Modelling of the thermodynamic properties of electrolyte soluions for industrial interests

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Introduction

Lots of processes in chemical engineering require the precise knowledge of thermodynamical properties of liquids. Typically, it may be crucial to anticipate the phase diagram and the heat capacity of a solvent. When the latter is a mixture of several molecules, it is also important to determine the activity coefficients of the various components. This point, together with economical constraints, prompts industrials to invest in research in chemical engineering. In that case, it may be useful to resort to an organism that aims at building links between the academic research and firms. This is for example the role of the AIF in Germany. More precisely, this organism finances the development of the modelling of thermodynamical properties of mixtures of electrolyte solutions.

The AiF is the German Federation of Industrial Research Associations "Otto von Guericke" (Arbeitsgemeinschaft industrieller Forschungsvereinigungen "Otto von Guericke" e.V.). The central concern of this registered non-profit association is the promotion of applied Research and Development (R&D) for the benefit of small and medium-sized enterprises (SME). Organized by industry, the AiF supports the efficient usage and advancement of R&D-programmes in order to increase the competitive strength of SMES. To this end, the AiF has created a unique infrastructure, comprising an industry-based innovations network covering over 100 industrial research associations, with approximately 50,000 SMES, and about 700 associated research institutions. Within this structure, the AiF's two offices in Cologne and Berlin provide practice-driven innovation consultancy promoting R&D on a national and, increasingly, an international scale. Since its foundation in 1954 the AiF has been a competent partner to the federal government - currently the Federal Ministries of Economics and Labour (BMWA) and of Education and Research (BMBF) - functioning as a bridge between industry and academy within the framework of various R&D-programmes. The AiF acts as an agency for the promotion of R&D for small and medium-sized enterprises in two ways: on the one hand, it lays the

foundations for industrial collective research for the benefit of entire industrial sectors; and on the other hand, the AiF acts as a programme managing executive for governmental R&D-support-measures for the benefit of individual companies and Universities of Applied Sciences (Fachhochschulen). Overall, the AiF has an annual budget of nearly 250 million Euros of public funds.

The investigation of thermodynamical properties of liquids is actually a difficult task which has attracted much interest in the academic research for a long time. The most simple modelling assumes that solution behaves like an ideal gas where all interactions are neglected. This model is not able to account for the experimental behaviour of mixtures containing molecules of very different nature. Moreover, in the case of electrolyte solutions, both the long-ranged electrostatic interactions between ions and the short-ranged interactions with solvent molecules have a huge influence on the properties of the whole fluid. The Debye-Hückel model [1] that treats ions as point charges allows one to describe the main features of structural and dynamical properties of very dilute electrolyte solutions. This model, whose main advantage is its simplicity, fails to describe ionic solutions at moderate and high concentration that may be used for practical applications. The Mean Spherical Approximation (MSA) [2] is used as a closure equation of the integral equations of statistical mechanics. It permits to better account for the experimental behaviour of such solutions. This model considers the solution in the framework of the continuous solvent model and regards ions as charged hard spheres. Moreover, it has the huge advantage to be anallytically solvable. Very recently, Papaiconomou et al. [3] have introduced MSA calculations in the Chen model [4]. The latter describes long-ranged electrostatic interactions by the Pitzer-Debye-Hückel equation and the short-ranged interactions in the framework of the (Nonrandom Two-Liquid) model. The aim of the PhD thesis of Papaiconomou, that was financed by AIF as is the present work, was to replace the Pitzer-Debye-Hückel equation [5] by the MSA and to better adapt the NRTL model to the case of electrolyte solutions. He obtained interesting results. However the model did not account for the solvation of ions.

In this context, the aim of the present thesis is to better model these short-ranged effects and also to implement the calculation of some specific thermodynamical quantities like the heat capacities and the heats of dilution. Latter calculations required to take into account the effect of the variation of temperature.

This manuscript is organized as follows. The first chapters (I to III) recall some general thermodynamical notions that are required to develop our model. Moreover, the various models for mixtures commonly used in chemical engineering are presented. Chapter IV is devoted to the model that we have developped to take into account solvation effects and possible association between ions of opposite charges

in solutions. Next, in chapter V we study temperature effects on properties such as heat molal enthalpies and heat capacities. Then, the sixth chapter is devoted to the presentation of the stepwise solvation-equilibrium model.

Bibliography

[1] R.A. Robinson, R.H. Stokes, Electrolyte Solutions, Second ed., London, 1965.

[2] L.Blum, Mol. Phys. 30 (1975) 1529.

[3] N. Papaiconomou, J.P. Simonin, O. Bernard, W. Kunz, Phys. Chem. Chem. Phys. 4 (2002) 4435-43.

[4] C.C. Chen, H.I. Britt, J.F. Boston, L.B. Evans, AICHE J. 28 (1982) 588.

[5] K.S. Pitzer, J. Phys. Chem. 77 (1973) 268.

Chapter 2

Thermodynamic properties of ionic solutions

2.1 Basic thermodynamics

2.1.1 Intensive and extensive variables:

Extensive variables depend on the size of the system, i.e. of the quantity of matter. Intensive variables do not depend on the size of the system. An intensive variable is a zero degree homogeneous function of the quantity of matter. An extensive variable is an homogeneous function of degree 1 of quantity of matter. By definition, $f(x_1, ..., x_k)$ is a homogeneous function of degree k of variables $x_1, ..., x_k$ if:

$$f(\lambda x_1, ..., \lambda x_k) = \lambda^k f(x_1, ..., x_k) \tag{2.1}$$

Euler theorem reads:

$$kf(x_1, ..., x_i, ...x_l) = \sum_i x_i \left(\frac{\partial f}{\partial x_i}\right)_{x_j \neq_i} \tag{2.2}$$

For a system of N components, where N_i is the number of particles i, one gets, for X an extensive variable:

$$X = \sum N_i \left(\frac{\partial X}{\partial N_i}\right)_{N_j \neq_i} \tag{2.3}$$

with $\left(\frac{\partial X}{\partial N_i}\right)_{T,P,N_j \neq_i}$ the partial molar quantity.

2.1.2 The chemical potential

The function μ_i is an intensive quantity which depends on temperature T, pressure P and mole fraction x_i of the system.

The chemical potential reads:

$$\mu_i = \mu_i^{\otimes} + kT \ln a_i \tag{2.4}$$

where a_i is called the activity by Lewis designated by the symbol a. The activity of a substance gives an indication of how active a substance is relative to its standard state because it provides a measure of the difference between the substance's chemical potential at the state of interest and that at its standard state. It depends on the composition. The standard state is indicated by a superscript $\otimes$. The activity coefficient f_i is defined from:

$$a_i = f_i x_i \tag{2.5}$$

So that

$$\mu_i = \mu_i^{\otimes} + kT \ln f_i x_i \tag{2.6}$$

On the molality scale (the molality m_i is the number of moles of species i per kilogram of solvent). The activity reads:

$$a_i = \gamma_i m_i \tag{2.7}$$

where γ_i is equal to one and $a_i = m_i$ for an ideal solution. γ_i is dimensionless.

2.1.3 The Gibbs-Duhem relation

The Gibbs free enthalpy G is extensive:

$$G(T, P, \lambda N_i) = \lambda G(T, P, N_i) \tag{2.8}$$

G is a homogeneous function of degree one of the N_i's, so that

$$G = \sum_i N_i \left(\frac{\partial G}{\partial N_i} \right)_{N_j \neq i, T, P} = \sum_i N_i \mu_i \tag{2.9}$$

Then, we have

$$dG = \sum_i \mu_i dN_i + \sum_i N_i d\mu_i \tag{2.10}$$

Hence

$$VdP - SdT = \sum_i N_i d\mu_i \tag{2.11}$$

This equation is the so-called Gibbs-Duhem (GD) relation which expresses the extensivity of G. A model for μ_i is self consistent if this necessary condition is satisfied. We will use this relation to check the validity of our models during this work. The GD relation is always satisfied if G has the form:

$$G = G(T, P, N_i) = N_{tot} G_N(T, P, x_1, ..., x_n) \tag{2.12}$$

where $G_N(T, P, x_1, ..., x_n)$ is the mean Gibbs energy per particule, with

$$x_i = N_i/N_{tot} \tag{2.13}$$

and

$$N_{tot} = N_1 + N_2 + ... + N_n \tag{2.14}$$

We have by definition of the chemical potential:

$$\mu_i = \frac{\partial G}{\partial N_i} = G_N + N_{tot}\left(\frac{\partial G_N}{\partial N_i}\right) \tag{2.15}$$

This yields

$$\frac{\partial G_N}{\partial N_i} = \frac{\partial G_N}{\partial x_i}\frac{\partial x_i}{\partial N_i} + \sum_{j\neq i}\frac{\partial G_N}{\partial x_j}\frac{\partial x_j}{\partial N_i} \tag{2.16}$$

$$= \frac{\partial G_N}{\partial x_i}\frac{N_{tot} - N_i}{N_{tot}^2} + \sum_{j\neq i}\frac{\partial G_N}{\partial x_j}\left(-\frac{N_j}{N_{tot}^2}\right) \tag{2.17}$$

Hence

$$\mu_i = G_N + (1 - x_i)\frac{\partial G_N}{\partial x_i} + \sum_{j\neq i}\frac{\partial G_N}{\partial x_j}(-x_j) \tag{2.18}$$

$$\mu_i = G_N + (1 - x_i)\frac{\partial G_N}{\partial x_i} - \sum_{j\neq i} x_j\frac{\partial G_N}{\partial x_j} \tag{2.19}$$

$$= G_N + \frac{\partial G_N}{\partial x_i} - \sum_{j} x_j\frac{\partial G_N}{\partial x_j} \tag{2.20}$$

The GD relation

$$\sum_i N_i d\mu_i = VdP - SdT \tag{2.21}$$

is automatically satisfied if $G = \sum_i N_i\mu_i$, which can be verified:

$$\sum_i N_i\mu_i = \sum_i N_i G_N + \sum_i N_i\frac{\partial G_N}{\partial x_i} - \sum_{j,i} x_j\frac{\partial G_N}{\partial x_j}N_i \tag{2.22}$$

$$= \sum_i N_i G_N + \sum_i N_i\frac{\partial G_N}{\partial x_i} - \sum_i\sum_j x_i\frac{\partial G_N}{\partial x_i}N_j \tag{2.23}$$

$$= \sum_i N_i G_N + \sum_i N_i\frac{\partial G_N}{\partial x_i} - \sum_i \frac{N_i\sum_j N_j}{N_{tot}}\frac{\partial G_N}{\partial x_i} \tag{2.24}$$

$$= \sum_i N_i G_N + \sum_i N_i\frac{\partial G_N}{\partial x_i} - \sum_i N_i\frac{\partial G_N}{\partial x_i} \tag{2.25}$$

$$= \sum_i N_i G_N = N_{tot}G_N \tag{2.26}$$

2.1.4 Relation between activity coefficients on different scales

In this work, we have used the mole fraction scale to express the composition because this scale was adopted to the thermodynamical models such as NRTL. The relation between activity coefficients on the molal and the mole fraction scales are:

$$\mu_i = \mu_i^{\otimes}(x) + RT \ln a_i(x) \tag{2.27}$$

$$\mu_i = \mu_i^{\otimes}(m) + RT \ln a_i(m) \tag{2.28}$$

where $\mu_i^{\otimes}(x)$ and $\mu_i^{\otimes}(m)$ are, respectively, the standard chemical potential of species i, where i is the solvent or the solute, on mole fraction and molal scales. Similarly, $a_i(x)$ and $a_i(m)$ are the activities, respectively on the mole fraction scale and on the molal scale:

$$a_i(x) = (x f_{\pm})^{\nu} \tag{2.29}$$

$$a_i(m) = (m \gamma_{\pm})^{\nu} \tag{2.30}$$

where m is the molality, $f_{\pm}$ and $\gamma_{\pm}$ are, respectively, the mean rational activity coefficient and the mean molal activity coefficient. Then one gets:

$$\ln \gamma_{\pm} = \frac{\mu_i^{\otimes}(x) - \mu_i^{\otimes}(m)}{\nu RT} + \ln \frac{x_s}{m} + \ln f_{\pm} \tag{2.31}$$

With x_s is the mole fraction of the salt, ν is the total number of moles of ions given by one mole of electrolyte. With the standard state conditions x_s and m tend towards zero, $\gamma_{\pm}$ and $f_{\pm}$ towards one. Thus:

$$\frac{\mu_i^{\otimes}(x) - \mu_i^{\otimes}(m)}{\nu RT} = -\ln \frac{1}{1/M_w + \nu m} \tag{2.32}$$

$$\lim_{x \to 0} \frac{\mu_i^{\otimes}(x) - \mu_i^{\otimes}(m)}{\nu RT} = M_w \tag{2.33}$$

Hence

$$\gamma_{\pm} = \frac{f_{\pm}}{1 + \nu m M_w} \tag{2.34}$$

where M_w is the molar mass of water.

Chapter 3

Common models used in chemical engineering for the thermodynamics of electrolytes in solvent mixtures

The aim of the following chapter is not to make an exhaustive review of thermodynamics but to summarise the main concepts and models used in chemical engineering thermodynamics for electrolyte solutions. We follow the book written by Prausnitz, Lichtenthaler and de Azevedo [1].

3.1 Models and theories of solutions

Most solutions are not ideal because of the interactions between the particles. Raoult's law $P_i = Px_i$ where P_i is the partial pressure, and x_i the mole fraction of i, is applicable when the components of the mixture become undistinguishable and it fails to represent the behavior of real solutions at high concentration. That is due to differences in molecular size, shape, and intermolecular forces of the components. However, Raoult's law may be regarded as a reference law in the study of real solutions.

3.1.1 Random mixture or not random mixture

A very important assumption is the following: when the molecules of two components are mixed, the arrangement of molecules is completely random, i.e. there is no preference in the choice of its neighbours. This assumption was made by Van Laar, Scatchard and Hildebrand [2]. In these conditions, when we have a mixture

of two liquids, there is no volume change ($v^E = 0$) and entropy of mixing ($s^E = 0$) corresponds to an ideal solution.

But generally the mixture is not completely random contrary to an ideal solution. In order to make a model which takes into account the fact that the solution is non-random, Guggenheim [3] constructed a lattice theory for molecules of equal size that form mixtures which are not necessarily random. No specific interaction like H bound and solvation is taken into account. There are three assumptions: consider that every N_A molecules of type A and every N_B molecules of type B has z nearest neighbours, (z is the coordination number). Suppose each molecule has z nearest neighbors.

For pure A

$$U_A = \frac{1}{2} N_A z w_{AA} \tag{3.1}$$

with U_A is the potential energy of A, N_A the number of molecules of type A, w_{AA} the mean interaction potentiel between A molecules. Similarly for B

$$U_B = \frac{1}{2} N_B z w_{BB} \tag{3.2}$$

with U_B is the potential energy of B, N_B the number of molecules of type B, w_{BB} the mean interaction potentiel between B molecules. And if we have a mixture of N_A molecules of type A and N_B molecules of type B

$$U = N_{AA} w_{AA} + N_{BB} w_{BB} + N_{AB} w_{AB} \tag{3.3}$$

with

$$z N_A = N_{AB} + 2 N_{AA} \tag{3.4}$$

$$z N_B = N_{AB} + 2 N_{BB} \tag{3.5}$$

where U is the total potentiel energy of the lattice. Thus

$$U = w_{AA} \left(\frac{z N_A - N_{AB}}{2} \right) + w_{BB} \left(\frac{z N_B - N_{AB}}{2} \right) + N_{AB} w_{AB} \tag{3.6}$$

$$U = \frac{1}{2} z N_A w_{AA} + \frac{1}{2} z N_B w_{BB} + N_{AB} \left(w_{AB} - \frac{1}{2} w_{AA} - \frac{1}{2} w_{BB} \right) \tag{3.7}$$

Hence

$$\Delta U_{mixt} = N_{AB} w \tag{3.8}$$

where $w = w_{AB} - \frac{1}{2} w_{AA} - \frac{1}{2} w_{BB}$ is the interchange energy. Eq. 3.7 gives the potential energy of a binary mixture and also that of a pure liquid: N_{AB} and either N_A or N_B are set equal zero. If $w = 0$ one speaks of the random mixtures and if $w \neq 0$ the mixtures are not random.

3.1.2 The Two-Liquid Theory

Several workers have derived thermodyanmic models to describe the excess properties of mixtures. Wilson and Abrams(1975) [4, 5] have developed, respectively, Wilson's equation and UNIQUAC. Both are based on the Two-Liquid Theory. Renon (1969) [6], used the derivation of the three parameters Wilson's equation. Maurer [7] adopted the local compositions related to overall compositions through Boltzmann factors. The notion of local composition results from The Two-Liquid Theory. We briefly expose in this paragraph the Two-Liquid Theory.

We consider a binary mixture of molecules of components 1 and 2, where molecules 1 and 2 have arbitrary size and shape. Each molecule is closely surrounded by other molecules of 1 and 2. We have two types of cells: one contains molecule 1 at its center and the other contains molecule 2 at its center. Suppose $M^{(1)}$ is an extensive property M of a fluid consisting only of cells of 1; in the same way, $M^{(2)}$ for a fluid of cells of 2. The Two-Liquid Theory assumes that the extensive property M_{mixt} of the mixture reads:

$$M_{mixt} = x_1 M^{(1)} + x_2 M^{(2)} \tag{3.9}$$

If we take the molar excess energy u^E as the extensive property, one has [4]:

$$u^E = x_1 q_1 \theta_{21} \Delta u_{21} + x_2 q_2 \theta_{12} \Delta u_{12} \tag{3.10}$$

with

$$\theta_{21} = \frac{\theta_2 \exp\left(-\frac{\Delta u_{21}}{RT}\right)}{\theta_1 + \theta_2 \exp\left(-\frac{\Delta u_{21}}{RT}\right)} \tag{3.11}$$

$$\theta_{12} = \frac{\theta_1 \exp\left(-\frac{\Delta u_{12}}{RT}\right)}{\theta_2 + \theta_1 \exp\left(-\frac{\Delta u_{12}}{RT}\right)} \tag{3.12}$$

and with

$$\theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2} \tag{3.13}$$

$$\theta_2 = \frac{x_2 q_2}{x_1 q_1 + x_2 q_2} \tag{3.14}$$

where

$$\Delta u_{21} = \frac{1}{2} z \left(U_{21} - U_{11}\right) N_{Av} \tag{3.15}$$

$$\Delta u_{12} = \frac{1}{2} z \left(U_{12} - U_{22}\right) N_{Av} \tag{3.16}$$

with θ is the surface fraction, U_{ij} is the potentiel energy of two nearest neighbors i and j, q is the external surface area, N_{Av} is the Avogadro number, and x the mole fraction. Eq.(3.10) is the fundamental relation based on two-fluid theory using the notion of local composition.

Wilson's equation

The Wilson's equation gives not only an expression for the activity coefficients as a function of composition but also the variation of the activity coefficient with temperature. It provides a good representation of excess Gibbs energies g^E for miscible mixtures, such as solutions of polar and associating components (alcohols) in non-polar solvents. Orye showed [8] that Wilson's equation is adapted to describe very well the activity coefficients of 100 binary mixtures. For a solution of m components, Wilson's equation is:

$$\frac{g^E}{RT} = -\sum_i x_i \ln\left(\sum_j x_j \Lambda_{ij}\right) \tag{3.17}$$

where

$$\Lambda_{ij} \equiv \frac{v_j}{v_i} \exp\left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right) \tag{3.18}$$

$$\Lambda_{ji} \equiv \frac{v_i}{v_j} \exp\left(-\frac{\lambda_{ji} - \lambda_{jj}}{RT}\right) \tag{3.19}$$

with λ_{ij} is the energy of interaction between the molecules i and j. The activity coefficient for a component k is given by:

$$\ln \gamma_k = -\ln\left(\sum_j x_j \Lambda_{kj}\right) + 1 - \sum_i \frac{x_i \Lambda_{ik}}{\sum_j x_j \Lambda_{ij}} \tag{3.20}$$

Therefore for a binary system, if we use indices 1 and 2, respectively, for the solvent and for the solute:

$$\frac{g^E}{RT} = -x_1 \ln\left(x_1 + \Lambda_{12} x_2\right) - x_2 \ln\left(x_2 + \Lambda_{21} x_1\right) \tag{3.21}$$

and the activity coefficients derived from this equation are:

$$\ln \gamma_1 = -\ln\left(x_1 + \Lambda_{12} x_2\right) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2}\right) \tag{3.22}$$

$$\ln \gamma_2 = -\ln\left(x_2 + \Lambda_{21} x_1\right) + x_1 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2}\right) \tag{3.23}$$

In Eq. 3.21 the excess Gibbs energy is defined by reference to an ideal solution in the sense of Raoult's law. This excess Gibbs energy obeys the boundary condition that g^E equals zero as either x_1 or x_2 is zero. Wilson's equation has two adjustable parameters

$$\Lambda_{12} = \frac{v_2}{v_1} \exp\left(-\frac{\lambda_{12} - \lambda_{11}}{RT}\right) \tag{3.24}$$

$$\Lambda_{21} = \frac{v_1}{v_2} \exp\left(-\frac{\lambda_{21} - \lambda_{22}}{RT}\right) \tag{3.25}$$

where v_i is the molar liquid volume of pure component i and the λ_{ij} is interaction energy between molecules i and j.

However, Wilson's equation has two disadvantages: first, Eqs (3.22-3.23) are not useful because they exhibit maxima or minima. Second, Wilson's equation is not able to predict limited miscibility. The liquid systems must be completely miscible or partially miscible with one liquid phase present.

The UNIQUAC equation

Abrams(1975) and Maurer(1978) attempted to derive a two parameters equation for g^E that retains the advantage of the Wilson's equation without restriction to completely miscible mixture. Abrams derived an equation that extends the quasichemical theory of Guggenheim for nonrandom mixtures to solutions containing molecules of different sizes. UNIQUAC (the Universal Quasi-Chemical theory) for g^E consists of two parts: on the one hand, a combinatorial part which describes the entropic contribution, and on the other hand a residual part which accounts for the intermolecular forces that are responsable for the enthalpy of mixing. The combinatorial part depends on the composition, the size and the shape of the molecules. The residual part depends on intermolecular forces.

$$\frac{g^E}{RT} = \left(\frac{g^E}{RT}\right)_{combinatorial} + \left(\frac{g^E}{RT}\right)_{residual} \tag{3.26}$$

For a solution of m components, the UNIQUAC equation for the molar excess Gibbs energy is the sum of two terms. The combinatorial part is

$$\frac{g^E}{RT} = \sum_i \ln \frac{\Phi_i^*}{x_i} + \frac{z}{2} \sum_i q_i x_i \ln \frac{\theta_i}{\Phi_i^*} \tag{3.27}$$

the residual part is:

$$\frac{g^E}{RT} = -\sum_i q^{'} x_i \ln \left(\sum_j \theta_j^{'} \tau_{ji} \right) \tag{3.28}$$

where Φ_i^*, θ and $\theta^{'}$ are, respectively, the segment fraction and the areas fractions:

$$\Phi_i^* = \frac{r_i x_i}{\sum_j r_j x_j} \tag{3.29}$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \tag{3.30}$$

$$\theta_i^{'} = \frac{q_i^{'} x_i}{\sum_j q_j^{'} x_j} \tag{3.31}$$

τ_{ij}, τ_{ji} are adjustable parameters:

$$\tau_{ij} = \exp\left(-\frac{a_{ij}}{T}\right) \tag{3.32}$$

$$\tau_{ji} = \exp\left(-\frac{a_{ji}}{T}\right) \tag{3.33}$$

where a_{ij} and a_{ji} are the binary energy parameters. r, q, and q' are pure-component molecular structure constants which depend on the molecular size and on the external surface areas. q_i and q_i' are the surface interactions and the geometric external surface. Except for water and lower alcohols, $q = q'$. The resulting activity coefficient of species i requires only pure-component and binary parameters. The activity coefficient of species i reads:

$$\ln \gamma_i = \ln \frac{\Phi_i^*}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i^*} + l_i - \frac{\Phi_i^*}{x_i} \sum_j x_j l_j - q_i^{'} \ln \left(\sum_j \theta_j^{'} \tau_{ji} \right) + q_i^{'} - q_i^{'} \sum_j \frac{\theta_j^{'} \tau_{ij}}{\sum_k \theta_k^{'} \tau_{kj}} \tag{3.34}$$

where

$$l_j = \frac{z}{2} (r_j - q_j) - (r_j - 1) \tag{3.35}$$

Eq.(3.34) requires only pure-component and binary parameters. UNIQUAC is widely used in the chemical industry in order to predict the thermodynamic behaviour of chemical mixtures. It is applicable to a wide variety of non-electrolyte mixtures. Polar or non-polar solvents, such as alcohols, ketones, hydrocarbons, or nitriles can be accurately described with the UNIQUAC model, including partially miscible mixtures, which can't be described by the Wilson model for instance. For example the VLE curve of the n-hexane and nitroethane system at $45°C$ [9] is shown in Figure 3.1. The pressure of the vapor phase is plotted as a function of the mole fraction of acetonitrile in the liquid phase. We observe a strong positive deviation from ideality in the sense of Raoul't law. Despite this deviation the experimental points are very well described within the UNIQUAC model.

NRTL equation

Renon and Prausnitz[6] used the concept of local composition in the derivation of NRTL (Nonrandom Two-Liquid) equation. This equation is applicable to partially miscible as well as completely miscible systems.

$$\frac{g^E}{RT} = \sum_i x_i \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} \tag{3.36}$$

where

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} \tag{3.37}$$

$$G_{ji} = \exp\left(-\alpha_{ji} \tau_{ji}\right) \tag{3.38}$$

$$\alpha_{ji} = \alpha_{ij} \tag{3.39}$$

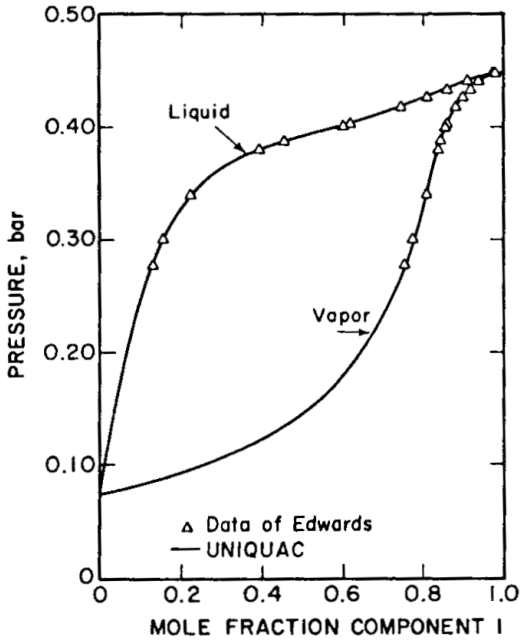

Figure 3.1: Strong positive deviations from ideality. Vapor-liquid equilibria for *n*-hexane (1)/nitroethane (2) system at 45°C. Taken from ref. [1].

The activity coefficient for any component i is given by:

$$\ln \gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{x_j G_{ij}}{\sum_k G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_l x_l \tau_{lj} G_{lj}}{\sum_k G_{kj} x_k} \right) \tag{3.40}$$

Eqs.(3.36) and (3.40) only contain parameters which can be obtained from binary data. The significance of g_{ij} is similar to that of λ_{ij} in Wilson's equation: g_{ij} is an energy parameter which is characteristic of the $i-j$ interaction. The NRTL model likewise the Wilson model describes multi-component systems only with the help of binary parameters.

3.1.3 Chen model: Electrolyte-NRTL model(Pitzer-Debye-Hückel NRTL model)

In 1982 Chen [10] proposed a model with local composition which described the excess Gibbs energy of single-solvent, single completely dissociated electrolyte systems over the entire range of temperature and concentration.

Chen made two assumptions about electrolyte systems which are critical to the local composition model development: first the local composition of cations around cations is zero. In other words the repulsive forces between ions of like charge are relatively large. Second the local electroneutrality assumption states that the

distribution of cations and anions around a central molecule is such that the local ionic charge is zero. It is these realistic assumptions, in conjunction with the local composition concept, that enable the new model to represent all kind of electrolyte systems. The excess Gibbs energy is the sum of two contributions: the long-range electrostatic forces between ions, and the short-range forces between all the species. For the long-range contribution Chen took the Pitzer-Debye-Hückel equation [11], and for the short-range contribution the NRTL (Nonrandom Two-Liquid) model [6]. Thus at infinite dilute solution for the electrolyte systems the model is reduced to the Debye-Hückel model. At higher concentrations the model reduces to the NRTL model. The short-range interaction contribution model is developed from a symmetric convention based on reference states of pure solvents.The long-range contribution is based on a asymmetric convention whose frame of reference is the infinite dilution. We have:

$$\frac{g^E}{RT} = \frac{g^{E,LR}}{RT} + \frac{g^{E,SR}}{RT} + \frac{g^{E,Born}}{RT} \tag{3.41}$$

where the superscript LR, SR and Born are, respectively, long-range, short-range and the Born's term.

Long-range interaction contribution

The Pitzer Debye-Hückel equation normalized to mole fractions of unity and zero for electrolytes is used to represent the long-range interaction contribution.

$$g^{E,LR} = -\left(\frac{1}{M_s}\right)^{1/2} 4A_\Phi \frac{I_x}{\rho} \ln\left(1 + \rho I_x^{1/2}\right) \tag{3.42}$$

where M_s is the molar mass of salt, $\rho = bM_m^{-1/2}$, M_m the molar mass of solvent, b being related to the closest approach distance between ions. I_x is the ionic strength on mole fraction basis:

$$I_x = \frac{1}{2}\sum_i z_i^2 x_i \tag{3.43}$$

where z_i is the charge of ion i, and A_Φ is the Debye-Hückel parameter

$$A_\phi = \frac{1}{3}\sqrt{2\pi N_{Av} d_m}\left(\frac{\beta e^2}{4\pi\epsilon_0\epsilon_m}\right)^{3/2} \tag{3.44}$$

where d_m is the solvent density, N_{Av} is the Avogadro's number, e is the elementary charge, ϵ_0 is the permittivity of a vacuum and ϵ_m is the relative permittivity of water. By differentiating with respect to N_i we obtain for the activity coefficient of species i:

$$\ln f_i^{*LR} = -\left(\frac{1000}{M_s}\right) A_\Phi [\frac{2Z_i^2}{\rho}\ln(1 + \rho I_x^{1/2}) + \frac{Z_i^2 I_x^{1/2} - 2I_x^{3/2}}{1 + \rho I_x^{1/2}}] \tag{3.45}$$

Short-range interaction contribution

As we have seen previously NRTL is based on the Two-Liquid Theory. The derivation that follows may be generalized to handle all types of electrolyte systems, in this work the derivation will be based on a system of single completely dissociated liquid electrolyte, cation, anion, and single solvent. In this type of mixture, it is assumed that there are three types of cells as shown in Figure 3.2. One type consists of a central solvent molecule with solvent molecules, anions, and cations in the immediate neighborhood. The local electroneutrality assumption is applied to cells of this type. The other two are based on the like-ion repulsion assumption and have either an anion or cation as the central species, and an immediate neighborhood consisting of solvent molecules and oppositely-charged ions, but no ions of like charge.

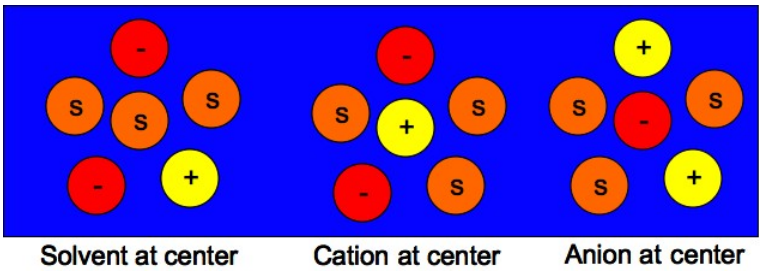

Figure 3.2: Three types of cells according to like-ion repulsion assumption and local electroneutrality assumption

The central particle may be either 1 or 2. 1 or 2 could be cation, anion or solvent respectively. The interaction parameter τ_{ij} is the interaction energy between two particles i and j.

$$\tau_{ji} = \beta(g_{ji} - g_{ii}) \tag{3.46}$$

with g_{ij}=g_{ji} For our exemple where the particle central is 1 or 2 we have:

$$\tau_{12} = \beta(g_{12} - g_{22}) \tag{3.47}$$

$$\tau_{21} = \beta(g_{21} - g_{11}) \tag{3.48}$$

The probability P_{ji} [12] is used here in place of G_{ji} [6, 10]. P_{ji} describes the probability of finding a particle of species j in the immediate vicinity of a central particle of species i. P_{ji} follows the Boltzmann distribution as

$$P_{ji} = \exp\left(-\alpha\tau_{ji}\right) \tag{3.49}$$

and

$$P_{ji,ki} = \exp\left(-\alpha\tau_{ji,ki}\right) \tag{3.50}$$

$P_{ji,ki}$ is the relative probability of finding a particle of species j near i compared to that of finding k near i. α is the so-called non-randomness parameter.

The last (closure) equation relates the local mole fractions of species j and k around central species i, X_{ji} and X_{ki} to the probabilities as

$$\frac{X_{ji}}{X_{ki}} = \frac{x_j P_{ji}}{x_k P_{ki}} \tag{3.51}$$

where j and i are ions or solvent. This relation was first proposed by Chen and Evans [10]. Later, it was modified with the introduction of the valence z_i [13]. We have

$$\sum_j X_{ji} = 1 \tag{3.52}$$

The assumption "no ions around an ion of like charge" must be present, thus

$$X_{ii} = X_{jj} = 0 \tag{3.53}$$

$$P_{ii} = P_{jj} = 0 \tag{3.54}$$

From 3.51 and 3.52 one gets

$$X_{ji} = \frac{x_j P_{ji}}{\sum_j x_j P_{ji}} \tag{3.55}$$

with x_j the mole fraction of species j in solution.

The Excess Gibbs energy per molecule of species i, G_i^{NRTL} is:

$$\bar{G_i}^{NRTL} = \sum_j X_{ji} g_{ji} \tag{3.56}$$

finally we have from 3.55

$$\bar{G_i}^{NRTL} = \frac{x_j P_{ji} g_{ji}}{\sum_j x_j P_{ji}} \tag{3.57}$$

The reference state G_i^{ref} is the pure solvent for the solvent and it is the central ion only surrounded by counter-ions for the ions, as defined by Chen and Evans [10].

$$\bar{G_m}^{ref,NRTL} = g_{mm} \tag{3.58}$$

$$\bar{G_c}^{ref,NRTL} = \bar{G_a}^{ref,NRTL} = g_{ca} \tag{3.59}$$

and

$$\bar{G}^{ref,NRTL} = \sum_k x_k \bar{G_k}^{ref,NRTL} \tag{3.60}$$

The NRTL deviation of excess Gibbs energy of the system

$$\Delta\bar{G}^{NRTL} = \sum_k x_k \Delta\bar{G}_k{}^{NRTL} \tag{3.61}$$

and the total deviation of the excess Gibbs energy of the system is

$$\Delta G^{NRTL} = N_{tot}\Delta\bar{G}^{NRTL} \tag{3.62}$$

where $N_{tot} = N_c + N_a + N_m$ is the total number of particles in solution. In the case of a mixture of one salt and several solvents that will be considered below, one gets, using Eqs. 3.55-6.14 the following equation [12]

$$\beta\Delta G^{NRTL} = \sum_i [x_c X_{mc}\tau_{mc,ac} + x_a X_{ma}\tau_{ma,ca} + x_m \sum_i X_{jm}\tau_{jm}] \tag{3.63}$$

Born term

The Born term in Eq. 3.41 is used to account for the Gibbs energy of transfer of ionic species from the infinite dilution state in a mixed-solvent to the infinite dilution state in aqueous phase.

$$\ln f_i^{Born} = \frac{\beta e^2}{8\pi\epsilon_0}\left(\frac{1}{\epsilon_m^{'}} - \frac{1}{\epsilon_m}\right)\sum_i \frac{x_i z_i^2}{r_i} \tag{3.64}$$

where $\epsilon_m^{'}$, ϵ_m are the relative permittivity of the solvent mixture and the relative permittivity of water, respectively, r_i is the Born ionic radius. For purely aqueous systems $\ln f_i^{Born} = 0$.

3.1.4 MSA-NRTL model

Papaiconomou et al. [12] developed a model which describes the electrolyte solutions with MSA (Mean Spherical Approximation) and NRTL models. It differs from the Chen et al. model (3.1.3) in the following aspects:

- They replaced the Pitzer DH term by the MSA expression for the long-range interaction. MSA is a well-based theoretical model which provided expressions for the free energy and the activity coefficients in the Mac Millan-Mayer framework where the solvent is regarded as a continuum. The MSA model is similar to the Debye-Hückel theory. However it differs from the latter in the fact that it better takes into account the sizes of the ions (excluded volume effect).

- First the interaction parameters τ_{ij} for the cations are the same as those for the anions in Chen's work [10]. In Papaiconomou's work τ_{ij} are different for cations and anions, thus τ_{cm} is different from τ_{am}. There were three independent parameters τ_{cm}, τ_{am} and $\tau_{mc,ac}$. We have the relation:

$$\tau_{ma,ca} = \tau_{mc,ac} + \tau_{am} - \tau_{cm} \tag{3.65}$$

  Second, $\tau_{mc,ac}$ was varied with composition of solution [18].

$$\tau_{mc,ac} = \tau^{(1)}_{mc,ac} + \tau^{(2)}_{mc,ac} x_m \tag{3.66}$$

  The τ_{ji} are adjustable parameters.

- The Born term is not taken into account because it is not relevant.

To sum up, what does MSA-NRTL describe ? Figure 3.3 provides an overall picture which makes it possible to visualize the two kinds of interactions: the long-range and the short-range interactions.

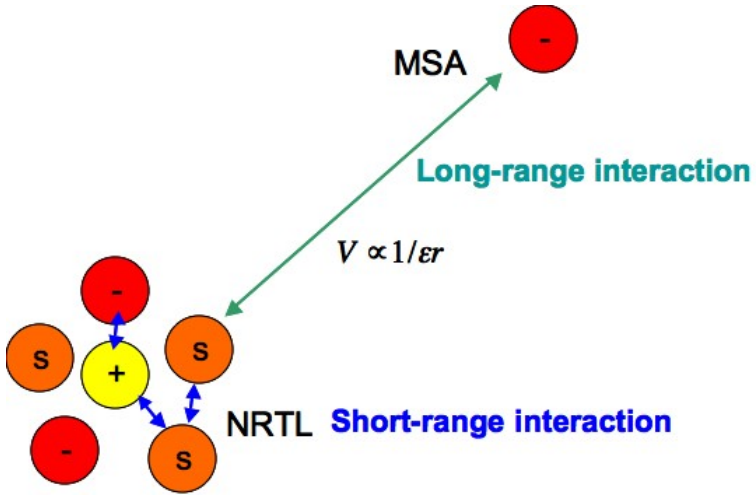

Figure 3.3: Long-range and short-range interactions in the MSA-NRTL model

Moreover, Papaiconomou et al. described the osmotic and activity coefficients of electrolyte solutions at 25°C. Nevertheless, in their work they studied the mean activity coefficient of salt in the solvent mixtures, but they did not take into account the effect of the temperature and the solvation.

Finally, the liquid vapor equilibria (L-V) were not described.

These are some remarks that show that the MSA-NRTL model can be improved and extended. In the next chapter, we will see how to improve MSA-NRTL model.

List of symbols

a_i	activity of species i
a_{ij}	binary energy parameters in UNIQUAC
A	anion
A_Φ	Debye-Hückel coefficient for the osmotic function
b	The closest approach distance between ions
C	cation
d_i	density of solvent i
e	charge of proton
f_i	activity coefficient of i on stoichiometric mole fraction scale
g_{ij}	Energy parameter in NRTL
G	Gibbs energy of solution
$\bar{G}$	partial molal excess Gibbs energy
$\mathcal{G}$	specific Gibbs energy
$\bar{G}_i$	Gibbs energy per particle of i
I	ionic strength
k_B	Boltzmann constant
l_{ij}	pair i-j interaction parameter
m	molality
M_i	molar mass of solvent i
n	mole number
N_{av}	Avogadro number
N_i	number of particles of i
P	Pression
P_{ik}, $P_{ik,jk}$	defined by eqs 6.61 and 6.62
q	External surface area
q_i	Constant parameters of Pitzer
r	distance of molecules
S_{model}	set of particle numbers within the model (eq 6.19)
S_{LR}	set of particle numbers at LR level (eq 6.20)
T	temperature
u	Molar excess energy
U	Potential energy
v	molar volume
V	volume of solution
W	water
w_{ij}	mean interaction potential
w	Interchange energy
X_{ij}	local mole fraction of species i and j
x_i	stoichiometric mole fraction
y_i	"true" mole fraction scale
z	Coordination number

Greek letters

α	NRTL random parameter
β	$= 1/k_B T$
θ	Surface fraction
$\gamma_\pm$	mean salt activity coefficient on molal scale
ε_i	relative permittivity of solvent i
ε_0	permittivity of a vacuum
κ	Debye screening parameter
Λ	Binary parameter in Wilson model
λ	Energy of parameter in Wilson equation
μ_i	chemical potential of species i
ν	$= \nu_C + \nu_A$
ν_i	stoichiometric number of species i in salt
Φ	segment fraction
ρ_i	molar density of species i
τ_{ij}, τ_{ji}	binary parameters in NRTL
σ_i	diameter of species i

Subscripts

1	total water
2	total solvent
W	free water
Z	free solvent
born	Born's term
s	salt
sol	Solution
T	Total

Superscripts

$\otimes$	reference state
(0)	value at T=298.15 K
el	electrostatic contribution
E	Excess
hyd	contribution from hydration
id	ideal contribution
MSA	contribution within mean spherical approximation
SR	contribution of short range forces

Bibliography

[1] J.M. Prausnitz, R.N. Lichtenthaler, E.G. de Azevedo, Third ed., Prentice Hall, New Jersey, 1999.

[2] G. Scatchard, Chem. Rev. 44 (1949) 7.

[3] E.A. Guggenheim, Mixtures, Oxford University Press, 1952.

[4] G.M. Wilson, J. Am. Chem. Soc. 86 (1964) 127.

[5] D.S. Abrams, J.M. Prausnitz, AIChE J. 21 (1975) 16.

[6] H. Renon, J.M. Prausnitz, AICHE J. 14 (1968) 135.

[7] G. Maurer, J.M. Prausnitz, Fluid Phase Equilib. 2 (1978) 91.

[8] R.V. Orye, J.M. Prausnitz, Ind. Eng. Chem. 57 (1965) 19.

[9] J.B. Edwards, Ph.D. Dissertation, Georgia Institute of Technology.

[10] C.C. Chen, H.I. Britt, J.F. Boston, L.B. Evans, AICHE J. 28 (1982) 588.

[11] K.S. Pitzer, J. Am. Chem. Soc. 102 (1980) 2902.

[12] N. Papaiconomou, J.P. Simonin, O. Bernard, W. Kunz, Phys. Chem. Chem. Phys. 4 (2002) 4435-43.

[13] C.C. Chen, L.B. Evans, AICHE J. 32 (1986) 444.

[14] J.K. Percus, G. Yevick, Phys. Rev. 136 (1964) B290.

[15] J.L. Lebowitz, J.K. Percus, Phys. Rev. 144 (1966) 251.

[16] E. Waisman, J.L. Lebowitz, J. Chem. Phys. 52 (1970) 4307.

[17] L.Blum, Mol. Phys. 30 (1975) 1529.

[18] V. Abovsky, Y. Liu, S. Watanasiri, Fluid Phase Equilib. 150-151 (1998) 277.

Chapter 4

Inclusion of ionic hydration and association in the MSA-NRTL model for a description of the thermodynamic properties of aqueous ionic solutions. Application to solutions of associating acids.

The purpose of this chapter is to further improve the MSA-NRTL model of Papaiconomou et al. [1], by introducing explicitly the solvation of ions.

Firt, we shortly discuss the importance of solvation through the behavior of osmotic coefficient as a function of the temperature.

The evolution of the effective potential when the temperature increases allow us to understand the evolution of LiCl and NaCl osmotic coefficients in Figure 4.1 [2].

4.1 Introduction

4.1.1 General considerations

The variation of ϕ as a function of temperature depends on the electrolyte. For HCl, LiCl, ϕ decreases whereas for NaCl , KCl, RbCl and C_SCl, for small temperature,

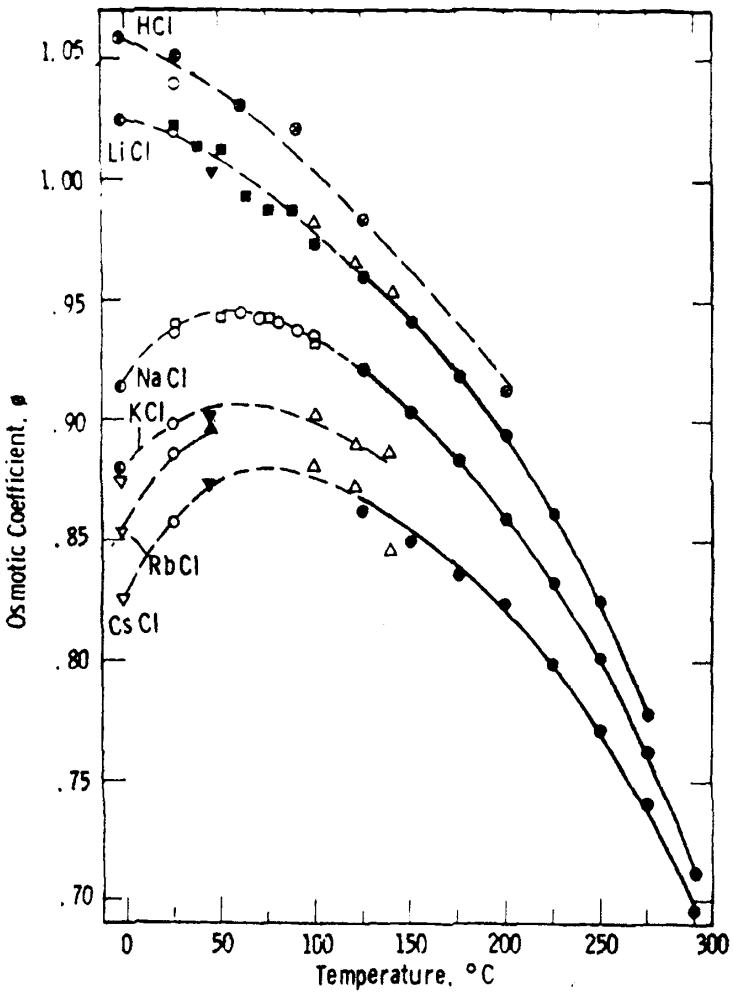

Figure 4.1: Temperature dependence of osmotic coefficients of 1m alkali metal chlorides and HCL. [2]

ϕ increases but it decreases at higher temperature. The difference between these curves may be understand in terms of hydrated ionic diameter which represents the solvation of the ion.

Indeed, for these concentrated solutions, the bigger the size of the ion, the greater ϕ. Thus for some electrolytes, the size always decreases as a function of T whereas for for other electrolytes it increases for the small temperature.

The difference in the temperature dependence corresponds to different solvation shells. In fact, the concept of the diameter simply expresses the short-range part of the effective ion-ion potential averaged over the configuration of the solvent. The latter can be calculated from MD (molecular dynamic) simulations (Figure 4.2).

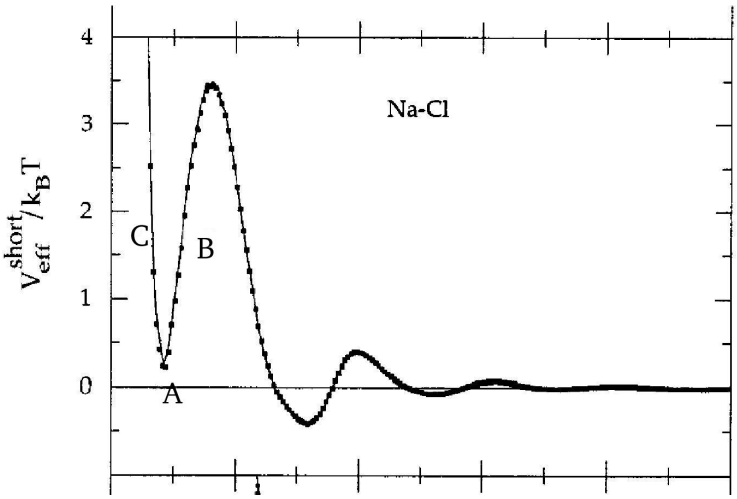

Figure 4.2: Short-range part of the effective potential between ion-ion pairs in aqueous NaCl electrolyte. Coutinuous line, 0.5 M; separate symbols, 1 M. In substracting Ewald potential. Dielectric constant of 79 and 78 for 0.5 M and 1 M solution, respectively. [3]

The accessible configurations are roughly situated below k_BT. If T increases, some ions will increase their diameter by exploring configuration at higher distances (penetration of on hydration shell) A $\rightarrow$ B. On the other hand, further ions will explore smaller distances (A $\rightarrow$ C). Thus, hydration is strongest for small ions. For instance, Li^+ is expected to be more hydrated than Na^+, K^+...

After we remark the relevant concept of solvation, we present the Stokes and Robinson model with constant solvation number.

4.1.2 Stokes and Robinson model for solvation

First of all we consider that any solute in aqueous solution is solvated i.e. cations or anions are surrounded by water molecules. In order to describre the solvation we use the mole fraction and molality scale because if we take the molarity scale we do not take into account the effect of solvent. We calculate the total Gibbs free energy in two ways : first the solute is not solvated, and second considering the solute solvated by h moles of solvent, h is constant. Thus, we have on one hand, h_1 moles of water combined with ν_1 moles of cations and on the other hand, h_2 moles of water combinated with the ν_2 moles of anions. The subscript 1 is for water, C and A for cations and anions respectively.

$$G = N_1\mu_1 + N_A\mu_A + N_C\mu_C \tag{4.1}$$

and

$$G = N_W\mu_W + N_A\mu_{A'} + N_C\mu_{C'} \tag{4.2}$$

in which $N_W = N_1 - h$, N_1, N_C, and N_A, are the particle number of free water, total water, of hydrated cations, of total cations, of anions, respectively, μ_i is the chemical potential of species i. Only the terms of solute are different because in one case it's ion and another case it's ion with water's molecules. We introduce the chemical potential in terms of the appropriate mole fraction and activity coefficient :

$$\mu_1 = \mu_1^{\otimes} + RT\ln a_1 \tag{4.3}$$

$$\mu_C = \mu_C^{\otimes} + RT\ln\frac{N_1}{N_1 + N_A + N_C} + RT\ln f_C \tag{4.4}$$

$$\mu_{C'} = \mu_{C'}^{\otimes} + RT\ln\frac{N_1}{N_W + N_A + N_C} + RT\ln f_{C'} \tag{4.5}$$

where $\mu_{C'}$ is the chemical potential of species for the hydrated solute, f_C, f_A, $f_{C'}$ and $f_{A'}$ are, respectively, the activity coefficient of cations, of anions, of hydrated cations and of hydrated anions on the mole fraction scale. Hence

$$h\mu_1 + N_C\mu_C - N_C\mu_{C'} + N_A\mu_A - N_A\mu_{A'} = 0 \tag{4.6}$$

We have :

$$h\mu_1^{\otimes} + N_C\Delta\mu_C^{\otimes} + N_A\Delta\mu_A^{\otimes} + hRT\ln a_1 + N_CRT\ln X + N_ART\ln X + N_CRT\ln f_C$$

$$+N_ART\ln f_A - N_CRT\ln f_C^{'} - N_ART\ln f_A^{'} = 0$$

where $X = \frac{N_W+N_C+N_A}{N_1+N_C+N_A}$

$$\Delta\mu_C^{\otimes} = \mu_C^{\otimes} - \mu_{C'}^{\otimes}$$

and

$$\Delta\mu_A^{\otimes} = \mu_A^{\otimes} - \mu_{A'}^{\otimes}$$

For N_1 going to infinity (infinite dilution), a_1, goes to unity. So, one gets:

$$h\mu_1^{\otimes} + N_C\left(\mu_C^{\otimes} - \mu_{C'}^{\otimes}\right) + N_A\left(\mu_A^{\otimes} - \mu_{A'}^{\otimes}\right) = 0 \tag{4.7}$$

Hence

$$N_C \ln f_C^{'} + N_A \ln f_A^{'} = N_C \ln f_C + N_A \ln f_A + h \ln a_1 + (N_C + N_A) \ln \frac{N_W + N_C + N_A}{N_1 + N_C + N_A} \tag{4.8}$$

Let us set $N_C = \nu_C N$ and $N_A = \nu_A N$ with $\nu = \nu_C + \nu_A$ where N is the total particle number.

$$\nu_C N \ln f_C^{'} + \nu_A N \ln f_A^{'} = \nu_C N \ln f_C + \nu_A N \ln f_A + h \ln a_1 + (N_C + N_A) \ln \frac{N_W + N_C + N_A}{N_1 + N_C + N_A} \tag{4.9}$$

Hence

$$\nu_C N \ln f_C^{'} + \nu_A N \ln f_A^{'} = \nu \ln f_{\pm}^{'} = (\nu_C + \nu_A) f_{\pm}^{'} \tag{4.10}$$

Similarly

$$\nu_C N \ln f_C + \nu_A N \ln f_A = \nu \ln f_{\pm} = (\nu_C + \nu_A) f_{\pm} \tag{4.11}$$

where $f_{\pm}$ and $f_{\pm}^{'}$ are, respectively, the mean activity coefficient of hydrated cations and of not hydrated cations on the mole fraction scale. with

$$f_{\pm}^{\nu} = f_C^{\nu_C} f_A^{\nu_A} \tag{4.12}$$

Hence

$$\ln f_{\pm}^{'} = \ln f_{\pm} + \frac{h}{N\nu} \ln a_1 + \ln \frac{N_W + N_C + N_A}{N_1 + N_C + N_A} \tag{4.13}$$

Stokes and Robinson assumed that the value of h in the actual solution is the same as at infinite dilution.

We used this model while adapting it in order to improve the model of N. Papaiconomou et al.

4.2 Inclusion of ionic hydration and association in the MSA-NRTL model for a description of the thermodynamic properties of aqueous ionic solutions. Application to solutions of associating acids.

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Ionic hydration and association are included in the MSA-NRTL model for a description of the thermodynamic properties of aqueous ionic solutions. Hydration effects are introduced using the classic model of Robinson and Stokes, in which hydration numbers that are independent of salt concentration. Association is accounted for through a mass action law. New compact conversion formulae are given expressing the individual ionic, and mean salt, activity coefficients at the Lewis-Randall level. The model is applied to the representation of strong and associating aqueous electrolytes. In the case of solutions of associating acids, its ability to describe also the speciation of the acid is examined.

Keywords: Thermodynamic properties; Ionic Solutions; Electrolytes; Hydration; MSA; NRTL.

4.2.1 Introduction

The representation of the thermodynamic properties of ionic solutions has been the subject of numerous studies in the past decades. For many practical applications, *e.g.* in physical chemistry, chemical engineering or atmospheric chemistry, it is useful to have analytical working equations at hand, capable of being easily translated into a software program running on a microcomputer [4].

A great number of such models has been devised that may roughly be classified in two categories. Firstly, following the original idea of van't Hoff [5] and the more general MacMillan-Mayer (MM) theory [6] in which the solute is regarded as a gas of particles, models have been developed based on a statistical mechanical treatment of the system. This is the case of the mean spherical approximation (MSA) [7, 8, 9, 10] in which ions are modeled as charged hard spheres. Secondly, more phenomenological models have been proposed that generally led to an expression for the Gibbs energy of solution, split into decoupled electrostatic (generally a Debye-Hückel term) and non-electrostatic interactions. Examples of this type of model are the well-known Pitzer model [11] in which the non-electrostatic contribution has the form of a virial expansion, and models based on a local composition description of the system as in the elec-NRTL [12, 13, 14, 15], with the nonrandom two liquid (NRTL) contribution [12, 13, 1] to account for the effect of non-electrostatic forces.

In a previous article, we presented the MSA-NRTL model [1] in which the MSA was used for the electrostatic contribution to the Gibbs energy, in place of the Pitzer-Debye-Hückel term as used by Chen *et al.* [12, 13]. As is well known, electrostatic forces govern the thermodynamic behaviour of an ionic solution at low salt concentration. As salt concentration is increased, the effect of other forces becomes comparatively more important because of the progressive screening of ion-ion interactions. In the NRTL model, these other forces are assumed to be short-range (SR) forces, occurring only between closest neighbors. In our model [1], the NRTL expressions introduce parameters that are characteristic of the mean interaction energies between pairs of different species. So, 3 such parameters are required for an aqueous ionic binary solution [1].

An effect that is missing in the first version of the MSA-NRTL model [1] is the inclusion of hydration. The importance of this phenomenon in the representation of departures from ideality has been known and described for a long time [16]. Recent studies bring additional support to this principle. Zavitsas has shown [17] that a pseudo-ideal behaviour can be obtained for some thermodynamic properties if a certain number of water molecules is assumed to be bound to a solute (electrolyte or nonelectrolyte). Besides, *ab initio* numerical simulations developed during the past decade confirm the old picture of a well-defined hydration shell around small

and/or plurivalent cations [18, 19, 20, 21, 22, 23]. By contrast, simple anions such as Cl^-, Br^- and I^- seem to have less defined hydration shells [24] and this type of ion is believed to be weakly hydrated [25].

A second effect that was not included in our former work [1] was ion association. The issue of association of acids has recently prompted renewed interest in the field of atmospheric chemistry because of their presence in many aerosols. So, the case of sulfuric acid has been addressed using a Pitzer-type model [26] for a description of speciation of sulfuric acid as a function of temperature. The case of nitric acid, which is believed to exhibit significant association in water [27, 28, 29], is also likely to be of interest for such representations. Besides, it may be put forward that the influence of the hydration of the two ions in acid solutions on the pairing process has not received enough attention. Furthermore, to our knowledge, the issue of developing solution models capable of representing the thermodynamic properties together with the speciation in an associating acid solution has not been addressed sufficiently in the literature.

In the present work, hydration is incorporated into the MSA-NRTL model by following a route similar to the one proposed by Robinson and Stokes [16], which consists of assuming that an ion bears a constant number of attached water molecules (independent of salt concentration). The elec-NRTL was modified recently by using this method [30]. The model of Robinson and Stokes has also been used in combination with UNIQUAC [31]. In the present paper, the new MSA-NRTL model is applied to represent the basic thermodynamic properties of various aqueous strong 1-1 and 2-1 electrolytes (the case of salts containing plurivalent ions was not approached in our earlier work [1]). A description of the thermodynamic properties of sulfuric acid and nitric acid solutions is developed by including association between hydrated H^+ cation and hydrated anion (SO_4^{2-} or NO_3^-). For these solutions, the capability of the model to represent the thermodynamic properties *and* the speciation of the acid is examined.

The next section presents the theoretical aspects of this work. The third section is devoted to the presentation of the results and to their discussion.

Most calculations were performed using the symbolic calculation device Maple$^{\mathrm{R}}$.

4.2.2 Theoretical

Let us consider an aqueous solution containing an electrolyte, $C_{\nu_C}A_{\nu_A}$, C being the cation and A the anion with stoichiometric numbers ν_C and ν_A, respectively. We denote by z_C the valence of the cation and by z_A that of the anion. Furthermore, we denote by h_C and h_A the hydration numbers of C and A, respectively. These numbers are supposed not to vary with salt concentration.

Hereafter we will use the subscripts W, C' and A' to designate the the *free* water (not bound to an ion), the *hydrated* cation and the *hydrated* anion, respectively (Figure 4.3). Quantities referring to the *total* water (bound plus free) will be designated by the subscript 1.

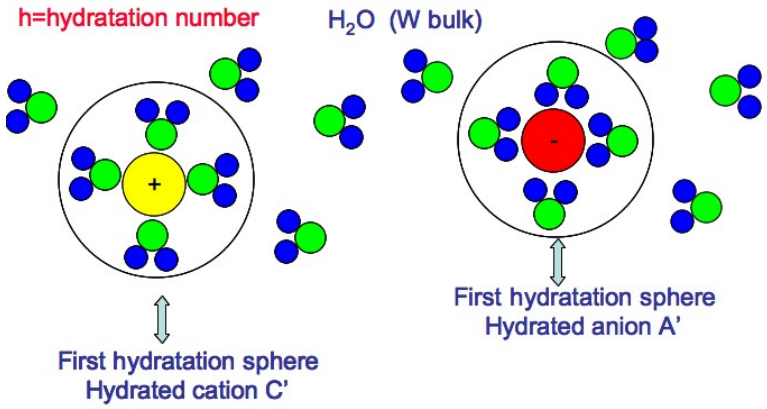

Figure 4.3: Hydration representation

We suppose that the hydrated cation and anion may associate to form the pair P=CA, of valence $z_C + z_A$ and hydration number h_P, according to the reaction

$$\mathrm{C(H_2O)}_{h_C} + \mathrm{A(H_2O)}_{h_A} \rightleftharpoons \mathrm{P(H_2O)}_{h_P} + (\mathrm{h}_C + \mathrm{h}_A - \mathrm{h}_P)\ \mathrm{H_2O}$$

the charges on the species being omitted for convenience. The association equilibrium constant for this reaction is

$$K = \frac{a_P a_W^{h_C + h_A - h_P}}{a_{C'} a_{A'}} \tag{4.14}$$

Basic thermodynamic relations.

The relevant set of particle numbers to be used in any model is

$$S_m \equiv \{N_W, N_{C'}, N_{A'}, N_P\} \tag{4.15}$$

Correspondingly, one may define the "true" mole fraction of a species i as

$$y_i \equiv \frac{N_i}{N_W + N_{C'} + N_{A'} + N_P} \tag{4.16}$$

Let us denote its activity coefficient at this level by g_i.

Any such activity coefficient, calculated using a given model, will have to be converted from the model level (with the set of variables S_m) to the Lewis-Randall

(LR) level, that is the level of the experimentalist, for which the relevant set of variables is

$$S_{LR} \equiv \{N_1, N_C, N_A\} \tag{4.17}$$

to which correspond the stoichiometric mole fractions

$$x_i \equiv \frac{N_i}{N_1 + N_C + N_A} \tag{4.18}$$

We will denote by f_i an activity coefficient on this mole fraction scale at the LR level.

According to the above assumptions, one has

$$N_C = N_{C'} + N_P \tag{4.19}$$

$$N_A = N_{A'} + N_P \tag{4.20}$$

$$N_1 = N_W + h_C N_{C'} + h_A N_{A'} + h_P N_P \tag{4.21}$$

The derivation of the activity coefficients of the species 1, C and A at the LR level from the activity coefficients of W, C' and A' at the model level may be deduced as follows.

For small variations of the particle numbers, the variation of the Gibbs energy of solution may be written as

$$\mathrm{d}G = \mu_W \mathrm{d}N_W + \mu_{C'} \mathrm{d}N_{C'} + \mu_{A'} \mathrm{d}N_{A'} + \mu_P \mathrm{d}N_P \tag{4.22}$$

for the set of variables S_m, at constant pressure and temperature. At the LR level, it is given by

$$\mathrm{d}G = \mu_1 \mathrm{d}N_1 + \mu_C \mathrm{d}N_C + \mu_A \mathrm{d}N_A \tag{4.23}$$

By replacing the LR variables by their expressions, eqs 4.19-4.21, in eq 4.23, one arrives at

$$\mathrm{d}G = \mu_1 \mathrm{d}N_W + (\mu_C + h_C\mu_1)\mathrm{d}N_{C'} + (\mu_A + h_A\mu_1)\mathrm{d}N_{A'} + (\mu_C + \mu_A + h_P\mu_1)\mathrm{d}N_P \tag{4.24}$$

Upon identification of this relation with eq 4.22 and considering that this equality holds for any small variation of S_m, one obtains

$$\mu_{C'} = \mu_C + h_C\mu_1 \tag{4.25}$$

$$\mu_{A'} = \mu_A + h_A\mu_1 \tag{4.26}$$

$$\mu_W = \mu_1 \tag{4.27}$$

$$\mu_P = \mu_C + \mu_A + h_P\mu_1$$

Henceforth, the use of eq 4.27 in eqs 4.25 and 4.26 leads to

$$\mu_X = \mu_{X'} - h_X \mu_W \tag{4.28}$$

for X= C or A, so giving the relation for the mean chemical potential of C or A at the LR level as a function of that for the hydrated ions and the free water, quantities that may be calculated in the framework of a suitable model.

Besides, one may write

$$\beta\mu_X = \beta\mu_X^{\otimes} + \ln(x_X f_X) \tag{4.29}$$

$$\beta\mu_{X'} = \beta\mu_{X'}^{\otimes} + \ln(y_{X'} g_{X'}) \tag{4.30}$$

for X= C or A, and

$$\beta\mu_W = \beta\mu_W^{\otimes} + \ln a_W \tag{4.31}$$

with $\mu_i^{\otimes}$ the standard chemical potential of species i and

$$\beta \equiv (k_B T)^{-1}$$

k_B being the Boltzmann constant and T the temperature.

Eqs 4.29-4.31 may be inserted into eq 4.28. The quantity $\mu_X^{\otimes}$ being independent of composition, one finds that

$$\mu_X^{\otimes} = \mu_{X'}^{\otimes} - h_X \mu_W^{\otimes} \tag{4.32}$$

by taking the limit of infinite dilution of salt. Then, by using eqs 4.29-4.32 in eq 4.28, we get

$$f_X = \frac{y_{X'}}{x_X a_W^{h_X}} g_{X'} \tag{4.33}$$

for X= C or A, which is the desired relation connecting the mean activity coefficient of X (X being in the form of X' and P), f_X, to the activity coefficient of the hydrated species X', $g_{X'}$.

Eq 4.33 provides a compact expression for converting the activity coefficient of an ion to the LR level. It is simpler than the usual two-step conversion method accounting for hydration and association (as explained for instance on pages 37 and 238 of ref. [16]).

The mean activity coefficient of salt in the LR system is

$$\ln f_\pm \equiv \frac{\nu_C}{\nu} \ln f_C + \frac{\nu_A}{\nu} \ln f_A \tag{4.34}$$

where $\nu \equiv \nu_C + \nu_A$.

Finally, the mean activity coefficient of salt on the molality scale, $\gamma_\pm$, is obtained using the classic conversion formula [1, 16]

$$\gamma_\pm = x_1 \, f_\pm \tag{4.35}$$

By combining eqs 4.33-4.35 and after rearrangement of terms, we find the new result

$$\ln \gamma_{\pm} = \ln g_{\pm} - \frac{h}{\nu} \ln a_W + \ln y_1 + \frac{1}{\nu}(\nu_C \ln \xi_C + \nu_A \ln \xi_A) \tag{4.36}$$

in which $g_{\pm}$ is the mean activity coefficient of the free ions C' and A', h is the total hydration number of free ions per molecule of salt

$$h \equiv \nu_C h_C + \nu_A h_A \tag{4.37}$$

y_1 is given formally by eq 4.16 applied to total water, and ξ_X is the fraction of free (non-associated) ion X. By introducing the fraction of associated anion (fraction of A forming the pair P), denoted by x, and the notation $a \equiv mM_1$, with m the molality of salt and M_1 the molar mass of solvent, it may be shown easily that

$$y_1 = \{1 + a[\nu - \nu_A x - h + \nu_A(h_C + h_A - h_P)x]\}^{-1} \tag{4.38}$$

$$\xi_C \equiv 1 - \frac{\nu_A}{\nu_C} x \tag{4.39}$$

$$\xi_A \equiv 1 - x \tag{4.40}$$

For a strong electrolyte ($x = 0$), eq 4.36 reduces to

$$\ln \gamma_{\pm} = \ln g_{\pm} - \frac{h}{\nu} \ln a_W + \ln y_1 \tag{4.41}$$

which is the result obtained by Robinson and Stokes (equation 9.17 of ref. [16]) since in that case (with $x = 0$ in eq 4.38)

$$y_1 = \frac{1}{1 + (\nu - h)a}$$

As for the solvent activity, eq 4.27 entails that

$$a_W = a_1 \tag{4.42}$$

because the two corresponding standard chemical potentials are equal.

By virtue of this equation, the osmotic coefficient can be calculated according to

$$\phi \equiv -\frac{x_1}{1 - x_1} \ln a_W \tag{4.43}$$

with

$$x_1 = 1/(1 + \nu a)$$

and

$$a_W = y_W g_W \tag{4.44}$$

The activity coefficients g_X may be calculated using the relation

$$\ln g_X \equiv \frac{\partial G}{\partial N_X} - \frac{\partial G}{\partial N_X}(N_C = N_A = 0) \tag{4.45}$$

with infinite dilution of salt as the reference state.

In this work, it is assumed that the Gibbs energy, G, may be split into decoupled long-range electrostatic ("el") and short-range contributions as

$$G = G^{el} + G^{SR} \tag{4.46}$$

Because of eq 4.45, it stems from this relation that

$$g_X = g_X^{el}\, g_X^{SR} \tag{4.47}$$

We now give the explicit forms taken for these contributions.

Electrostatic contribution to Gibbs energy.

Following our previous work [1], we take the restricted primitive MSA expression [7] for the electrostatic part of G, and extend it to the case of associating electrolytes. One then has

$$\beta G^{el} = -\lambda \frac{\Gamma}{1+\Gamma\sigma}\left(z_C^2 N_{C'} + z_A^2 N_{A'} + z_P^2 N_P\right) + \frac{\Gamma^3}{3\pi} V \tag{4.48}$$

with V being the volume of solution, σ the mean ionic diameter in water, λ the Bjerrum distance (*ca.* 0.7 nm for water at 25°C) and Γ the MSA screening parameter,

$$\Gamma = \frac{1}{2\sigma}\left(\sqrt{1+2\kappa\sigma} - 1\right) \tag{4.49}$$

with κ the Debye screening parameter

$$\kappa = \sqrt{4\pi\lambda(\rho_{C'} z_C^2 + \rho_{A'} z_A^2 + \rho_P z_P^2)}$$

Using eqs 4.45 and 4.48 for Y= C', A' or W (with $z_W = 0$), one finds

$$\ln g_Y^{el} = -\lambda \frac{\Gamma}{1+\Gamma\sigma} z_Y^2 + \frac{\Gamma^3}{3\pi}\frac{\partial V}{\partial N_Y} \tag{4.50}$$

with the differentiation of eq 4.48 being performed at constant Γ [1]. In the second term of the r.h.s. of this equation, application of the chain rule for partial derivatives for the sets of variables S_m and S_{LR} leads to

$$\left[\frac{\partial V}{\partial N_{C'}}\right]_{N_W,N_{A'},N_P} = \left[\frac{\partial V}{\partial N_C}\right]_{N_A,N_1}\left[\frac{\partial N_C}{\partial N_{C'}}\right]_{N_W,N_{A'},N_P} + \left[\frac{\partial V}{\partial N_1}\right]_{N_C,N_A}\left[\frac{\partial N_1}{\partial N_{C'}}\right]_{N_W,N_{A'},N_P}$$

and a similar result for the differentiation w.r.t. $N_{A'}$, and

$$\left[\frac{\partial V}{\partial N_W}\right]_{N_{C'},N_{A'},N_P} = \left[\frac{\partial V}{\partial N_1}\right]_{N_C,N_A}\left[\frac{\partial N_1}{\partial N_W}\right]_{N_{C'},N_{A'},N_P}$$

By using these last two equations together with eqs 4.19-4.21, one gets in more compact form (without mentioning the variables kept constant in the differentiation)

$$\frac{\partial V}{\partial N_{X'}} = \frac{\partial V}{\partial N_X} + h_X \frac{\partial V}{\partial N_1} \tag{4.51}$$

for X= C or A, and

$$\frac{\partial V}{\partial N_W} = \frac{\partial V}{\partial N_1} \tag{4.52}$$

Following ref. [1], we make the simplification that

$$\frac{\partial V}{\partial N_C} = \frac{\partial V}{\partial N_A} = 0 \tag{4.53}$$

which avoids the knowledge of solution densities and constitutes a good approximation [1]. Thus,

$$\frac{\partial V}{\partial N_1} = M_1/\mathcal{N}d_1$$

with $\mathcal{N}$ the Avogadro number and d_1 the density of water.

With this simplification, we obtain from eqs 4.50-4.53

$$\ln g^{el}_{X'} = -\lambda \frac{\Gamma}{1+\Gamma\sigma} z_X^2 + h_X \frac{\Gamma^3}{3\pi}\frac{\partial V}{\partial N_1} \tag{4.54}$$

$$\ln g^{el}_{W} = \frac{\Gamma^3}{3\pi}\frac{\partial V}{\partial N_1} \tag{4.55}$$

SR contribution to Gibbs energy.

For the SR part of G, we use the NRTL model for the system composed of the species: the *hydrated* cation C', the *hydrated* anion A' and the free water W.

The NRTL model is a local composition model that was proposed by Renon and Prausnitz [32]. It has relationship [33] with Guggenheim's quasi-chemical lattice theory [34]. The main features of its application to ionic solutions have been reported in earlier work [12, 13, 1]. Below we recall the basic ingredients of the model. We also discuss how it may be applied to solutions of plurivalent and associating electrolytes.

In the NRTL model, the excess SR Gibbs energy per particle i is given by

$$\bar{G}_i^{NRTL} = \sum_j x_j p_{ji} w_{ji} / \sum_j x_j p_{ji} \tag{4.56}$$

where

$$p_{ji} = \exp(-\alpha\beta w_{ji}) \tag{4.57}$$

is proportional to the "probability" of finding a particle of type j in the close vicinity of particle i, with w_{ji} the i-j interaction energy ($w_{ij} = w_{ji}$) and α the non-random parameter related to the mean coordination number, Z, appearing in the lattice model of Guggenheim for nonrandom mixtures [34] as [32, 33]

$$\alpha = \frac{2}{Z} \tag{4.58}$$

In eq 4.56, the quantity p_{ji} is responsible for non-randomness in the distribution of species around a given particle (randomness corresponding to $\alpha = 0$ or $\beta = 0$, $p_{ji} = 1$). Here we take $\alpha = 0.3$, meaning that each species (*hydrated* ion or solvent molecule) has *ca.* 6 closest neighbors according to eq 4.58.

If we set

$$\tau_{ji} \equiv \beta(w_{ji} - w_{ii}) \tag{4.59}$$

then eq 4.56 may be rewritten as

$$\bar{G}_i^{NRTL} = \sum_j x_j P_{ji} w_{ji} / \sum_j x_j P_{ji} \tag{4.60}$$

with

$$P_{ji} = \exp(-\alpha \tau_{ji}) \tag{4.61}$$

The advantage of the transformation of Eq 4.56 into Eq. 4.60 is to reduce the number of parameters, and becomes more obvious in Eq 4.68-4.74 (one fewer parameter). Eq 4.60 may be written more simply as a function of the τ parameters by introducing suitable NRTL reference energies [12, 13]. By writing [1]

$$\Delta \bar{G}_i^{NRTL} \equiv \bar{G}_i^{NRTL} - \bar{G}_i^{NRTL,ref} \tag{4.62}$$

it may be easily shown that the use of these quantities in eq 4.45 leads to the same expressions for the activity coefficients as when using the true excess energies (eq 4.60).

If i is not charged, then $P_{ii} = 1$ because $\tau_{ii} = 0$. Thus, taking $\bar{G}_i^{NRTL,ref} = w_{ii}$ yields

$$\Delta \bar{G}_i^{NRTL} = \frac{\sum_{j \neq i} x_j P_{ji} \tau_{ji}}{\sum_{j \neq i} x_j P_{ji} + x_i} \tag{4.63}$$

If i is charged, we adopt the simplification [12] $P_{ii} = 0$ because of electrostatic mutual exclusion of like charged ions. In that case, one may take $\bar{G}_i^{NRTL,ref} = w_{ki}$ where k is a counterion for i ($z_k z_i < 0$), which gives

$$\Delta \bar{G}_i^{NRTL} = \frac{\sum_{j \neq i} x_j P_{ji,ki} \tau_{ji,ki}}{\sum_{j \neq i} x_j P_{ji,ki}} \tag{4.64}$$

with

$$\tau_{ji,ki} \equiv \beta(w_{ji} - w_{ki}) \tag{4.65}$$

$$P_{ji,ki} \equiv \exp(-\alpha\tau_{ji,ki}) = P_{ji}/P_{ki} \tag{4.66}$$

One notices that $P_{ji,ki} = 0$ if j and i have the same charge sign ($z_j z_i > 0$) and $P_{ji,ki} = 1$ if $j = k$.

Finally, activity coefficients arising from the SR interaction may be obtained by differentiation of the SR Gibbs energy (according to eq 4.45), given by

$$G^{SR} = N_W \Delta\bar{G}_W^{NRTL} + N_{C'} \Delta\bar{G}_{C'}^{NRTL} + N_{A'} \Delta\bar{G}_{A'}^{NRTL} + N_P \Delta\bar{G}_P^{NRTL} \tag{4.67}$$

It is worth noting that, in the present work, we treat monovalent and plurivalent electrolytes on an equal footing in the NRTL model framework. So, we do not introduce the valences of the ions in the NRTL expressions as done elsewhere [12, 13], for which we do not see any clear justification. On the other hand, the stoichiometric numbers ν_i have a direct and obvious effect on the relative populations of C', A' and P and this effect is included in the above NRTL expressions (for instance, $x_{C'}/x_{A'} = \nu_C/\nu_A$ for a strong electrolyte).

Negatively charged pair. In the case that the pair P is negatively charged (as in the case of sulfuric acid), the application of eq 4.60 yields

$$\bar{G}_W^{NRTL} = \frac{x_{C'} P_{C'W} w_{C'W} + x_{A'} P_{A'W} w_{A'W} + x_P P_{PW} w_{PW} + x_W w_{WW}}{x_{C'} P_{C'W} + x_{A'} P_{A'W} + x_P P_{PW} + x_W} \tag{4.68}$$

$$\bar{G}_{C'}^{NRTL} = \frac{x_{A'} P_{A'C'} w_{A'C'} + x_P P_{PC'} w_{PC'} + x_W P_{WC'} w_{WC'}}{x_{A'} P_{A'C'} + x_P P_{PC'} + x_W P_{WC'}} \tag{4.69}$$

$$\bar{G}_{A'}^{NRTL} = \frac{x_{C'} P_{C'A'} w_{C'A'} + x_W P_{WA'} w_{WA'}}{x_{C'} P_{C'A'} + x_W P_{WA'}} \tag{4.70}$$

the expression for $\bar{G}_P^{NRTL}$ being obtained by replacing A' by P in eq 4.70. One notices that, besides the mutual exclusion of cations C ($P_{C'C'} = 0$) and anions ($P_{A'A'} = 0$), no PP or A'P term appears in these expressions ($P_{PP} = P_{A'P} = 0$) because of electrostatic repulsion between these species.

As indicated by eq 4.62, the reference energies w_{WW}, w_{PC}, $w_{C'A'}$, $w_{C'P}$ may be subtracted from $\bar{G}_W^{NRTL}$, $\bar{G}_{C'}^{NRTL}$, $\bar{G}_{A'}^{NRTL}$ and $\bar{G}_P^{NRTL}$, respectively. Thus, after some simple algebra, one gets

$$\Delta\bar{G}_W^{NRTL} = \frac{x_{C'} P_{C'W} \tau_{C'W} + x_{A'} P_{A'W} \tau_{A'W} + x_P P_{PW} \tau_{PW}}{x_{C'} P_{C'W} + x_{A'} P_{A'W} + x_P P_{PW} + x_W} \tag{4.71}$$

$$\Delta\bar{G}_{C'}^{NRTL} = \frac{x_{A'} P_{A'C',PC'} \tau_{A'C',PC'} + x_W P_{WC',PC'} \tau_{WC',PC'}}{x_{A'} P_{A'C',PC'} + x_P + x_W P_{WC',PC'}} \tag{4.72}$$

$$\Delta\bar{G}_{A'}^{NRTL} = \frac{x_W P_{WA',C'A'} \tau_{WA',C'A'}}{x_{C'} + x_W P_{WA',C'A'}} \tag{4.73}$$

$$\Delta\bar{G}_P^{NRTL} = \frac{x_W P_{WP,C'P}\tau_{WP,C'P}}{x_{C'} + x_W P_{WP,C'P}} \tag{4.74}$$

The NRTL Gibbs energies (eqs 4.71-4.74) are expressed as a function of 5 independent interaction parameters: $\tau_{C'W}$, $\tau_{A'W}$, τ_{PW}, $\tau_{WC',A'C'}$ and $\tau_{WC',PC'}$, that is 1 fewer parameter than the 6 independent w_{ij} parameters. The other parameters are given by the following relations

$$\tau_{WX,C'X} = \tau_{WC',XC'} + \tau_{XW} - \tau_{C'W} \tag{4.75}$$

for X= A' or P, and

$$\tau_{A'C',PC'} = \tau_{WC',PC'} - \tau_{WC',A'C'} \tag{4.76}$$

Uncharged pair. In the case that the pair is not charged, as for nitric acid, eqs 4.73 and 4.74 must be modified to allow for the presence of P in the vicinity of A' and P. Eqs 4.71 and 4.72 remain unchanged.

With the reference Gibbs energies $w_{C'A'}$ and w_{PP} for A and P, respectively, one gets

$$\Delta\bar{G}_{A'}^{NRTL} = \frac{x_P P_{PA',C'A'}\tau_{PA',C'A'} + x_W P_{WA',C'A'}\tau_{WA',C'A'}}{x_{C'} + x_P P_{PA',C'A'} + x_W P_{WA',C'A'}} \tag{4.77}$$

$$\Delta\bar{G}_P^{NRTL} = \frac{x_{C'} P_{C'P}\tau_{C'P} + x_{A'} P_{A'P}\tau_{A'P} + x_W P_{WP}\tau_{WP}}{x_{C'} P_{C'P} + x_{A'} P_{A'P} + x_P + x_W P_{WP}} \tag{4.78}$$

These relations involve 7 independent parameters: $\tau_{C'W}$, $\tau_{A'W}$, τ_{PW}, $\tau_{C'P}$, $\tau_{A'P}$, τ_{WP} and $\tau_{WC',A'C'}$. The other parameters contained in eqs 4.71, 4.72, 4.77 and 4.78 are related to this set through the following relations. The parameter $\tau_{WA',C'A'}$ is given by eq 4.75 and one has the relations

$$\tau_{WC',PC'} = \tau_{WP} - \tau_{C'P} + \tau_{C'W} - \tau_{PW} \tag{4.79}$$

and

$$\tau_{PA',C'A'} = \tau_{A'P} - \tau_{WP} + \tau_{PW} - \tau_{C'W} + \tau_{WC',A'C'} \tag{4.80}$$

$$\tau_{A'C',PC'} = -\tau_{PA',C'A'} + \tau_{A'P} - \tau_{C'P} \tag{4.81}$$

Strong electrolytes. The case of strong electrolytes may be approached by using eqs 4.71-4.73 and setting $x_P = 0$, involving 3 independent NRTL interaction parameters: $\tau_{C'W}$, $\tau_{A'W}$, $\tau_{WC',A'C'}$.

Solution of association equilibrium.

Eq 4.14 may be rewritten as follows

$$x - K\,\frac{a(\nu_C - \nu_A x)(1-x)}{1 + a[\nu - \nu_A x - h + \nu_A x(h_C + h_A - h_P)]}\,\frac{g_{C'}g_{A'}}{g_P a_W^{h_C+h_A-h_P}} = 0 \tag{4.82}$$

in which a_W is given by eq 4.44 and the activity coefficients g_i may be computed according to eqs 4.45 and 4.47.

Eq 4.82 was solved numerically for x by using a Newton-Raphson algorithm. The activity coefficients of the species C', A', P and W were computed as a function of x, by utilizing eq 4.47. This procedure gives the composition of solution for given values of K and of the model parameters.

4.2.3 Dependence of thermodynamic quantities vs. hydration numbers.

An important question that arises within the present framework is the following. For a given binary aqueous solution, can a fit of the thermodynamic properties give information on the individual ionic hydration numbers, h_C and h_A ?

Close examination of eqs 4.41 and 4.43 shows that, for a strong electrolyte, $\gamma_\pm$ and ϕ are functions of h only (h is defined through eq 4.37). This may be seen by developing eq 4.41 as

$$\ln \gamma_\pm = \frac{1}{\nu}\left(\nu_C \ln g_C^{el} + \nu_A \ln g_A^{el} - h \ln g_W^{el}\right) + \ln g_\pm^{SR} - \frac{h}{\nu}\ln(y_W g_W^{SR}) - \ln[1 + (\nu - h)a] \tag{4.83}$$

In the first term of the r.h.s. of this relation, the hydration numbers h_C and h_A contained in $\ln g_C^{el}$ and $\ln g_A^{el}$ (see eq 4.54) turn out to be cancelled by the term $h \ln g_W^{el}$. Note that the same result holds if the approximation expressed by eq 4.53 is relaxed. The other terms of this relation are functions of h, because h_C and h_A only appear in

$$N_W = N_1 - hN_{salt}$$

according to eqs 4.21 and 4.37, with N_{salt} the number of salt molecules introduced in solution. For the same reason, ϕ is a function of h.

Therefore, for a strong electrolyte, the present model may allow the determination of the sole h, not h_C or h_A individually.

The situation for an associating electrolyte requires more scrutiny, showing that the result depends on the stoichiometry of the salt.

In the case of symmetric electrolytes, that is for salts such that $\nu_C = \nu_A = \nu_i$, the conclusion is identical to that for a strong electrolyte, which may be understood as follows. Besides the fact that the hydration numbers again cancel in the term $\nu_C \ln g_C^{el} + \nu_A \ln g_A^{el} - h \ln g_W^{el}$, all terms turn out to be functions of $h_C + h_A$, as for instance in y_1 (eq 4.38). Since in that case $h_C + h_A = h/\nu_i$, it stems that $\ln \gamma_\pm$ is a function of h, and so does ϕ.

On the other hand, in the case of asymmetric associating electrolytes ($\nu_C \neq \nu_A$), the expressions of $\ln \gamma_\pm$ and ϕ cannot be handled so as to become functions of h

alone. Obviously, this result is due to the fact that the cation/anion molar ratio, equal to $(\nu_C - \nu_A x)/(\nu_A - \nu_A x)$, varies with the association rate x.

These conclusions should be independent of the model used for electrostatic and SR interactions, provided the latter are expressed in terms of the variables contained in S_m (definition 4.15).

4.2.4 Results and discussion

In the first place, it was verified numerically that the osmotic coefficient ϕ and the mean salt activity coefficient $\gamma_\pm$, given respectively by eqs 4.43 and 4.35, accurately satisfy the Gibbs-Duhem relation. This was done for strong electrolytes and for associating acids. This precaution gives strong support to the validity of the whole procedure of calculating the thermodynamic quantities at the LR level.

Parameter values were adjusted by simultaneously fitting experimental osmotic and activity coefficients data for strong electrolytes [35] at 25°C, using a least-square minimization algorithm of the Marquardt type. The numerical values for these thermodynamic quantities were obtained from the NIST databank [36], in which primary data for uni-univalent salts are taken from the compilation of Hamer and Wu [37]. In the fits, the minimum salt concentration was 0.1 mol kg^{-1} and the maximum salt concentration was limited to 6 mol kg^{-1} for 1-1 salts and acids, and to 4 mol kg^{-1} for 2-1 salts, except for those salts whose saturation point is below these values, as is the case for KCl (5 mol kg^{-1}), KBr (5.5 mol kg^{-1}), KI (4.5 mol kg^{-1}) and CaI_2 (1.915 mol kg^{-1}).

For a given fit, the average absolute relative deviation (AARD) was computed and taken as an indicator of the quality of fit.

Strong electrolytes.

The advantage of introducing hydration numbers in the MSA-NRTL model is shown in Table 1 in which results are given for fits with fixed hydration number value, in the case of LiCl and $MgCl_2$ aqueous solutions. It is seen that outside intervals of 3-5 for LiCl and 8-10 for $MgCl_2$ the quality of fits is not satisfactory (Figure 4.4).

It is worth of note that these figures coincide with the order of magnitude that may be expected for h if one adds a small chloride hydration number (of the order of unity) to the likely hydration number values for these cations, namely $h_{Li^+} \simeq 4$ [19, 25] and $h_{Mg^{2+}} = 6$ [22, 25].

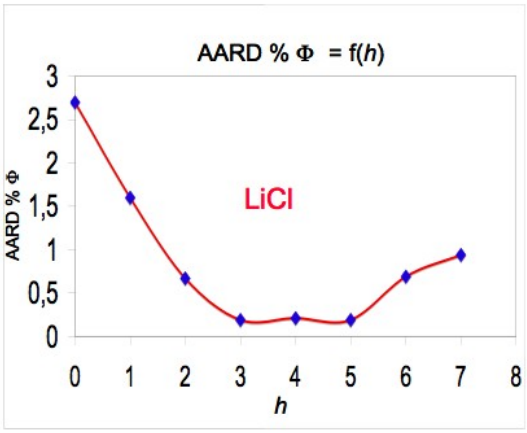

Figure 4.4: Value effect of hydration number as a function of the osmotic coefficient

Table 1. Results of fits for various values of the total hydration number, h (eq 4.37), in the case of LiCl (range= 0.1-6 mol kg^{-1})and $MgCl_2$ (range= 0.1-4 mol kg^{-1}) aqueous solutions.

Salt	h	$\tau_{C'W}$	$\tau_{A'W}$	$\tau_{WC',A'C'}$	σ^a	AARD$_\phi{}^b$ (%)	$AARD_{\gamma_\pm}{}^c$
LiCl	0	16.4	-3.70	-4.07	0.135	2.7	4.4
	1	22.6	-3.19	-3.99	0.259	1.6	2.8
	2	53.4	-2.68	-4.11	0.389	0.67	1.1
	3	1.36	-2.21	-8.45	0.475	0.19	0.21
	4	-1.57	-0.853	0.678	0.484	0.21	0.24
	5	-2.37	-1.74	3.39	0.468	0.19	0.22
	6	-1.50	-1.50	2.82	0.568	0.69	1.1
	7	4.04	4.04	0.272	0.638	0.94	1.5
$MgCl_2$	4	53.0	-2.86	-4.19	0.421	2.6	4.1
	5	-0.113	-2.35	-3.04	0.468	1.6	2.3
	6	194	-2.40	0.261	0.529	0.71	0.99
	7	-2.92	-0.665	-0.529	0.529	0.68	0.95
	8	-2.60	-1.17	0.993	0.537	0.57	0.78
	9	-2.58	-1.38	1.91	0.545	0.45	0.60
	10	-2.72	-1.54	2.70	0.559	0.40	0.64
	11	-2.51	-1.32	2.50	0.613	0.85	2.2
	12	-2.16	-1.02	2.16	0.663	1.6	3.6
	13	2.58	3.08	-0.464	0.749	2.7	5.8

^{a} the mean ionic size of the ion in nm; ^{b}Average Absolute Relative Deviation (AARD) for ϕ; ^{c}AARD for $\gamma_\pm$.

Table 2. Results for parameter values: 1-1 electrolytes (range= 0.1-6 mol kg^{-1}) and 2-1 electrolytes (range= 0.1-4 mol kg^{-1}).

Salt	$\tau_{C'W}$	$\tau_{A'W}$	$\tau_{WC',A'C'}$	σ^a	h	AARD$_\phi{}^b$ (%)	$AARD_{\gamma_\pm}{}^c$
HCl	-1.90	-1.40	1.82	0.473	4.15	0.10	0.14
HBr	-1.90	-1.60	2.15	0.512	5.07	0.12	0.19
HI	-1.90	-1.82	2.39	0.699	4.98	0.19	0.25
LiCl	-1.60	-1.40	2.22	0.489	4.94	0.23	0.28
LiBr	-1.60	-1.60	2.04	0.443	4.75	0.20	0.28
LiI	-1.60	-1.82	3.05	0.755	6.49	0.43	0.48
NaCl	-0.80	-1.40	2.97	0.440	5.61	0.15	0.20
NaBr	-0.80	-1.60	2.62	0.446	4.39	0.16	0.20
NaI	-0.80	-1.82	2.58	0.487	4.13	0.07	0.08
KCl	1.00	-1.40	2.45	0.407	3.27	0.05	0.05
KBr	1.00	-1.60	2.02	0.420	2.11	0.07	0.06
KI	1.00	-1.82	1.01	0.484	0.842	0.09	0.08
$MgCl_2$	-2.71	-1.40	2.22	0.550	9.50	0.41	0.55
$MgBr_2$	-2.71	-1.60	1.27	0.554	7.83	0.21	0.29
MgI_2	-2.71	-1.82	0.908	0.565	7.76	0.31	0.57
$CaCl_2$	-2.32	-1.40	2.37	0.522	9.25	0.17	0.21
$CaBr_2$	-2.32	-1.60	2.43	0.585	9.53	0.13	0.16
CaI_2	-2.32	-1.82	2.14	0.609	8.87	0.17	0.16
Li_2SO_4	-1.60	-2.25	4.67	0.434	9.56	0.30	0.19

[a]In nm; [b]Average Absolute Relative Deviation (AARD) for ϕ; [c]AARD for $\gamma_\pm$.

Next, the hydration number h was also regressed. The results for some 1-1 and 2-1 salts in water are shown in Table 2. Common values were determined for the τ parameters. So, the value obtained for $\tau_{Li^+{}'W}$ is common for all salts containing the lithium cation and similarly $\tau_{Cl^-{}'W}$ is the same for all chlorides. On the other hand, the total hydration number h and the parameters $\tau_{WC',A'C'}$ and σ, are characteristic of each salt.

The set of values of Table 2 was determined by first fitting the data for the alkaline earth halides MgX_2 and CaX_2, X being an halide, with initial values for the τ's and for h that were set to 0 and 8, respectively. The plots of experimental and calculated osmotic coefficient are shown in the Figure 4.5 and 4.6. The fits of the osmotic coefficient for 1-1 and 2-2 electrolytes are satisfactory.

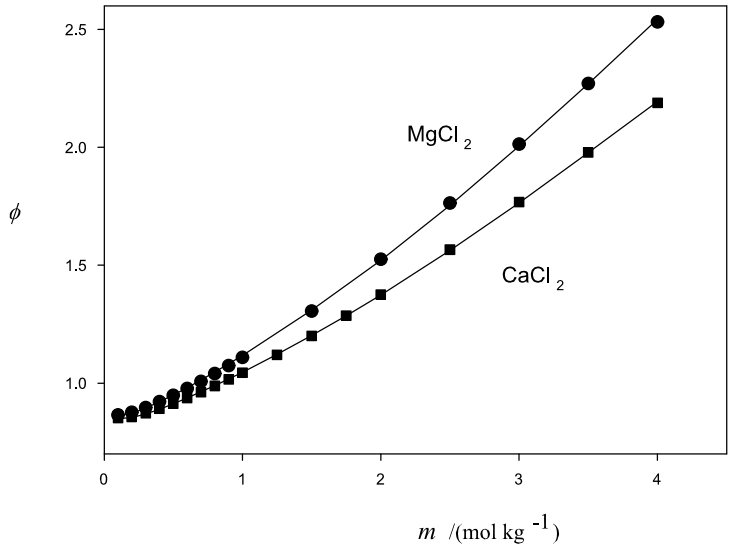

Figure 4.5: Osmotic coefficient as a function of molality for $MgCl_2$ aqueous solution. Symbols: experimental data. Solid line: result of fit.

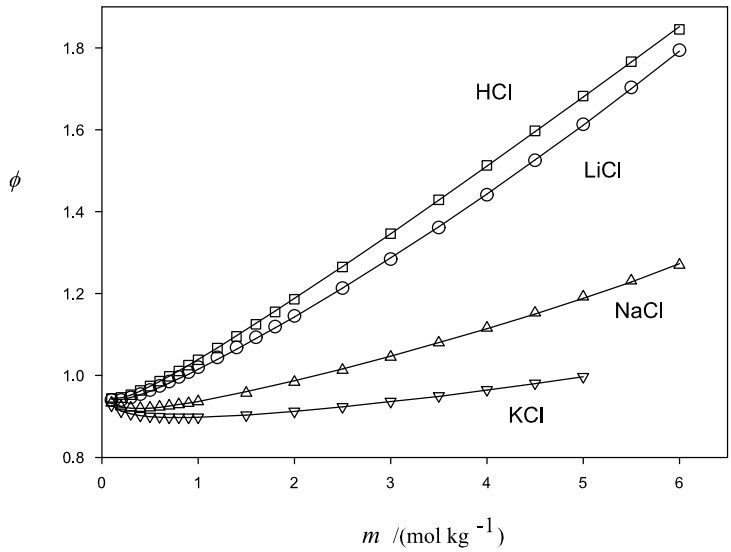

Figure 4.6: Osmotic coefficient as a function of molality for 1-1 salt aqueous solution. Symbols: experimental data. Solid line: result of fit.

It was noticed that the resulting values for $\tau_{C'W}$ and $\tau_{A'W}$ were weakly dependent on the nature of A and C, respectively. Moreover, the results of fits were found to be relatively insensitive to the initial parameter values. Therefore it was felt that these values for the τ's could constitute an "optimum" set, and the $\tau_{A'W}$ values for the halides were used to fit the data for the alkali halides and the simple acids HCl, HBr and HI. Thus, common $\tau_{C'W}$ values for the alkali cations and H^+ were determined. Let us mention that the latter are indicative values in the case of the alkali cations because the fits for the 3 halides did not point to consistent common values for $\tau_{C'W}$ for a given alkali cation. On the other hand, the value $\tau_{H^+W} = -1.9$ may be regarded as an "optimum" one because fitting the 3 acids approximately gave this common value.

The following comments may be made concerning the results of Table 2.

It is observed that the values found for h exhibit a clear gap between 1-1 and 2-1 salts, with values of 4.9 $\pm$ 0.7 for the former (without taking into account potassium salts for which h is lower) and of 8.8 $\pm$ 0.8 for the latter. Again, and somewhat surprisingly, these average values are reasonable orders of magnitude for h, as may be inferred for these salts from experimental and simulation studies. Indeed, one recovers these figures if one relies on typical h_C values of 4 and 6 for monovalent [18, 19, 20, 25] and divalent [22, 23, 25] cations, respectively, and if one takes $h_A \simeq 1$ for halide anions. The latter is plausible in view of experimental [38, 39, 40] and simulation [24] studies suggesting that the halides Cl^-, Br^- and I^- be weakly hydrated as compared to small and/or plurivalent cations.

Despite the reservation made in the case of alkali cations and although the τ parameters do not have a clear physical meaning, it is observed that the value of the quantity $-\tau_{C'W}$ increases with the polarizing power of the cation C (in particular for small and doubly charged ions). It increases in the order K< Na < Li < H < Ca < Mg . Let us recall that, according to eq 4.59, a negative value of $\tau_{C'W}$ indicates that the C'-W interaction (C' representing the hydrated cation), $w_{C'W}$, is stronger than the WW interaction, w_{WW}. The values of the parameter $\tau_{A'W}$ are of the same order of magnitude for the halide anions, Cl^-, Br^- and I^-. It is observed that they are more negative for the more polarizable anions, the quantity $-\tau_{A'W}$ being in the order I>Br>Cl. The parameter $\tau_{WC',A'C'}$ has an average value of the order of 2, with values between *ca.* 0.9 and 3 for the halide salts. Besides, the value of the mean ionic diameter, σ, has a reasonable magnitude and, as expected, it increases when going from the smaller halide (Cl^-) to the bigger one (I^-) for a given cation, except for LiBr.

Let us mention that, as compared to our previously reported results [1], the present values for $\tau_{C'W}$ and $\tau_{WC',A'C'}$ are significantly smaller in absolute value. Thus, instead of $\tau_{H^+W} = -8.5$ in our former work [1], we now get $\tau_{H^+{}'W} = -1.9$. This result is consistent with the expectation, mentioned in the Introduction section, that the characteristic cation-water interaction should be weaker in a model separately accounting for hydration. In our previous MSA-NRTL model, τ_{CW} was supposed to account for the (bare) cation-water interaction in which the water belonged to the first and second hydration shells. In the present model, the cation-first hydration shell water interaction is accounted for by attaching water molecules to the cation and $\tau_{C'W}$ is supposed to describe the expected weaker C'-second hydration shell water interaction.

The Li_2SO_4 solution was considered for a determination of the $\tau_{SO_4{}^{2-}{}'W}$ parameter, for which the fit gave a value of *ca.* -2.25, to be used in the next section in the case of sulfuric acid.

Aqueous sulfuric acid solutions.

The experimental values given by the NIST databank originate from the work of Rard *et al.* [41]. The osmotic and activity coefficients for aqueous sulfuric acid solutions were fitted in the range 0.1-6 mol kg^{-1}.

The τ values determined in the previous section for the H^+ and SO_4^{2-} ions, $\tau_{H^+{}'W} = -1.90$ and $\tau_{SO_4{}^{2-}{}'W} = -2.25$, were utilized for this calculation. The remaining adjustable NRTL parameters are τ_{PW}, $\tau_{WC',A'C'}$ and $\tau_{WC',PC'}$. The other parameters are K, σ, h_C, h_A and h_P. This is a great number of adjustable parameters. However, the thermodynamic quantities are very sensitive to the values of K and of the hydration numbers, and to the size σ at low salt concentration, which favors the determination of a unique set of "optimum" parameter values in the fit. Fitting the proportion of association together with the thermodynamic quantities further enhances this feature.

Let us notice that, in all the fits, the resulting value for h_P was zero, indicating an unhydrated bisulfate anion, which is not irrealistic for this big monovalent anion.

The association constant K is related to its equivalent K_m, defined on the molality scale, according to the relation [16], $K = K_m/M_1$. Values of between *ca.* 83 and 97 kg mol^{-1} have been reported [42, 43, 44] for K_m.

First, the value adopted by Pitzer *et al.* [44], $K_m = 95.2$ kg mol^{-1}, was adopted and the parameters τ_{PW}, $\tau_{WC',A'C'}$, $\tau_{WC',PC'}$, σ, h_C, h_A (and h_P) were adjusted. This led to the parameter set no. 1 presented in Table 3, with a good fit of both thermodynamic quantities and plausible values for the hydration numbers h_C and h_A. The value $h_C = 4.07$ is of the same order as for HCl and the value $h_A = 7.1$ is

Table 3. Results for parameter values in the case of sulfuric acid, with $\tau_{H^+{}'W} = -1.9$ and $\tau_{SO_4{}^{2-}{}'W} = -2.25$ (values taken from Table 2). In all cases, $h_P = 0$.

Set no.[a]	K_m[b]	τ_{PW}	$\tau_{WC',A'C'}$	$\tau_{WC',PC'}$	σ[c]	h_C	h_A	AARD$_\phi$[d]	$AARD_{\gamma_\pm}$[e]
1	95.2	-3.44	5.77	5.73	0.517	4.07	7.10	0.16	0.09
2	96.8	-3.53	5.78	5.95	0.559	3.95	7.98	0.13	0.08
3	85.5	-3.71	5.13	5.59	0.291	2.55	5.26	0.36	0.28

[a] See text for meaning; [b] In units of kg mol^{-1}; [c] In nm; [d] Average Absolute Relative Deviation (AARD) in % for ϕ; [e] (AARD) in % for $\gamma_\pm$.

at the lower end of the range determined experimentally (7-12) for the number of water molecules in the first hydration shell of SO_4^{2-} [25].

In a second step, it was chosen to also adjust K_m, together with the other parameters. This gave the results of set no. 2. The parameter values and the quality of fit are not greatly modified as compared to the set no. 1.

Lastly, it was attempted to fit at the same time ϕ, $\gamma_\pm$ and the proportion of associated sulfate (the bisulfate ion HSO_4^-), x. In the least-square minimization procedure, a smaller weight of 0.2 was given to the effect of the deviation of x because the experimental values of x are quite scattered. The latter were taken from the Raman data of Chen and Irish [45], Knopf *et al.* [26] and Lund Myrhe *et al.* [46]. The fit led to the parameter values of set no. 3 in Table 3. The corresponding plots of the experimental and calculated osmotic and activity coefficients are shown in Figures 4.7 and 4.8, respectively. The plot of the proportion of bisulfate HSO_4^-, x, vs. molality is shown in Figure 4.9. It exhibits a sinuous profile, similar to the experimental profile obtained by Young [47], plotted in ref. [45].

These satisfying results are obtained with parameter values that are appreciably different from those of sets no. 1 and 2. In particular, K_m is significantly smaller, although in the admitted range of 83-97 [42, 43, 44], and the mean ionic size and the hydration numbers h_C and h_A are greatly decreased. The parameters σ and h_C are much smaller than for the acids HCl, HBr and HI. The hydration number h_A is smaller than the reported lower bound of 7 [25]. We note that considering only the higher x values of Chen and Irish (empty circles in (Figure 4.9) in the fit only slightly modifies these values. Therefore, the model experiences some difficulties in

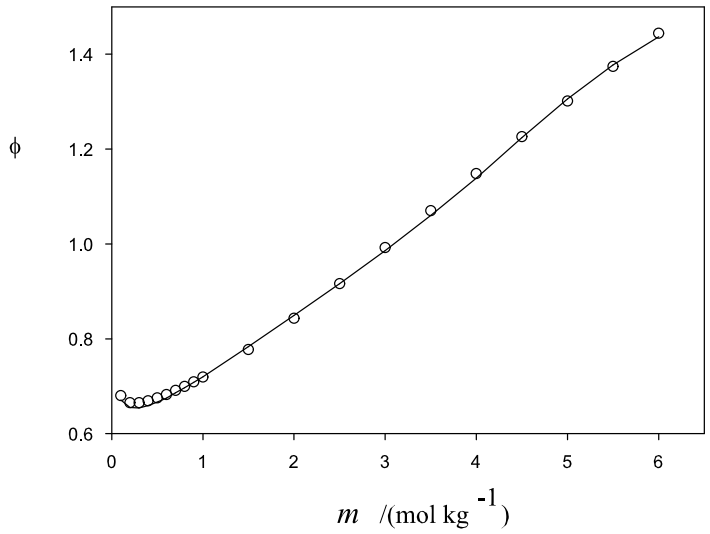

Figure 4.7: Osmotic coefficient as a function of molality for aqueous sulfuric acid solution. Symbols: experimental data. Solid line: result of fit.

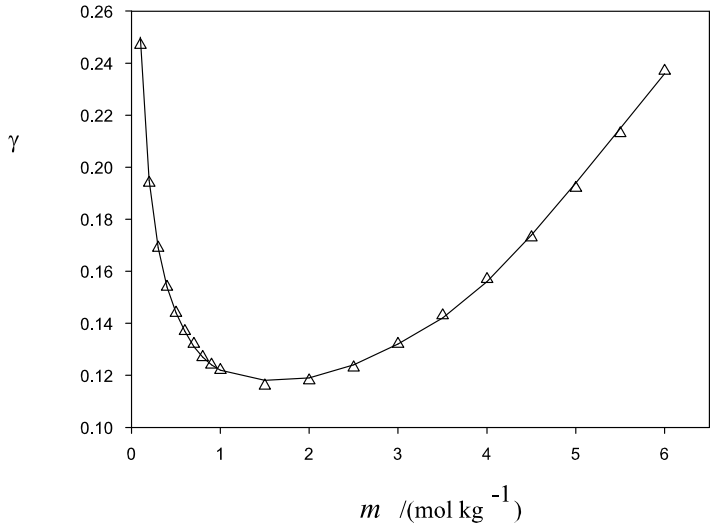

Figure 4.8: Activity coefficient as a function of molality for aqueous sulfuric acid solution. Symbols: experimental data. Solid line: result of fit.

this double representation, which may originate from inadequacies in the model or from experimental issues, as suggested by the large scatter of the data.

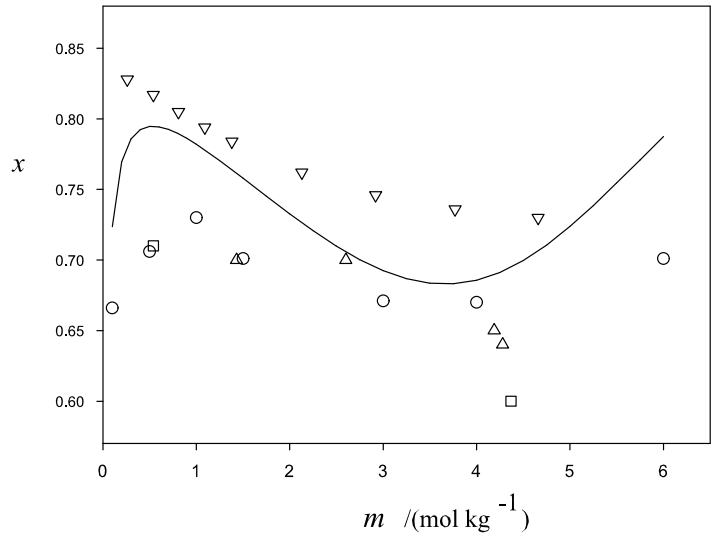

Figure 4.9: Degree of association of sulfate ion (forming HSO_4^-) as a function of molality. Symbols: experimental data of Chen and Irish [45] ($\bigtriangledown$), Knopf *et al.* [26] (empty square), Lund Myrhe [46] ($\bigtriangleup$) and Young [47] ($\circ$). Solid line: result of fit.

Aqueous nitric acid solutions.

As shown above the adjustable NRTL parameters in this case are $\tau_{C'W}$, $\tau_{A'W}$, τ_{PW}, $\tau_{C'P}$, $\tau_{A'P}$, τ_{WP} and $\tau_{WC',A'C'}$. In order to reduce the number of parameters, it was assumed that the HNO_3 pair has the same NRTL interaction parameters as water, which simplification amounts to

$$\tau_{PW} = \tau_{WP} = 0 \qquad \tau_{C'P} = \tau_{C'W} \qquad \tau_{A'P} = \tau_{A'W}$$

and leaves 3 NRTL adjustable parameters: $\tau_{C'W}$, $\tau_{A'W}$ and $\tau_{WC',A'C'}$. This assumption may be justified by the fact that H_2O and HNO_3 are neutral species, and have comparable dipole moments (1.85 D and 2.22 D in vacuum respectively). However it is clear that this simplification is appreciably arbitrary. Nevertheless any other assumption would be as arbitrary.

The τ value of Table 2 for the H^+'-W interaction was used, that is $\tau_{H^{+\prime}W} = -1.90$. In contrast with the case of sulfuric acid, the parameter $\tau_{A'W}$ was fitted for HNO_3 solution because it could not be assigned a clear value when considering the $LiNO_3$ solution (non associating electrolyte). Therefore, one is left with 5 parameters,

Table 4. Results for parameter values in the case of nitric acid, with $\tau_{H^+W} = -1.9$ and $h_P = 0$.

Set no.[a]	K_m [b]	$\tau_{A'W}$	$\tau_{WC',A'C'}$	σ [c]	h	AARD$_\phi$ [d] (%)	$AARD_{\gamma_\pm}$ [e] (%)
1	0	-1.68	2.92	0.527	2.93	0.08	0.08
2	0.0378	-1.41	3.17	0.586	5.85	0.25	0.31

[a]See text for meaning; [b]In units of kg mol^{-1}; [c]In nm; [d]Average Absolute Relative Deviation (AARD) for ϕ; [e]AARD for $\gamma_\pm$.

namely $\tau_{A'W}$, $\tau_{WC',A'C'}$, σ, h and K. The hydration number for the HNO_3 pair was assigned the value $h_P = 0$ because it is a neutral species.

As for sulfuric acid, the association constant K is related to K_m, as $K = K_m/M_1$. An empirical value of 0.045 kg mol^{-1} for K_m, proposed by Hood *et al.* [48], may be corrected [49] to give $K_m \simeq 0.1$ kg mol^{-1}.

First, the thermodynamic data ϕ and $\gamma_\pm$ were fitted together by least-square adjustment of the 5 model parameters. This gives the set no. 1 in Table 4. This procedure yields a good fit with an adjusted value of zero for K (no association).

Next, the thermodynamic data ϕ and $\gamma_\pm$ were fitted together with the association fraction x, with a weight of 0.2 being given to the latter in the fit. Experimental data for x were taken from the work of Krawetz [27]. These results, obtained in 1955 using Raman spectroscopy, have been confirmed in recent studies [28, 29]. This new fit led to the results of set no. 2 in Table 4. For this set, the osmotic and activity coefficients are plotted in Figure 4.10 and the association fraction x is shown in Figure 4.11.

As compared to the set no. 1, the fact of also fitting x increases the total hydration number value to 5.85, only a little larger than in the case of halide acids, which is reasonable since the nitrate ion is also believed to be weakly hydrated [50, 51]. The K_m value of 0.0378 kg mol^{-1}, is coincidentally [49] close to the old value of Hood *et al.* [48] of 0.045 kg mol^{-1}. The AARDs of fit are clearly larger than for the set no. 1 but are quite acceptable.

The main conclusion of this part is that both types of quantities can be accurately described by the model.

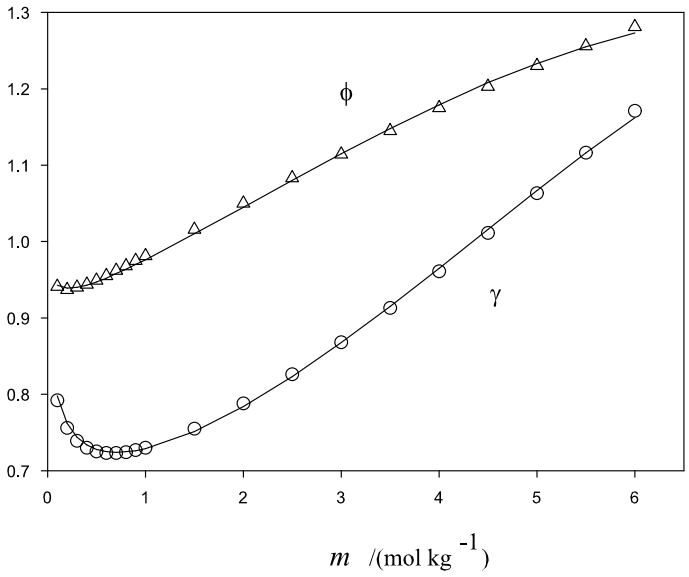

Figure 4.10: Osmotic and activity coefficient as a function of molality for aqueous nitric acid solution. Symbols: experimental data. Solid lines: result of fit.

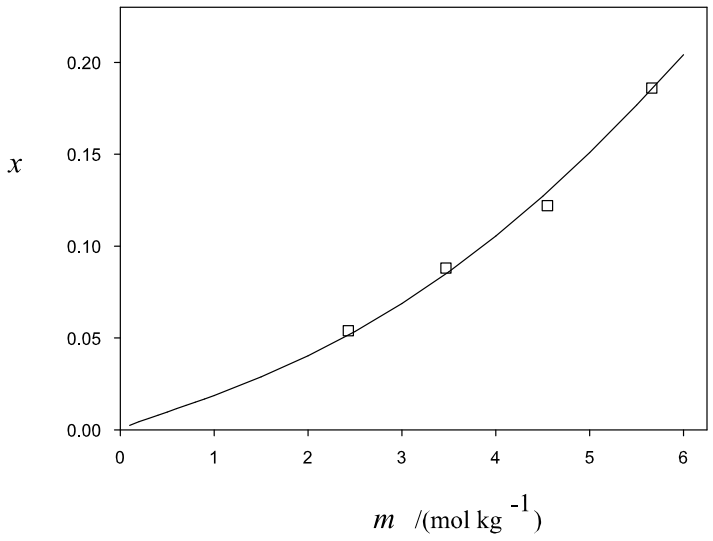

Figure 4.11: Degree of association of nitrate ion (forming HNO_3) as a function of molality. Symbols: experimental data of Krawetz [27]. Solid line: result of fit.

4.2.5 Conclusion

The model of Robinson and Stokes, in which constant hydration numbers are attributed to ions in solution, has been combined with the MSA-NRTL model and applied to aqueous solutions of alkali and alkaline earth halides and to acids. The formulae of Robinson and Stokes, converting the individual and mean salt activity coefficients to the LR level, have been compacted and extended to the case of associating electrolytes.

Good representations of the osmotic and activity coefficients for strong electrolytes are obtained. A consistent set of values is proposed for the individual NRTL parameters $\tau_{C'W}$ and $\tau_{A'W}$. The adjusted total hydration numbers have reasonable orders of magnitude.

In the case of associating acids, the model can be adjusted to represent the thermodynamic properties and the speciation of the acid. However, it seems to perform better for nitric acid than for sulfuric acid.

These representations will be used in subsequent work for thermodynamic descriptions of mixed aqueous solvent electrolytes.

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List of symbols

a_i	activity of species i
A	anion
C	cation
C$'$	cation hydrated
d_i	density of solvent i
e	charge of proton
f_i	activity coefficient of i on stoichiometric mole fraction scale
g_i	activity coefficient of i on "true" mole fraction scale
G	Gibbs energy of solution
$\bar{G}$	partial molal excess Gibbs energy
$\mathcal{G}$ specific Gibbs energy	
$\bar{G}_i$	Gibbs energy per particle of i
h_i	hydration number of cation by solvent i
k_B	Boltzmann constant
m	molality
M_i	molar mass of solvent i
n	mole number
N_{av}	Avogadro number
N_i	number of particles of i
P_{ik}, $P_{ik,jk}$	defined by eqs 6.61 and 6.62
S_{model}	set of particle numbers within the model (eq 6.19)
S_{LR}	set of particle numbers at LR level (eq 6.20)
T	temperature
V	volume of solution
W	water
x_i	stoichiometric mole fraction
y_i	"true" mole fraction scale
z	Electronic charge
z_i	valence of ion i
Z	coordination number

Greek letters

α	NRTL random parameter
β	$= 1/k_B T$
$\gamma_\pm$	mean salt activity coefficient on molal scale
Γ	MSA screening parameter
ε_i	relative permittivity of solvent i
ε_0	permittivity of a vacuum
κ	Debye screening parameter
λ	Bjerrum length
μ_i	chemical potential of species i
ν	$= \nu_C + \nu_A$
ν_i	stoichiometric number of species i in salt
ϕ	osmotic coefficient
ρ_i	number density of species i
σ_i	diameter of species i

Subscripts

1	total water
2	total solvent
W	free water
Z	free solvent

Superscripts

$\otimes$	reference state
(0)	value at T=298.15 K
el	electrostatic contribution
hyd	contribution from hydration
id	ideal contribution
MSA	contribution within mean spherical approximation
SR	contribution of short range forces

Bibliography

[1] Papaiconomou, N.; Simonin, J.P.; Bernard, O.; Kunz, W. MSA-NRTL Model for the Description of the Thermodynamic Properties of Electrolyte Solutions. *Phys. Chem. Chem. Phys.* **2002**, *4*, 4435.

[2] W.T. Lindsay, C.T. Liu, J. Phys. Chem. 75 (1971) 3723-3727.

[3] A.P. Lyubartsev, S. Marcelja, Physical Review E 65 (2002) 041202-1-6.

[4] Liu, Y.; Watanisiri S. Successfully Simulate Electrolyte Systems. *Chem. Eng. Prog.* October **1999**, 25.

[5] van't Hoff, J.H. Die Rolle des osmotischen Druckes in der Analogie zwischen Lösungen und Gasen. *Z. Phys. Chem.* **1887**, *1*, 481.

[6] McMillan, W.G.; Mayer, J.E. The Statistical Thermodynamics of Multicomponent Systems. *J. Chem. Phys.* **1945**, *13*, 276.

[7] Blum, L.; Høye, J.S. Mean Spherical Model for Asymmetric Electrolytes 2. Thermodynamic Properties and the Pair Correlation Function. *J. Phys. Chem.* **1977**, *81*, 1311.

[8] Triolo, R.; Blum, L.; Floriano, M.A. Simple Electrolytes in the Mean Spherical Approximation. 2. Study of a Refined Model. *J. Phys. Chem.* **1978**, *82*, 1368.

[9] Simonin, J.P.; Blum, L.; Turq, P. Real Ionic Solutions in the Mean Spherical Approximation. 1. Simple Salts in the Primitive Model. *J. Phys. Chem.* **1996**, *100*, 7704.

[10] Simonin, J.P. Real Ionic Solutions in the Mean Spherical Approximation. 2. Pure Strong Electrolytes up to Very High Concentrations, and Mixtures, in the Primitive Model. *J. Phys. Chem.* **1997**, *101*, 4313.

[11] Pitzer, K.S.; Mayorga, G. Thermodynamics of Electrolytes. II. Activity and Osmotic Coefficients for Strong Electrolytes with One or Both Ions Univalent. *J. Phys. Chem.* **1973**, *77*, 2300.

[12] Chen, C.C.; Britt, H.I.; Boston, J.F.; Evans, L.B. Local Composition Model for Excess Gibbs Energy of Electrolyte Systems. *AIChE J.* **1982**, *28*, 588.

[13] Chen, C.C.; Evans, L.B. A Local Composition Model for the Excess Gibbs Energy of Aqueous Electrolyte Systems.*AIChE J.* **1986**, *32*, 444.

[14] Kolker, A.; de Pablo, J.J. Thermodynamic Modeling of Concentrated Aqueous Electrolyte and Nonelectrolyte Solutions. *AIChE J.* **1995**, *41*, 1563.

[15] Abovsky, V.; Liu, Y.; Watanasiri, S. Representation of Nonideality in Concentrated Electrolyte Solutions using the Electrolyte NRTL model with Concentration-Dependent Parameters. *Fluid Phase Equilibria* **1998**, *150-151*, 277.

[16] Robinson, R.A.; Stokes, R.H. *Electrolyte Solutions*; Butterworths: London, 1959.

[17] Zavitsas, A.A. Properties of Water Solutions of Electrolytes and Nonelectrolytes. *J. Phys. Chem. B* **2001**, *105*, 7805.

[18] Botti, A.; Bruni, F.; Imberti, S.; Ricci, M.A.; Soper, A.K. Ions in Water: The Microscopic Structure of a Concentrated HCl Solution. *J. Chem. Phys.* 2004, *121*, 7840.

[19] Lyubartsev, A.P.; Laasonen, K.; Laaksonen, A. Hydration of Li^+ Ion. An Ab Initio Molecular Dynamics Simulation. *J. Chem. Phys.* **2001**, *114*, 3120.

[20] Rempe, S.R.; Pratt, L.R. The Hydration Number of Na^+ in Liquid Water. *Fluid Phase Equilibria* **2001**, *183-184*, 121.

[21] Ramaniah, L.M.; Bernasconi, M.; Parrinello, M. Ab Initio Molecular-Dynamics Simulation of K^+ Solvation in Water. *J. Chem. Phys.* **1999**, *111*, 1587.

[22] Lightstone, F.C.; Schwegler, E.; Hood, R.Q.; Gygi, F.; Galli, G. A First Principles Molecular Dynamics Simulation of the Hydrated Magnesium Ion. *Chem. Phys. Lett.* **2001**, *343*, 549.

[23] Naor, M.N.; van Nostrand, K.; Dellago, C. Car-Parrinello Molecular Dynamics Simulation of the Calcium Ion in Liquid Water. *Chem. Phys. Lett.* **2003**, *369*, 159.

[24] Grossfield, A. Dependence of Ion Hydration on the Sign of the Ion's Charge. *J. Chem. Phys.* 2005, *122*, 024506.

[25] Ohtaki, H.; Radnai, T. Structure and Dynamics of Hydrated Ions. *Chem. Rev.* **1993**, *93*, 1157.

[26] Knopf, D.A.; Luo, B.P.; Krieger, U.K.; Koop, T. Thermodynamic Dissociation Constant of the Bisulfate Ion from Raman and Ion Interaction Modeling Studies of Aqueous Sulfuric Acid at Low Temperature. *J. Phys. Chem. A* **2003**, *107*, 4322.

[27] Krawetz, A.A. A Raman Spectral Study of Equilibria in Aqueous Solutions of Nitric Acid. Ph. D. Thesis, University of Chicago, 1955.

[28] Lund Myrhe, C.A.; Grothe, H.; Gola, A.A.; Nielsen, C.J. Optical Constants of HNO_3/H_2O and $H_2SO_4/HNO_3/H_2O$ at Low Temperatures in the Infrared Region. *J. Phys. Chem. A* **2005**, *109*, 7166.

[29] Moisy, P. Unpublished results.

[30] Chen, C.C.; Matjias, P.M.; Orbey, H. Use of Hydration and Dissociation Chemistries with the Electrolyte-NRTL Model. *AIChE J.* **1999**, *45*, 1576.

[31] Lu, X.; Zhang, L.; Wang, Y.; Shi, J.; Maurer, G. Prediction of Activity Coefficients of Electrolytes in Aqueous Solutions at High Temperatures. *Ind. Eng. Chem. Res.* **1996**, *35*, 1777.

[32] Renon, H.; Prausnitz, J.M. Local Composition in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.*, 1968, *14*, 135.

[33] Renon, H.; Prausnitz, J.M. Derivation of the Three-Parameter Wilson Equation for the Excess Gibbs Energy of Liquid Mixtures. *AIChE J.* **1969**, *15*, 785.

[34] Guggenheim, E.A. *Mixtures*; Clarendon Press: Oxford, 1952.

[35] Sillen, L.G.; Martell, A.E. *Stability Constants of Metal-Ion Complexes* and *Supplement no. 1*; The Chemical Society: London, 1964.

[36] Goldberg, R.N.; Manley, J.L.; Nuttal, R.L. *Program Gamphi for Calculating Activity and Osmotic Coefficients of Aqueous Electrolyte Solutions at 298.15 K*, National Bureau of Standards, Chemical Thermodynamics Division, U.S.A., 1984.

[37] Hamer, W.J.; Wu, Y.C. Osmotic Coefficients and Mean Activity Coefficients of Uni-univalent Electrolytes in Water at 25 °C. *J. Phys. Chem. Ref. Data* **1972**, *1*, 1047.

[38] Hertz, H.G. in *Water: A Comprehensive Treatment*, vol. 3, F. Franks, Plenum: New York, 1973.

[39] Hewish, N.A.; Neilson, G.W.; Enderby, J.E. Environment of Ca^{2+} ions in aqueous solvent. *Nature* **1982**, *297*, 138.

[40] Copestake, A.P.; Neilson, G.W.; Enderby, J.E. The Structure of a Highly Concentrated Aqueous Solution of Lithium Chloride. *J. Phys. C Solid State Phys.* **1985**, *18*, 4211.

[41] Rard, J.A.; Habenschuss, A.; Spedding, F.H. A Review of the Osmotic Coefficients of Aqueous H_2SO_4 at 25 °C. *J. Chem. Eng. Data* **1976**, *21*, 374.

[42] Nair, V.S.K.; Nancollas, G.H. Thermodynamics of Ion Association. Part V. Dissociation of the Bisulphate Ion. *J. Chem. Soc.* **1958**, 4144.

[43] Dunsmore, H.S.; Nancollas, G.H. Dissociation of the Bisulfate Ion. *J. Phys. Chem.* **1964**, *68*, 1579.

[44] Pitzer, K.S.; Roy, R.N.; Silvester, L.F. Thermodynamics of Electrolytes. 7. Sulfuric Acid. *J. Am. Chem. Soc.* **1977**, *99*, 4930.

[45] Chen, H.; Irish, D.E. A Raman Spectral Study of Bisulfate-Sulfate Systems. II. Constitution, Equilibria, and Ultrafast Proton Transfer in Sulfuric Acid. *J. Phys. Chem.* **1971**, *75*, 2672.

[46] Lund Myrhe, C.E.; Christensen, D.H.; Nicolaisen, F.M.; Nielsen, C.J. Spectroscopic Study of Aqueous H_2SO_4 at Different Temperaures and Compositions: Variations in Dissociation and Optical Properties. *J. Phys. Chem. A* **2003**, *107*, 1979.

[47] Young, T.F. Recent Developments in the Study of Interactions between Molecules and Ions, and of Equilibria in Solutions. *Rec. Chem. Prog.* **1951**, *12*, 81.

[48] Hood, G.C.; Redlich, O.; Reilly, C.A. Ionization of Strong Electrolytes. III. Proton Magnetic Resonance in Nitric, Perchloric, and Hydrochloric Acids. *J. Chem. Phys.* **1954**, *22*, 2067.

[49] Vilariño, T.; Bernard, O.; Simonin, J.P. Ionic Solutions in the Bindind Mean Spherical Approximation. Thermodynamics of Associating Electrolytes up to Very High Concentrations. *J. Phys. Chem. B* **2004**, *108*, 5763.

[50] Gonzalez Lebrero, M.C.; Bikiel, D.E.; Elola, M.D.; Estrin, D.A.; Roitberg, A.E. Solvent-induced Symmetry Breaking of Nitrate Ion in Aqueous Clusters: A Quantum-Classical Simulation Study. *J. Chem. Phys.* **2002**, *117*, 2718.

[51] Neilson, G.W.; Enderby, J.E. The Structure around Nitrate Ions in Concentrated Aqueous Solutions. *J. Phys. C Solid State Phys.* **1982**, *15*, 2347.

Chapter 5

Enthalpy effects in electrolyte solutions described using the MSA-NRTL model (including ion solvation)

5.1 Introduction

The modeling of the thermodynamic properties of ionic solutions is the subject of continuing fundamental investigations [4]. Generally, this type of study concerns aqueous solutions at ambient temperature. While they may be useful in atmospheric chemistry and geochemistry after suitable extension to a wide range of temperatures, these models are of limited interest for industrial applications in which aqueous solvent mixtures are often involved. Such systems still require the use of more or less empirical models to tackle many issues in chemical engineering thermodynamics [5, 6, 7].

There is indeed a significant demand from the industry for software programs running on microcomputers, capable of predicting the thermodynamic behavior of "complex" solutions. These solutions may contain several salts and several solvents, at temperatures different from 25°C. The modeling of these systems is not an easy task, in particular because the structure of this type of solution is still poorly known, especially as a function of temperature. In this context, the development of more or less empirical or phenomenological models, based on a reasonable picture of solution, seems a good means of providing efficient tools for the chemical industry. The present paper is a part of our continuing effort in that direction.

An important process occurring in ionic solutions is solvation. Here, by solvation,

we mean the event in which a number of solvent molecules remain in the close vicinity of an ion for a time significantly larger than the corresponding time in bulk solvent. In most models, this process is modeled by assuming that a definite number of solvent molecules are "firmly" bound to an ion. It may be noticed that, while a large body of experimental data has been gathered about the hydration of common ions at 25°C [8], ionic solvation in solvent mixtures (and the notion of "preferential solvation") is much more uncertain [9, 10, 11, 12, 13, 14].

Recently, we presented a model [15] combining the Mean Spherical Approximation (MSA) and the Non-Random Two-Liquid (NRTL) expressions for the electrostatic and short-range (SR) contributions to the Gibbs energy, respectively. The model was applied to strong and associated aqueous ionic solutions at 25°C. As compared to our previous work [16], the hydration of the ions was accounted for by introducing a constant hydration number, as in the classic model of Robinson and Stokes [17], already used by Chen et al. [18]. In a recent study [19], we used the stepwise solvation-equilibrium model of Stokes and Robinson [17] to account for the variation of solvation with salt concentration.

The purpose of the present work is to extend our previous model [15], with solvation number independent of salt concentration, to the case of strong electrolytes in water and in solvent mixtures at temperatures higher than 25°C. The thermodynamic properties represented include: the osmotic coefficient, the dilution enthalpy, the solute partial entropy at infinite dilution and the solution heat capacity in the case of purely aqueous solutions; the activity coefficients of solute and solvents in the case of aqueous solvent mixtures, all of these properties being studied in the temperature range 25°C-100°C. The partial salt heat capacity at infinite dilution is discussed in terms of influence of the ion on the water structure.

The next section presents the theoretical aspects of this work. The third section is devoted to the presentation of the results and to their discussion. Finally the conclusion will present the perspectives of our future work.

Most calculations were performed using the symbolic calculation device Maple^R.

5.2 Basic relations

Pitzer has extended his equations to treat enthalpies and heat capacities.

The basic equations for enthalpy and heat capacity are derived in general form for an electrolyte with ionic charges z_C and z_A for the positive and negative ions. The total excess Gibbs energy is [1]:

$$G^{ex} = n_w \nu m RT \left(1 - \phi + \ln \gamma_{\pm}\right) \tag{5.1}$$

where n_w is the number of kilograms of solvent, m is the molality, ν is the number of the ions of each type $\nu = \nu_C + \nu_A$, R is the gas constant, T designates the temperature in K, ϕ is the osmotic coefficient, and $\gamma_\pm$ is the activity coefficient. One gets:

$$G^{ex} = n_1 \bar{G}_1^{ex} + n_2 \bar{G}_2^{ex} \tag{5.2}$$

where n_1 and n_2 are the number of moles of solvent and solute, respectively, and $\bar{G}_1^{ex}$ is the partial molal excess Gibbs energy of the solvent, $\bar{G}_2^{ex}$ is the partial molal excess Gibbs energy of the solute.

Hence

$$\bar{G}_1^{ex} = \left(\nu \frac{n_2}{n_1}\right) RT\,(1-\phi) \tag{5.3}$$

$$\bar{G}_2^{ex} = (\nu RT \ln \gamma_\pm) \tag{5.4}$$

In the Chap 3 we have seen the Pitzer's equations for the aqueous electrolytes which lead to the following equations for ϕ and $\ln \gamma_\pm$ of a pure electrolyte:

$$\phi - 1 = -|z_C z_A| A_\Phi \frac{I^{1/2}}{1 + bI^{1/2}}$$

$$+m \frac{2\nu_C \nu_A}{\nu} \left(\beta_{CA}^{(0)} + \beta_{CA}^{(1)} exp^{-\alpha I^{1/2}}\right) + m^2 \frac{2\left(\nu_C \nu_A\right)^{3/2}}{\nu} C_{CA}^{\Phi}$$

and

$$\ln \gamma_\pm = -|z_C z_A| A_\Phi \left(\frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln\left(1 + bI^{1/2}\right)\right)$$

$$+m \frac{2\nu_C \nu_A}{\nu} \left(2\beta_{CA}^{(0)} + \frac{2\beta_{CA}^{(1)}}{\alpha^2 I}\left(1 - \left(1 + \alpha I^{1/2} - \frac{\alpha^2 I}{2}\right) exp^{-\alpha I^{1/2}}\right)\right) + \frac{3m^2}{2}\left(\frac{2\left(\nu_C \nu_A\right)^{3/2}}{\nu}\right) C_{CA}^{\Phi}$$

where I is the ionic strength

$$I = \frac{1}{2} \sum_i m_i z_i \tag{5.5}$$

and A_Φ is the Debye-Hückel coefficient for the osmotic function given as

$$A_\Phi = \frac{1}{3}\left(\frac{2\pi N_{av} \rho_w}{1000}\right)^{1/2} \left(\frac{e^2}{DkT}^{3/2}\right) = \frac{A_\gamma}{3} \tag{5.6}$$

where N_{av} is Avogadro's number, ρ_w is the density of the solvent, and D the static dielectric constant of pure water, k is Boltzmann's constant, and e is the absolute electronic charge. The first terms in equations of ϕ and $\ln \gamma\pm$ arises from the long range electrostatic interactions. The coefficients $\beta_{CA}^{(0)}$ and $\beta_{CA}^{(1)}$ account for various types of short-range interactions betweeen C and A, and for indirect forces arising

from the solvent. C^{Φ}_{CA} is for the triple ion interactions and is important only at high concentrations. The parameter b was given the value 1.2 for all electrolytes and α is 2 for all 1-1 and most other solutes. b and α are taken as temperature independent. $\beta^{(0)}_{CA}$,$\beta^{(1)}_{CA}$, and C^{Φ}_{CA} are adjusted for a given salt at fixed temperature by a fit of osmotic and activity coefficient data. The standard state are the pure solvent for the solvent and the infinite dilution for the solute.

The relative enthalpy L of an electrolyte solution is defined:

$$L = H - H^{\otimes} \tag{5.7}$$

where H is the total enthalpy of solution and $H^{\otimes}$ that at infinite dilution. L is related to G^{ex} by:

$$L = -T^2 \left(\frac{\partial \left(\frac{G^{ex}}{T} \right)}{\partial T} \right)_{p,m} \tag{5.8}$$

Eq. 5.1 and 5.8 yield for L:

$$L = \nu m R T^2 [\left(\frac{\partial \phi}{\partial T} \right)_{P,m} - \left(\frac{\partial \ln \gamma_{\pm}}{\partial T} \right)_{P,m}] \tag{5.9}$$

The apparent relative molal enthalpy, Φ_L is defined as:

$$\Phi_L = \frac{L - n_1 \bar{L_1}^{\otimes}}{n_2} = \frac{L}{n_2} \tag{5.10}$$

Hence

$$\Phi_L = \nu |z_C z_A| \left(\frac{A_H}{3.6} \right) \ln \left(1 + 1.2 I^{1/2} \right) - 2 \nu_C \nu_A R T^2 \left(m B'_{CA} + m^2 C'_{CA} \right) \tag{5.11}$$

where

$$B'_{CA} = \left(\frac{\partial B_{CA}}{\partial T}_{I,P} \right) \tag{5.12}$$

$$B_{CA} = \beta^{(0)}_{CA} + \left(\frac{2 \beta^{(1)}_{CA}}{\alpha^2 I} \right) [1 - \left(1 + \alpha I^{1/2} \right) exp \left(-\alpha I^{1/2} \right)] \tag{5.13}$$

$$C'_{CA} = \frac{1}{2} \left(\nu_C \nu_A \right)^{1/2} \left(\frac{\partial C^{\Phi}_{CA}}{\partial T} \right)_{I,P} \tag{5.14}$$

The quantity A_H is the Debye-Hückel coefficient for enthalpy:

$$A_H = -9 A_{\Phi} R T^2 [T^{-1} + \left(\frac{\partial D}{\partial T} \right)_P + \frac{\alpha_w}{3}] \tag{5.15}$$

where $\alpha_w = \left(\frac{\partial \ln V}{\partial T} \right)_P$ is the coefficient of thermal expansion of water.

The total relative heat capacity J is defined as:

$$J = C_P - C^{\otimes}_P = C_P - \left(n_1 C^{\circ}_{P_1} + n_2 \bar{C}^{\otimes}_{P_s} \right) \tag{5.16}$$

where $\bar{C}^{\otimes}_{P_s}$ is the partial molal heat capacity of the solute at infinite dilution and $C^{\circ}_{P_1}$ is the molal heat capacity of pure water.

$$J = \frac{\partial L}{\partial T} \tag{5.17}$$

The apparent molal heat capacity Φ_{C_P} is defined as:

$$\Phi_{C_P} = \frac{C_P - n_1 C^{\circ}_{P_1}}{n_2} \tag{5.18}$$

From Eq. 5.10 and 5.17 we find that:

$$\Phi_{C_P} - \bar{C}^{\otimes}_{P_s} = \left(\frac{\partial \Phi_L}{\partial T}\right)_{P,m} \tag{5.19}$$

The temperature derivative of Eq. 5.11 yields:

$$\Phi_{C_P} = \bar{C}^{\otimes}_{P_s} + |z_C z_A| \left(\frac{A_H}{3.6}\right) \ln\left(1 + 1.2I^{1/2}\right) - 2\nu_C \nu_A RT^2 \left(mB^{"}_{CA} + m^2 C^{"}_{CA}\right) \tag{5.20}$$

where

$$B^{"}_{CA} = \left(\frac{\partial^2 B_{CA}}{\partial T^2}\right) + \frac{2}{T}\left(\frac{\partial B_{CA}}{\partial T}\right)_{P,m} \tag{5.21}$$

and

$$C^{"}_{CA} = \frac{1}{2}\left(\nu_C \nu_A\right)^{1/2} \left[\left(\frac{\partial^2 C^{\Phi}_{CA}}{\partial T^2}\right)_{P,m} + \frac{2}{T}\left(\frac{\partial C^{\Phi}_{CA}}{\partial T}\right)_{P,m}\right] \tag{5.22}$$

with

$$A_J = \left(\frac{\partial C^{\Phi}_{CA}}{\partial T}\right)_P \tag{5.23}$$

The parameters A_Φ, A_H, and A_J depend only on the thermodynamic and electrostatic properties of water.

Application to NaCl aqueous solution:

The temperature dependence of $\beta^{(0)}$, $\beta^{(1)}$, and C^{Φ} are the following general forms:

$$\beta^{(0)} = q_1 + q_2\left(\frac{1}{T} - \frac{1}{T^{(0)}}\right) + q_3 \ln\left(\frac{T}{T^{(0)}}\right) + q_4\left(T - T^{(0)}\right) + q_5\left(T^2 - (T^{(0)})^2\right) \tag{5.24}$$

$$\beta^{(1)} = q_6 + q_9\left(T - T^{(0)}\right) + q_{10}\left(T^2 - (T^{(0)})^2\right) \tag{5.25}$$

$$C^{\Phi} = q_{11} + q_{12}\left(\frac{1}{T} - \frac{1}{T^{(0)}}\right) + q_{13} \ln\left(\frac{T}{T^{(0)}}\right) + q_{14}\left(T - T^{(0)}\right) \tag{5.26}$$

where T_r is the temperature at 298.15 K, the values of q_1, q_6, and q_{11} for NaCl at 25° C are given by Pitzer and Mayorga [2].

The heat capacity data at each experimental temperature were fitted to Eq. 5.20 and one gets $\bar{C}^{\otimes}_{P_s}$ by:

$$\bar{C}^{\otimes}_{P_s} = \bar{C}^{\otimes}_{P_{sol}}(T) + q_{17} + 2q_{18}T + 3q_{19}T^2 \tag{5.27}$$

where $\bar{C}^{\otimes}_{P_{sol}}(T)$ is the heat capacity of the solid reported by Kelley [3]

$$\bar{C}^{\otimes}_{P_{sol}}(T) = 10.98 + 0.0039T \tag{5.28}$$

with $T \geq 298.15K$.

Pitzer has 19 parameters for the description of NaCl electrolyte solution.

5.3 Theoretical

We consider a solvent mixture, composed of two solvents denoted by symbols 1 and 2, containing a strong electrolyte $C_{\nu_C}A_{\nu_A}$, C being the cation and A the anion with stoichiometric numbers ν_C and ν_A, respectively. We denote by h_{Ci} and h_{Ai} the solvation numbers of C and A in solvent i, respectively. These numbers are supposed not to vary with salt concentration. The symbols z_C and z_A stand for the valences of C and A, respectively.

Hereafter we will use the subscripts W, Z, C' and A' to designate the *free* solvents 1 and 2 (not bound to an ion), the *solvated* cation and the *solvated* anion, respectively. In this work, the symbols 1 and W will refer to water, but the treatment below is general as long as the electrolyte is completely dissociated in the solvent mixture. For commodity, the subscripts 1 and 2 will be used to designate quantities for the *total* solvents (bound plus free).

5.3.1 Basic thermodynamic relations.

In this section, the framework presented in previous work [15] for binary aqueous electrolyte solutions is extended (straightforwardly) to the case of ternary (one salt + two solvents) mixtures.

The relevant set of particle numbers to be used in any model is

$$S_m \equiv \{N_W, N_Z, N_{C'}, N_{A'}\} \tag{5.29}$$

with the corresponding so-called "true" mole fraction of a species i defined by

$$y_i \equiv \frac{N_i}{N_W + N_Z + N_{C'} + N_{A'}} \tag{5.30}$$

Any activity coefficient, g_i calculated using a model in terms of the set of variables S_m, must be converted to the experimental, Lewis-Randall (LR), level at which the relevant set of variables is

$$S_{LR} \equiv \{N_1, N_2, N_C, N_A\} \tag{5.31}$$

In this reference system, the stoichiometric mole fractions are defined as

$$x_i \equiv \frac{N_i}{N_1 + N_2 + N_C + N_A} \tag{5.32}$$

We will denote by f_i the activity coefficient on this mole fraction scale at the LR level.

According to the above assumptions, one has

$$N_1 = N_W + h_{C1} N_{C'} + h_{A1} N_{A'} \tag{5.33}$$

$$N_2 = N_Z + h_{C2} N_{C'} + h_{A2} N_{A'} \tag{5.34}$$

where h_{Xn} is the solvation number of species X (=C or A) by solvent n (=1 or 2).

The relation between the activity coefficients f_i and g_i is derived as follows.

For small variations of the number of particles, the variation of the Gibbs energy of solution may be written as

$$\mathrm{d}G = \mu_W \mathrm{d}N_W + \mu_Z \mathrm{d}N_Z + \mu_{C'} \mathrm{d}N_{C'} + \mu_{A'} \mathrm{d}N_{A'} \tag{5.35}$$

when using the set of variables S_m, at constant pressure and temperature. In terms of the set S_{LR} at the LR level, it is given by

$$\mathrm{d}G = \mu_1 \mathrm{d}N_1 + \mu_2 \mathrm{d}N_2 + \mu_C \mathrm{d}N_C + \mu_A \mathrm{d}N_A \tag{5.36}$$

The LR variables may be replaced by their expressions (Eqs. 5.33,5.34) in Eq. 5.36. Then, identification of the obtained relation with Eq. 5.35, and since this equality holds for any small variation of S_m, one gets

$$\mu_{X'} = \mu_X + h_{X1} \mu_1 + h_{X2} \mu_2 \tag{5.37}$$

$$\mu_W = \mu_1 \tag{5.38}$$

$$\mu_Z = \mu_2 \tag{5.39}$$

Then, inserting Eqs. 5.38 and 5.39 in Eq. 5.40 leads to

$$\mu_X = \mu_{X'} - h_{X1} \mu_W - h_{X2} \mu_Z \tag{5.40}$$

which expresses the relation for the mean chemical potential of C and A at the LR level as a function of that for the hydrated ions and the free water, quantities that may be calculated in the framework of a suitable model.

Besides, one may write

$$\beta \mu_X = \beta \mu_X^{\otimes} + \ln(x_X f_X) \tag{5.41}$$

$$\beta\mu_{X'} = \beta\mu^{\otimes}_{X'} + \ln(y_{X'} g_{X'}) \tag{5.42}$$

for X= C or A, and

$$\beta\mu_W = \beta\mu^{\otimes}_W + \ln a_W \tag{5.43}$$

$$\beta\mu_Z = \beta\mu^{\otimes}_Z + \ln a_Z \tag{5.44}$$

with $\mu_i^{\otimes}$ the standard chemical potential of species i and

$$\beta \equiv (k_B T)^{-1}$$

k_B being Boltzmann constant and T the temperature.

Eqs 5.41, 5.44 may be inserted into Eq. 5.40. The quantity $\mu_X^{\otimes}$ being independent of composition, one finds by taking the limit of infinite dilution of salt

$$\beta(\mu^{\otimes}_X - \mu^{\otimes}_{X'} - h_{X1}\mu^{\otimes}_W - h_{X2}\mu^{\otimes}_Z) = -\ln\left((a_1^{\circ})^{h_{X1}}(a_2^{\circ})^{h_{X2}}\right) \tag{5.45}$$

where the superscript $\circ$ denotes a quantity in the salt-free mixture. It results from Eqs. 5.41-5.45 that

$$f_X = g_{X'}\,\frac{y_{X'}}{x_X}\,\left(\frac{a_1^{\circ}}{a_W}\right)^{h_{X1}}\,\left(\frac{a_2^{\circ}}{a_Z}\right)^{h_{X2}} \tag{5.46}$$

which gives the desired relation between the LR activity coefficient of X (=C or A), f_X, and the activity coefficient of the solvated species X', $g_{X'}$.

The mean activity coefficient of salt at the LR level is

$$\ln f_{\pm} \equiv \frac{\nu_C}{\nu}\ln f_C + \frac{\nu_A}{\nu}\ln f_A \tag{5.47}$$

where $\nu \equiv \nu_C + \nu_A$.

Finally, the mean activity coefficient of salt on the molal scale, $\gamma_{\pm}$, is obtained using the conversion formula [17, 16]

$$\gamma_{\pm} = (x_1 + x_2)\, f_{\pm} \tag{5.48}$$

By combining Eqs. 5.46-6.42 and rearranging terms, we obtain

$$\ln\gamma_{\pm} = \ln g_{\pm} + \frac{h_1}{\nu}\ln\frac{a_1^{\circ}}{a_W} + \frac{h_2}{\nu}\ln\frac{a_2^{\circ}}{a_Z} + \ln(y_1 + y_2) \tag{5.49}$$

where

$$h_i \equiv \nu_C h_{Ci} + \nu_A h_{Ai}$$

is the total solvation number of salt by solvent i, m is the molality of salt, M_i is the molar mass of solvent i, and y_1 and y_2 are given formally by Eq. 5.30 applied to total amounts of solvents 1 and 2. If the proportion of solvent i is given as mass fraction in the salt-free solvent mixture, denoted by w_i°, one has

$$y_1 + y_2 = \frac{\frac{w_1^{\circ}}{M_1} + \frac{w_2^{\circ}}{M_2}}{(\nu - h_1 - h_2)m + \frac{w_1^{\circ}}{M_1} + \frac{w_2^{\circ}}{M_2}}$$

As for the solvent activities, Eqs. 5.38 and 5.39 entail that

$$a_1 = a_W \tag{5.50}$$

$$a_2 = a_Z \tag{5.51}$$

with $a_i = x_i f_i$ $(i = 1, 2)$, $a_Y = y_Y g_Y$ (Y=W,Z).

An activity coefficient g_X may be calculated using the relation

$$\ln g_X \equiv \frac{\partial G}{\partial N_X} - \frac{\partial G}{\partial N_X}(N_C = N_A = 0) \tag{5.52}$$

with infinite dilution of salt as the reference state.

In this work, it is assumed that the Gibbs energy, G, may be split into long-range electrostatic (el) and short-range (SR) contributions as

$$G = G^{el} + G^{SR} \tag{5.53}$$

Because of Eq. 5.52, it stems from this relation that

$$g_X = g_X^{el}\, g_X^{SR} \tag{5.54}$$

The explicit forms taken for these contributions are now given explicitly.

5.3.2 Electrostatic and SR contributions to Gibbs energy.

It is proposed to express the electrostatic contribution, G^{el}, by simply regarding the solvent mixture as a continuum of relative permittivity ε, whose value is known from experiment.

As in our previous work [16, 15], we take the restricted primitive MSA expression [20]

$$\beta G^{el} = -\lambda \frac{\Gamma}{1+\Gamma\sigma}\left(z_C^2 N_{C'} + z_A^2 N_A\right) + \frac{\Gamma^3}{3\pi} V \tag{5.55}$$

where V is the volume of solution, σ is the mean ionic size, λ is the Bjerrum distance

$$\lambda = \frac{1}{4\pi\varepsilon_0}\frac{\beta e^2}{\varepsilon} \tag{5.56}$$

where ε_0 is the permittivity of a vacuum, ϵ is the relative permittivity of the solvent mixture, Γ is the MSA screening parameter,

$$\Gamma = \frac{1}{2\sigma}\left(\sqrt{1+2\kappa\sigma} - 1\right) \tag{5.57}$$

with κ the Debye screening parameter

$$\kappa = \sqrt{4\pi\lambda(\rho_C z_C^2 + \rho_A z_A^2)}$$

in which ρ_i stands for the number density of species i.

Using Eqs. 5.52 and 5.55 for Y= C', A', W or Z (with $z_W = 0$ and $z_Z = 0$), one finds

$$\ln g_Y^{el} = -\lambda \frac{\Gamma}{1+\Gamma\sigma} z_Y^2 + \frac{\Gamma^3}{3\pi} \frac{\partial V}{\partial N_Y} \tag{5.58}$$

with the differentiation of Eq. 5.55 being performed at constant Γ [16].

In Eq. 5.58, the term $\partial V/\partial N_Y$ (Y being a species of S_m) can be expressed at the LR level (S_{LR} system) by using the chain rule for partial derivatives, which leads to [15]

$$\left[\frac{\partial V}{\partial N_{C'}}\right]_{N_W,N_Z,N_{A'}} = \left[\frac{\partial V}{\partial N_C}\right]_{N_1,N_2,N_A} \left[\frac{\partial N_C}{\partial N_{C'}}\right]_{N_W,N_Z,N_{A'}}$$
$$+ \left[\frac{\partial V}{\partial N_1}\right]_{N_2,N_C,N_A} \left[\frac{\partial N_1}{\partial N_{C'}}\right]_{N_W,N_Z,N_{A'}} + \left[\frac{\partial V}{\partial N_2}\right]_{N_1,N_C,N_A} \left[\frac{\partial N_2}{\partial N_{C'}}\right]_{N_W,N_Z,N_{A'}} \tag{5.59}$$

and a similar relation for A'. Moreover,

$$\left[\frac{\partial V}{\partial N_W}\right]_{N_Z,N_{C'},N_{A'}} = \left[\frac{\partial V}{\partial N_1}\right]_{N_2,N_C,N_A} \left[\frac{\partial N_1}{\partial N_W}\right]_{N_Z,N_{C'},N_{A'}}$$

$$\left[\frac{\partial V}{\partial N_Z}\right]_{N_W,N_{C'},N_A} = \left[\frac{\partial V}{\partial N_2}\right]_{N_1,N_C,N_A} \left[\frac{\partial N_2}{\partial N_Z}\right]_{N_W,N_{C'},N_A}$$

By using these last two equations together with Eqs. 5.33, 5.34, one gets in more compact form (without mentioning the variables kept constant in the differentiation)

$$\frac{\partial V}{\partial N_{X'}} = \frac{\partial V}{\partial N_X} + h_{X1} \frac{\partial V}{\partial N_1} + h_{X2} \frac{\partial V}{\partial N_2} \tag{5.60}$$

for X= C or A, and

$$\frac{\partial V}{\partial N_W} = \frac{\partial V}{\partial N_1} \tag{5.61}$$

$$\frac{\partial V}{\partial N_Z} = \frac{\partial V}{\partial N_2} \tag{5.62}$$

Following references [16, 15], we make the simplification that

$$\frac{\partial V}{\partial N_C} = \frac{\partial V}{\partial N_A} = 0 \tag{5.63}$$

which avoids the knowledge of solution densities and constitutes a good approximation [16]. This approximation amounts to neglecting the effect of salt on the volume of solution, which is therefore given by

$$V = (x_1^\circ M_1 + x_2^\circ M_2)/d_m N_{av} \tag{5.64}$$

where N_{av} is Avogadro number and d_m is the density of the salt-free solvent mixture.

With this simplification, we obtain from Eqs. 5.58-5.63

$$\ln g^{el}_{X'} = -\lambda \frac{\Gamma}{1+\Gamma\sigma} z_X^2 + h_{X1}\frac{\Gamma^3}{3\pi}\frac{\partial V}{\partial N_1} + h_{X2}\frac{\Gamma^3}{3\pi}\frac{\partial V}{\partial N_2} \tag{5.65}$$

$$\ln g^{el}_{W} = \frac{\Gamma^3}{3\pi}\frac{\partial V}{\partial N_1} \tag{5.66}$$

$$\ln g^{el}_{Z} = \frac{\Gamma^3}{3\pi}\frac{\partial V}{\partial N_2} \tag{5.67}$$

For the SR part of G, we take the NRTL expression for the system composed of the species: the solvated cation C', the solvated anion A', the free water W, and the free solvent Z. For one salt in a solvent mixture it is given by [16]

$$\beta\Delta G^{SR} = \sum_{m=W,Z}\left(y_{C'} X_{mC'}\tau_{mC',A'C'} + y_{A'} X_{mA'}\tau_{mA',C'A'} + y_m \sum_{j=W,Z,C',A'} X_{jm}\tau_{jm} \right) \tag{5.68}$$

in which

$$X_{ji} = y_j \exp(-\alpha\tau_{ji}) / \sum_k y_k \exp(-\alpha\tau_{ki})$$

In these formulas, α is the NRTL nonrandom parameter (hereafter we take the common value $\alpha = 0.3$) and $\tau_{ji} = \beta(w_{ji} - w_{ii})$, with w_{ji} the $i-j$ interaction energy.

Finally, we note that Eq. 5.49 may be rearranged by using Eqs. 5.65-5.67 to yield

$$\ln\gamma_\pm = -\lambda\frac{z_C^2\nu_C + z_A^2\nu_A}{\nu}\frac{\Gamma}{1+\Gamma\sigma} + \ln g_\pm^{SR} + \frac{h_1}{\nu}\ln\frac{a_1^\circ}{y_w g_w^{SR}} + \frac{h_2}{\nu}\ln\frac{a_2^\circ}{y_z g_z^{SR}} + \ln(y_1+y_2) \tag{5.69}$$

where $a_i^\circ = x_i^\circ f_i^{\circ SR}$ for $i = 1 or 2$ (salt-free solvent mixture), because the hydration numbers h_1 and h_2 contained in the expressions of $\ln g_C^{el}$ and $\ln g_A^{el}$ (see Eq. 5.65) turn out to be cancelled by the term $h_1 \ln g_W^{el}$ and $h_2 \ln g_Z^{el}$ (Eqs. 5.66 and 5.67).

5.3.3 Liquid-vapor equilibrium

The experimental values for the activity coefficients of solvents were computed as follows.

The vapor-liquid equilibrium may be cast into the equation [21]

$$x_i^G P\varphi_i^G = x_i^L f_i P_i^{sat}\varphi_{i,pure}^G \exp[v_i^L(P - P_i^{sat})/RT] \tag{5.70}$$

where x_i^G and x_i^L are, respectively, the mole fractions of component i in vapor and liquid phase, P is total pressure, P_i^{sat} is saturation pressure of pure solvent i, φ_i^G is

the fugacity coefficient of component i in the vapor phase, $\varphi^G_{i,pure}$ is that for pure solvent i (at the same temperature T), f_i is the experimental activity coefficient of i in the liquid phase. The last (exponential) term is the Poynting correction, with v_i^L the molar volume of solvent i and R is the gas constant.

The fugacity coefficient φ_i^G was estimated using the virial equation, truncated at the second virial coefficient, which gives

$$\varphi_i^G = \exp[\left(2\sum_j x_i^G B_{ij} - B\right) P/RT] \tag{5.71}$$

where B is the second virial coefficient for the mixture

$$B = (x_1^G)^2 B_{11} + 2x_1^G x_2^G B_{12} + (x_2^G)^2 B_{22} \tag{5.72}$$

with B_{ij} the second virial coefficient characterizing interactions between i and j molecules. B_{ii} may be obtained from experiment. For B_{12} we used the classic approximation [21]

$$B_{12} = (B_{11} + B_{22})/2$$

5.3.4 Description of the effect of temperature

The temperature was introduced into the various model parameters as follows.

As concerns the solvation numbers, it was assumed that the total solvation number $h_i(T)$ by solvent i in the solvent mixture was proportional to the fraction of solvent i on a salt-free basis, and that it varied linearly with T, that is

$$h_i = x_i^\circ [h_i^{(0)} + h_i^{(1)} \left(T - T^{(0)}\right)] \tag{5.73}$$

with $h_i^{(0)}$ the solvation number by pure solvent i at the reference temperature $T^{(0)}$ (here we took $T^{(0)} = 298.15$ K) and $h_i^{(1)}$ a parameter accounting for temperature dependency.

For the MSA mean ionic size in solvent i, we took

$$\sigma_i(T) = \sigma_i^{(0)} + \sigma_i^{(1)} \left(T - T^{(0)}\right) \tag{5.74}$$

For the $\tau_{ji}(T)$ interaction parameters, it was found that the following dependencies

$$\tau_{ji}(T) = \tau_{ji}^{(0)} + \tau_{ji}^{(1)} \left(1/T - 1/T^{(0)}\right) \tag{5.75}$$

and a similar relation for $\tau_{ji,ki}$ were sufficient for a description of the thermodynamic properties in the temperature range investigated here (25°C-100°C).

Besides, experimental values for the physical quantities, namely the relative permittivity and the density of a solvent i, were fitted according to the following functions.

$$\varepsilon_i(T) = \varepsilon_i^{(0)} + \varepsilon_i^{(1)} \left(T - T^{(0)}\right) + \varepsilon_i^{(2)} \left(T - (T^{(0)})\right)^2 \tag{5.76}$$

$$d_i(T) = d_i^{(0)} + d_i^{(1)} \left(T - T^{(0)}\right) + d_i^{(2)} \left(T - (T^{(0)})\right)^2 \tag{5.77}$$

The values of σ, ε and d for the solvent mixture at a temperature T were estimated by using the simple mixing relation

$$\Pi = x_1^{\circ}\Pi_1 + x_2^{\circ}\Pi_2 \tag{5.78}$$

for $\Pi = \sigma$, ϵ, d.

5.3.5 Dilution enthalpy and heat capacity.

This section is restricted to the case of purely aqueous solutions.

We have verified that NaCl at 100°C does not present any association.

Figure 5.1 [22] shows a surface in 3 dimensions which represents the negative logarithm of the equilibrium constant for the dissociation of NaCl into Na^+ and Cl^- solution as a function of the temperature between 400°C and 800°C and of the logarithm of the density of water.(-0.52 to -0.12 i.e. 0.01 to 0.1 molal)

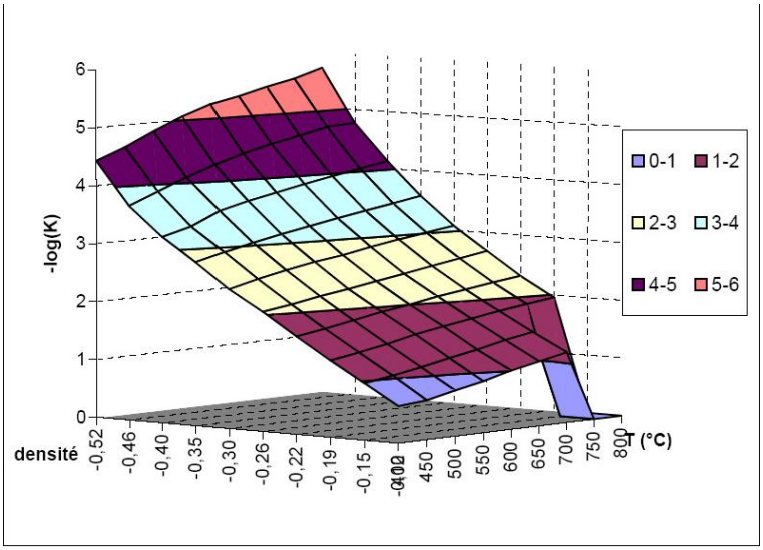

Figure 5.1: The negative logarithm of the equilibrium constant for the dissociation of NaCl at 0.1 to 0.01 molal as a function of the temperature and the logarithm of the density log d (gcm^{-3})

We used the data to obtain by extrapolation the equilibrium constant for the dissociation at 100°C: We plot on Figure 5.2 -log K as a function of the temperature for each density value. Fitting each curve we obtain a straight line.

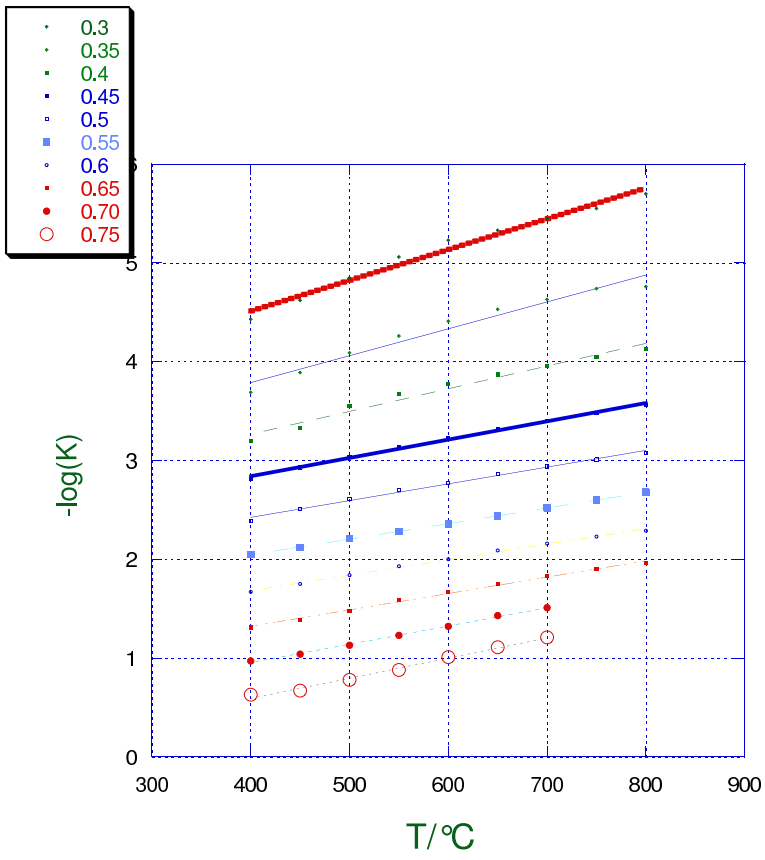

Figure 5.2: The curves of negative logarithm of the equilibrium constant for the dissociation of NaCl at 0.01 to 0.1 molal as a function of the temperature for one density d (gcm^{-3})

For each density value d we obtain, a relation -log K=a+bT, a, b and r (regression coefficients). Coefficients are reported in Table 1. Then, we evaluate K as a function of d at T=100°C. We obtain a straight line in Figure 5.3.

We find for the equilibrium constant a value of 26.91 by taking a density of 0.96 for water at 100°C in replacing this value in the following equation

$$-\log K = 5.51 - 7.22 * 0.96 \tag{5.79}$$

d (g.cm−3)	a	b (K^{-1})	r
0.3	3.2676	0.0031133	0.98888
0.35	2.6973	0.0027267	0.98262
0.4	2.3456	0.0023	0.9878
0.45	2.1022	0.00185	0.9973
0.5	1.7473	0.0016933	0.99688
0.55	1.4142	0.00158	0.99987
0.6	1.0516	0.0015733	0.9985
0.65	0.65533	0.0016633	0.9976
0.7	0.21536	0.00185	0.99882
0.75	0.22107	0.0020357	0.99521

Table 5.1: Fitting parameters for -log$K$= a+bT as a function of T and d.

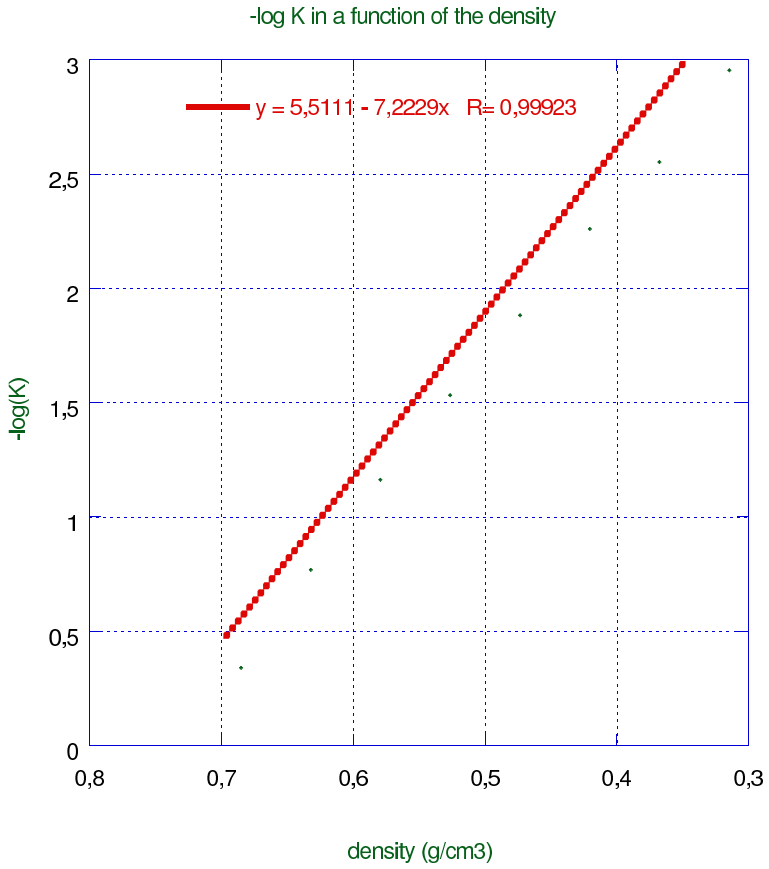

Figure 5.3: The curves of negative logarithm of the equilibrium constant for the dissociation of NaCl at 0.01 to 0.1 molal as a function of the density d (gcm^{-3})

thus

$$K = 10^{1.43} = 26.91 \tag{5.80}$$

The dissociation constant writes

$$K = \frac{[Na^+][Cl^-]}{[NaCl]} \tag{5.81}$$

and with α the dissociated fraction of NaCl we have

$$K = \frac{\alpha^2 m}{1-\alpha} \tag{5.82}$$

where m is the molality of salt.

Let us now discuss the validity of this constant value:

Taking a molality of 0.1 molal we obtain resolving Eq. 5.81, a dissociated fraction:

$$\alpha = \frac{-K \pm \sqrt{(}K(K+4m))}{2m} \tag{5.83}$$

$$\alpha = \frac{-26.91 \pm \sqrt{(}26.91(26.91+4*0.1))}{0.2} \tag{5.84}$$

We find a dissociated fraction of 0.996. We can thus consider that NaCl is nearly totally dissociated in a solution of 0.1 molal. As K is high it means there is not association at 6 molal.

As knowing this, we can express the excess Gibbs energy of solution per kilogram of water, denoted by $\mathcal{G}^{\mathcal{E}}$, which is given by [1, 23]

$$\mathcal{G}^E = \nu m RT(1 - \phi + \ln \gamma_{\pm}) \tag{5.85}$$

which is equivalent to $\sum_i N_i \mu_i^E$. In this equation, m is the molality of salt, $\gamma_{\pm}$ is given by Eq. 5.69 and ϕ is the osmotic coefficient

$$\phi \equiv -\frac{x_1}{1-x_1} \ln a_1 \tag{5.86}$$

in which $a_1 = a_W$ (Eq. 5.50)

The relative enthalpy per kilogram of water, L, is expressed as [23]

$$L = -T^2 \frac{\partial \mathcal{G}^{\mathcal{E}}/\mathcal{T}}{\partial T} \tag{5.87}$$

Then the apparent relative molal enthalpy [23] reads

$$\Phi_L = L/m \tag{5.88}$$

The apparent molal heat capacity, defined as

$$\Phi_{C_p} = \left(C_p - \frac{1}{M_1} C^{\circ}_{p_1} \right) /m \tag{5.89}$$

where C_p is the heat capacity of solution (for 1 kg of water) and $C^\circ_{p_1}$ is the heat capacity of pure water, is also given by [23]

$$\Phi_{C_p} = \bar{C}^\otimes_{p_s} + \frac{\partial \Phi_L}{\partial T} \tag{5.90}$$

in which $\bar{C}^\otimes_{p_s}$ is the partial molal heat capacity of salt at infinite dilution.

We now give below a few relations showing the connections between the above Eqs. 5.87-5.90.

The total relative heat capacity, J, is defined as [24]

$$J = C_p - C^\otimes_p = C_p - \left(n_1 C^\circ_{p_1} + n_s \bar{C}^\otimes_{p_s}\right) \tag{5.91}$$

where $C^\circ_{p_1}$ is the molal heat capacity of pure water, and n_1 and n_s are the mole numbers of water and solute, respectively. For 1 kg of water, one has

$$n_1 = 1/M_1 \quad n_s = m$$

In Eq. 5.91, $C^\otimes_p$ is the (hypothetical) heat capacity of a solution of the same composition, in which the components would have the same properties (same partial heat capacities) as at infinite dilution.

If we divide the total relative heat capacity by the mole number of solute one gets

$$\frac{J}{n_s} = \frac{C_p}{n_s} - \frac{n_1}{n_s} C^\circ_{p_1} - \bar{C}^\otimes_{p_s} \tag{5.92}$$

The total heat capacity reads:

$$C_p = C^\otimes_p + C^E_p \tag{5.93}$$

where C^E_p is the excess molal heat capacity

$$\frac{J}{n_s} = \frac{n_1 C^\circ_{p_1} + n_s \bar{C}^\otimes_{p_s} + C^E_p}{n_s} - \frac{n_1}{n_s} C^\circ_{p_1} - \bar{C}^\otimes_{p_s} = \frac{C^E_p}{n_s} \tag{5.94}$$

It may be shown using Eqs. 5.89, 5.90 and 5.87 that

$$\frac{J}{n_s} = \frac{C^E_p}{n_s} = \frac{\partial \Phi_L}{\partial T} \tag{5.95}$$

Thus,

$$\frac{\partial \Phi_L}{\partial T} = \frac{C_p}{n_s} - \frac{n_1 C^\circ_{p_1} + n_s \bar{C}^\otimes_{p_s}}{n_s} \tag{5.96}$$

$$= \frac{C_p(m) - C_p(\infty)}{n_s} \tag{5.97}$$

By definition $C_p = \frac{\partial H(m)}{\partial T}$ at constant pressure.

Hence

$$\frac{\partial \Phi_L}{\partial T} = \frac{\frac{\partial H(m)}{\partial T} - \frac{\partial H(\infty)}{\partial T}}{n_s} \tag{5.98}$$

where $\frac{\partial H(m)}{\partial T}$ and $\frac{\partial H(\infty)}{\partial T}$ are, respectively, the molal heat capacity at molality m calculated from the enthalpy, and that at infinite dilution from the enthalpy at infinite dilution.

Hence,

$$\Phi_L = \frac{H(m) - H(\infty)}{n_s} = \frac{H^E}{n_s} \tag{5.99}$$

where H^E is the enthalpy.

One gets

$$\frac{\partial \Phi_L}{\partial T} = \frac{\partial \left(\frac{H^E}{n_s}\right)}{\partial T} \tag{5.100}$$

$$= \frac{C_p}{n_s} - \frac{n_1 C^\circ_{p_1} + n_s \bar{C}^\otimes_{p_s}}{n_s} \tag{5.101}$$

$$\frac{\partial \Phi_L}{\partial T} = \Phi_{C_p} - \bar{C}^\otimes_{p_s} \tag{5.102}$$

with

$$\Phi_{C_p} = \frac{C_p - n_1 C^\circ_{p_1}}{n_s} \tag{5.103}$$

where Φ_{C_p} is the apparent molal heat capacity.

Unlike C_p and $C^\circ_{p_1}$, $\bar{C}^\otimes_{p_s}$ is not an experimentally measurable quantity.

$$\bar{C}^\otimes_{p_s} = \Phi_{c_p} - \frac{\partial \Phi_L}{\partial T} \tag{5.104}$$

$\bar{C}^\otimes_{p_s}$ is the heat capacity of solute at infinite dilution.

It should be noted that Φ_{C_p}, C_p and $\frac{\partial \Phi_L}{\partial T}$ depend on the concentration.

$$\frac{\partial \Phi_L}{\partial T} = \frac{C_p - n_1 C^\circ_{p_1} - n_s \bar{C}^\otimes_{p_s}}{n_s} \tag{5.105}$$

But $\bar{C}^\otimes_{p_s}$ does not depend on the concentration because it is defined at the reference state.

5.3.6 Relation between partial heat capacity, entropy and chemical potential at infinite dilution

The partial heat capacity of an ion i (= C or A), $\bar{C}_{p,i}$, is related to its partial entropy, $\bar{S^\otimes_i}$, through

$$\bar{C}^\otimes_{p,i} = T \frac{\partial \bar{S^\otimes_i}}{\partial T} \tag{5.106}$$

This relation can be easily demonstrated from the relations $H = G + TS$ and $S = -\partial G/\partial T$, and the definition

$$C_p = \frac{\partial H}{\partial T}$$

The partial entropy $\bar{S_i^{\otimes}}$ is

$$\bar{S_i^{\otimes}} = \left(\frac{\partial S^{\otimes}}{\partial N_i}\right) \tag{5.107}$$

where i=A,C.

Besides,

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N_j} \tag{5.108}$$

Hence, using Eqs. 5.107,5.108

$$\bar{S_i^{\otimes}} = -\left(\frac{\partial^2 G^{\otimes}}{\partial N_i \partial T}\right)_{P,N_{j\neq i}} \tag{5.109}$$

The solvation entropy of solute at infinite dilution is defined as

$$\bar{S}_s^{\otimes} = \nu_C \bar{S}_{C'}^{\otimes} + \nu_A \bar{S}_{A'}^{\otimes} \tag{5.110}$$

Using Eq. 5.107, one has that

$$\bar{S_i^{\otimes}} = \frac{\partial S^{\otimes}}{\partial N_i} = -\frac{\partial \left(\frac{\partial G^{\otimes}}{\partial T}\right)}{\partial N_i} = -\frac{\partial^2 G^{\otimes}}{\partial T \partial N_i}$$

from which it stems that

$$\bar{S_i^{\otimes}} = -\frac{\partial \mu_i^{\otimes}}{\partial T} \tag{5.111}$$

In the framework of our model, the chemical potential of i at infinite dilution, $\mu_i^{\otimes}$, may be decomposed as

$$\mu_i^{\otimes} = \mu_i^{\otimes,id} + \mu_i^{\otimes,SR} \tag{5.112}$$

because it is clear that the excess electrostatic part, $\mu_i^{\otimes,el}$, vanishes at infinite dilution of salt.

It results from Eqs. 5.111 and 5.112 that the partial entropy at infinite dilution is

$$\bar{S}_i^{\otimes} = \bar{S}_i^{\otimes,id} + \bar{S}_i^{\otimes,SR} \tag{5.113}$$

The chemical potential of solute at infinite dilution reads

$$\mu_s^{\otimes} \equiv \nu_C \mu_C^{\otimes} + \nu_A \mu_A^{\otimes} \tag{5.114}$$

The partial molal heat capacity of solute at infinite dilution, defined by

$$\bar{C}_{p,s}^{\otimes} \equiv \nu_C \bar{C}_{p,C}^{\otimes} + \nu_A \bar{C}_{p,A}^{\otimes}$$

is related to the entropy of solute at infinite dilution by [25]

$$\bar{C}^{\otimes}_{p,s} = -T\frac{\partial^2 \mu^{\otimes}_s}{\partial T^2} \tag{5.115}$$

which can be shown by using Eqs. 5.106, 5.111 and 5.114.

5.4 Results and Discussion

5.4.1 Case of aqueous solutions

We have represented the following thermodynamic properties: the osmotic coefficient, ϕ, the molal heat enthalpy, Φ_L, and the apparent molal heat capacity, Φ_{C_p}, for some "simple" binary aqueous electrolytes (water + one salt) as a function of the temperature.

These quantities could be fitted *simultaneously* in the case of LiCl and KCl solutions.

Our MSA-NRTL model with hydration was used to compute the various thermodynamic quantities under consideration. The osmotic coefficient, ϕ, was calculated using Eqs. 5.50 and 6.43. The molal heat enthalpy, Φ_L, was computed from Eqs. 5.85, 5.87 and 5.88. The apparent molal heat capacity, Φ_{C_p}, was deduced from Eq. 5.90. These tedious algebraic calculations were performed using the Maple software.

First, as usual, we performed the test consisting of verifying numerically that the osmotic coefficient, ϕ, and the mean salt activity coefficient, $\gamma_{\pm}$, accurately satisfy the Gibbs-Duhem relation. Then, the parameter values of our model were adjusted by simultaneously fitting experimental values for ϕ, Φ_L and Φ_{C_p}.

Experimental data were taken from the following sources.

For LiCl solutions, data for ϕ are given at 25°C by Hamer and Wu [26]. For temperatures between 25°C and 100°C, Gibbard [27] gives values up to 6 M for ϕ and for Φ_L. Values for Φ_{C_p} were taken from Rüterjans et al. [28].

For NaCl solutions, Gibbard and Scatchard [29] reported values for ϕ and Φ_L between 25°C and 100°C up to 6 molal.

For KCl solutions, Snipes and Ensor [30] reported values for ϕ and Φ_L between 25°C and 100°C. Tanner and Lamb [31] measured molal heat capacities up to 4 mol kg^{-1}.

For LiBr solutions, data for ϕ are given by Hamer and Wu [26] at 25°C. Values for Φ_L are available from Harned and Owen [24] at 25°C.

For NaBr solutions, Hamer and Wu [26] reported values of ϕ at 25°C and for Φ_L from Harned and Owen's values [24].

Table 2. Results of fits for various salts as a function of the temperature (range= 0.1-6 mol kg^{-1})(except KCl for which range= 0.1-4 mol kg^{-1}) aqueous solutions.

Salt	$\tau_{WC,AC}^{(0)}$	$\tau_{CW}^{(0)}$	$\tau_{AW}^{(0)}$	$\tau_{WC,AC}^{(1)}{}^{a}$	$\tau_{CW}^{(1)}$	$\tau_{AW}^{(1)}$	$\sigma_1^{(0)}$	$\sigma_1^{(1)b}$	$h_1^{(0)}$	$h_1^{(1)c}$
LiCl	2.07	-1.36	-1.47	52.8	-36.5	9.98	0.49	-0.005	4.8	-0.0100
NaCl	-90.8	-2.63	91.72	-25646	-612	27764	0.469	0	2.39	-0.01
KCl	3.46	1.69	-1.43	1026	-904	9.56	0.403	0.003	4.85	-0.022
NaBr	3.23	-2.5	-1.25	1166	-2376	258	0.446	3.9210^{-3}	4.39	0.016
LiBr	4.44	-3.18	-2.06	102	-470	-876	0.443	7.9210^{-2}	4.75	0.08

^{a} in K, ^{b} in nm, ^{c} in K^{-}1.

Table 3. Results of fits of osmotic coefficient, dilution enthalpies and heat capacities.

Ref.	Salt	T (/K)	AARD$_\phi{}^{b}$	$AARD_{\Phi_L}{}^{c}$	$AARD_{\Phi_{C_p}}{}^{d}$
[27, 28]	LiCl	298-373	0.176	11.15	3.52
[29]	NaCl	298-373	0.07	9.68	
[30, 31]	KCl	298-358	0.06	7.88	6.19
[26, 24]	NaBr	298	0.247	5.82	
[26, 24, 32]	LiBr	298	1.15	23.3	

^{b}Average Absolute Relative Deviation (AARD) in % for ϕ; ^{c}(AARD) in % for Φ_L; ^{d}(AARD) in % for Φ_{C_p}.

Results for some aqueous 1-1 electrolyte solutions between 25°C and 100°C are collected in Tables 2 and 3. Plots of ϕ are shown in Figures 5.4-5.7 in the case of LiCl, NaCl, KCl and NaBr, respectively. Plots of Φ_L are shown in Figures 5.8-5.11 for the same electrolytes. The Φ_{C_p} is represented for LiCl and KCl in Figures 5.13 and 5.14.

The LiCl and KCl systems were represented with the use of a total of 10 adjustable model parameters for the simultaneous representation of ϕ, Φ_L and Φ_{C_p}. Namely, these parameters were $p^{(0)}$ and $p^{(1)}$ with $p = \tau_{CW}, \tau_{AW}, \tau_{WC,AC}, \sigma_1$ and h_1. For comparison, Silvester and Pitzer [23] introduced 19 parameters to describe the same properties for NaCl solutions in the (wider) range 0-300°C. We are not aware of similar results for LiCl or KCl solutions. As seen in Figures 5.4,5.8,5.13 for LiCl,

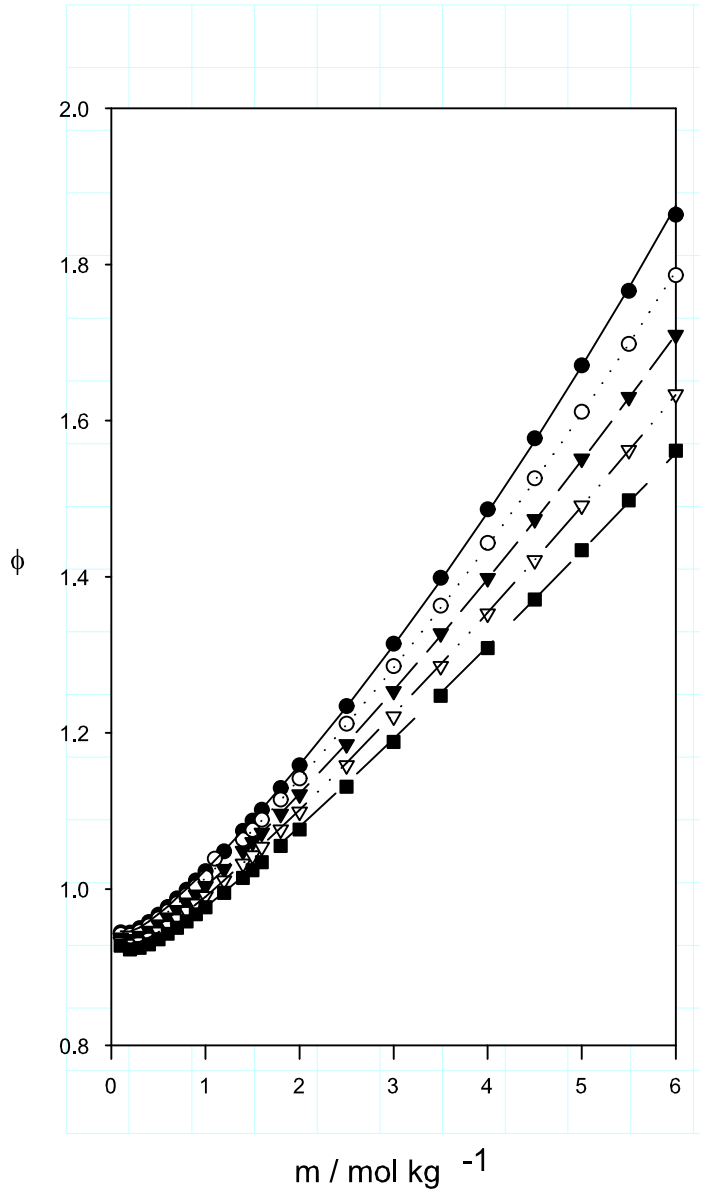

Figure 5.4: Osmotic coefficient as a function of molality for aqueous LiCl solution. Symbols are experimental data [26, 27]: (●) 273 K, (○) 298 K, (▼) 323 K, (▽) 348 K, (■) 373 K

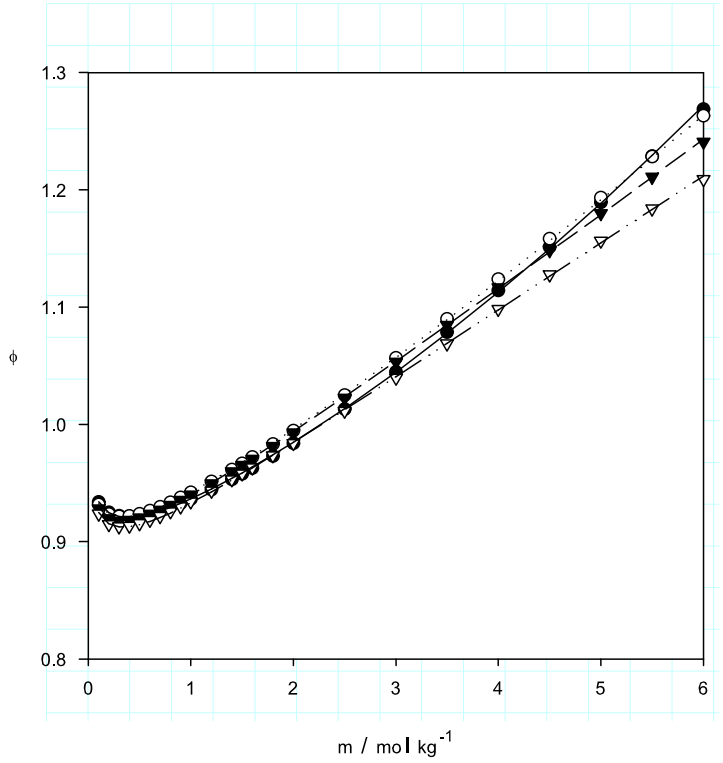

Figure 5.5: Osmotic coefficient as a function of molality for aqueous NaCl solution. Symbols are experimental data [29]: (●) 298 K, (○) 323 K, (▼) 348 K, (▽) 373 K

and 5.6,5.10,5.14 for KCl, and in Table 3 giving the average absolute relative deviation (AARD) of fits, the representations of the 3 properties for these two solutions are quite satifactory.

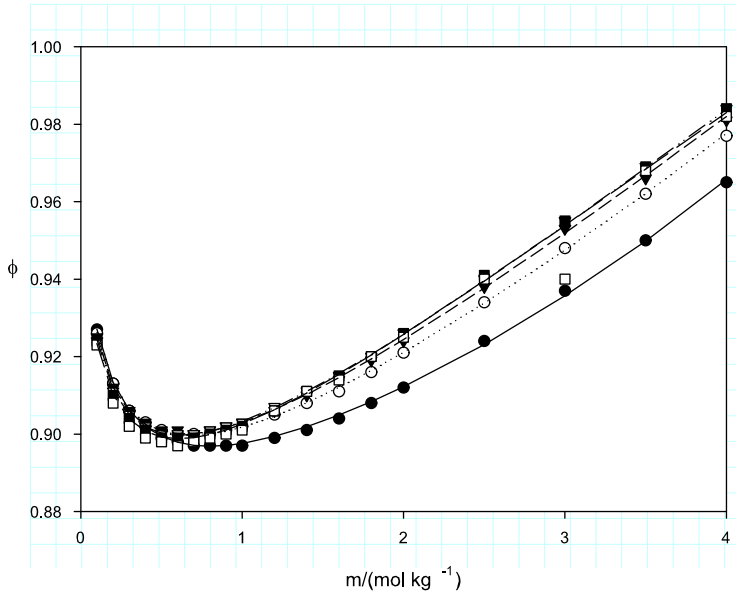

Figure 5.6: Osmotic coefficient as a function of molality for aqueous KCl solution. Symbols are experimental data [30]: (•) 298 K, (○) 313 K, (▼) 323 K, (▽) 333 K, (■) 343 K, (□) 353 K

We notice in Figure 5.4 that ϕ decreases with temperature for all molalities. It is opposite for KCl, as seen in Figures 5.6. For NaCl in Figure 5.5 ϕ does not exhibit a monotonous behavior as a function of T contrary of LiCl. The quality of fit is satisfactory. However the magnitude of the parameters in Table 1 is large. The behavior of NaCl is intermediate between that of LiCl and KCl with an initial increase followed by a decrease, for moderate molalities. It is similar to LiCl at 6 mol kg^{-1}. We notice that this peculiarity makes NaCl solutions difficult to model as compared to other solutions. In Figure 5.7 the quality of fit of NaBr is satisfactory.

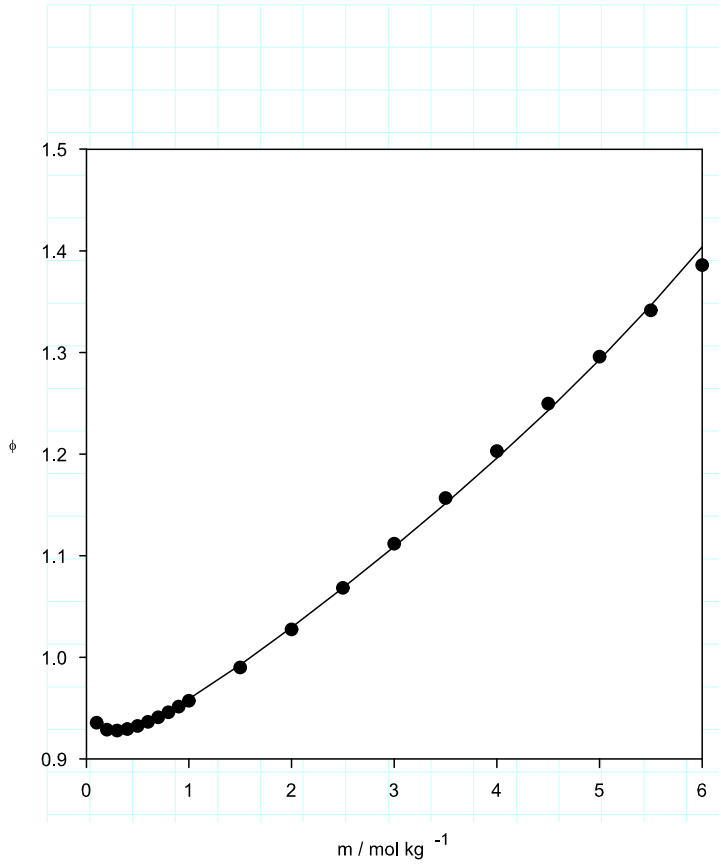

Figure 5.7: Osmotic coefficient as a function of molality for aqueous NaBr solution. Symbols are experimental data [26]: (•) 298 K

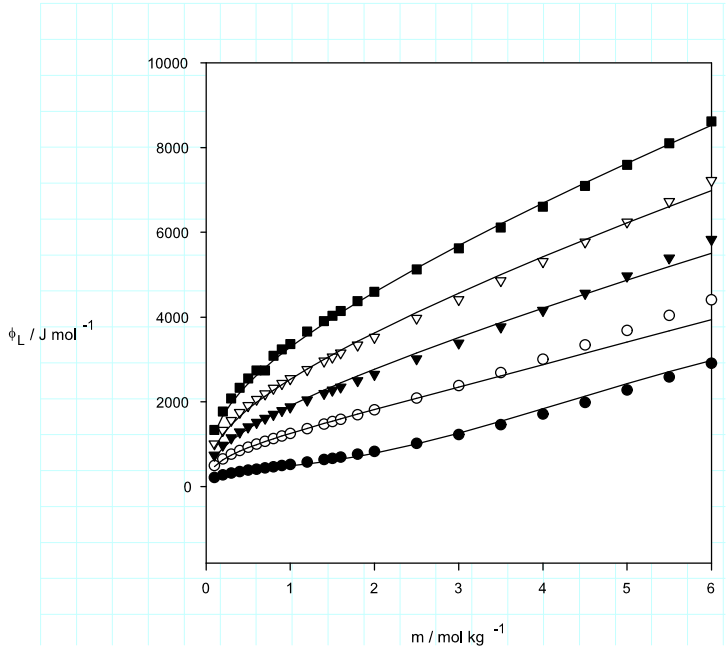

Figure 5.8: Molal heat enthalpy as a function of molality for aqueous LiCl solution. Symbols are experimental data [27]: (●) 273 K, (○) 298 K, (▼) 323 K, (▽) 348 K, (■) 373 K

The values of the deviations in the fit of molal heat enthalpies, shown in Table 3, are rather satisfactory, except in the case of LiBr.

The molal heat enthalpies, Φ_L, of LiCl, NaCl, KCl and NaBr solutions increase with temperature (Figures 5.8-5.11). Figure 5.12 summarizes the results for the molal heat enthalpies at different temperatures for several salts.

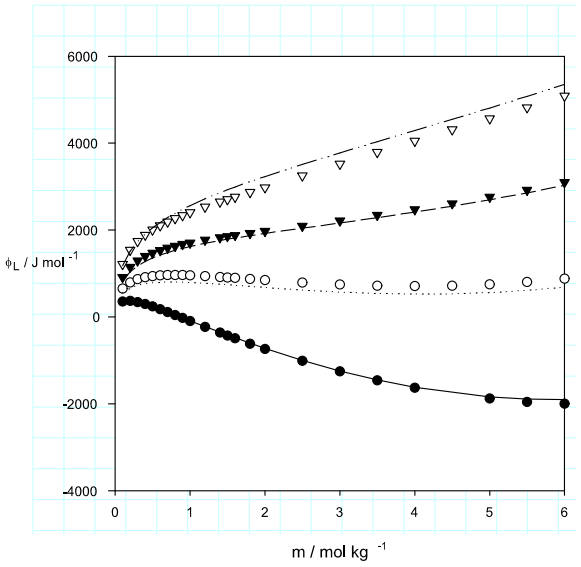

Figure 5.9: Molal heat enthalpy as a function of molality for aqueous NaCl solution. Symbols are experimental data [29]: (●) 298 K, (○) 323 K, (▼) 348 K, (▽) 373 K

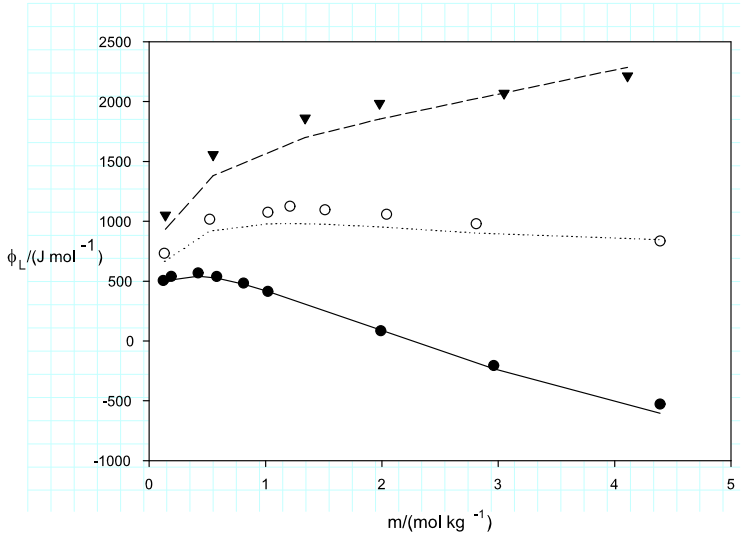

Figure 5.10: Molal heat enthalpy as a function of molality for aqueous KCl solution. Symbols are experimental data [30]: (●) 313 K, (○) 333 K, (▼) 353 K

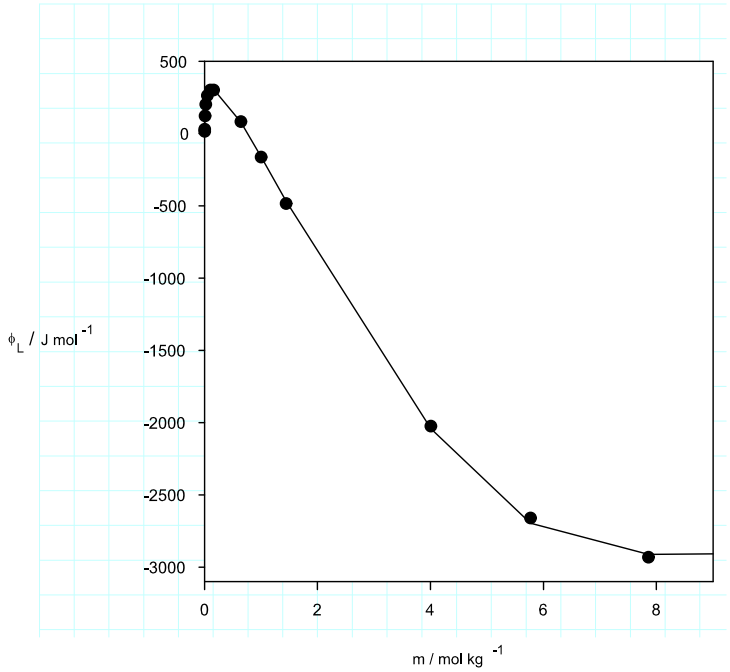

Figure 5.11: Molal heat enthalpy as a function of molality for aqueous NaBr solution. Symbols are experimental data [24]: (•) 298 K

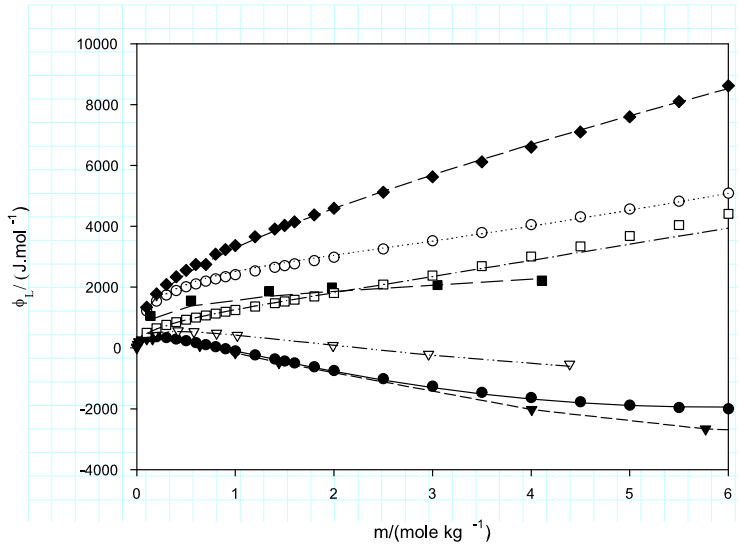

Figure 5.12: Recapitulation of molal heat enthalpies as a function of molality for aqueous solutions at different temperatures. Symbols are experimental data: For LiCl: (□) 298 K, (♦) 373 K, for KCl: (▽) 313 K, (■) 353 K, for NaCl: (•) 298 K, (○) 373 K, for NaBr: (▼) 298 K

As regards the heat capacities, it is important to notice that the standard partial molal heat capacity of a salt, $\bar{C}^{\otimes}_{p,s}$, was taken as an adjustable parameter in the fit of Φ_{C_p} (Eq. 5.90) because this quantity is not measurable experimentally.

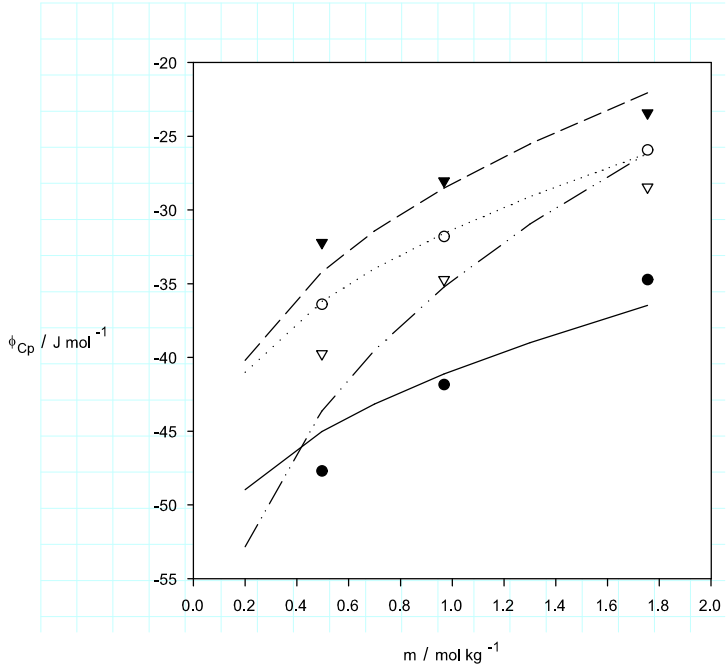

Figure 5.13: Molal heat capacity as a function of molality for aqueous LiCl solution. Symbols are experimental data [28]: (●) 303 K, (○) 323 K, (▼) 343 K, (▽) 373 K

Our fitted values of $\bar{C}^{\otimes}_{p,s}$ are given in Table 4. They may be compared with the results reported in references [28, 33]. It is seen in Figure 5.15 that our set of values is in reasonable agreement with these previously published values.

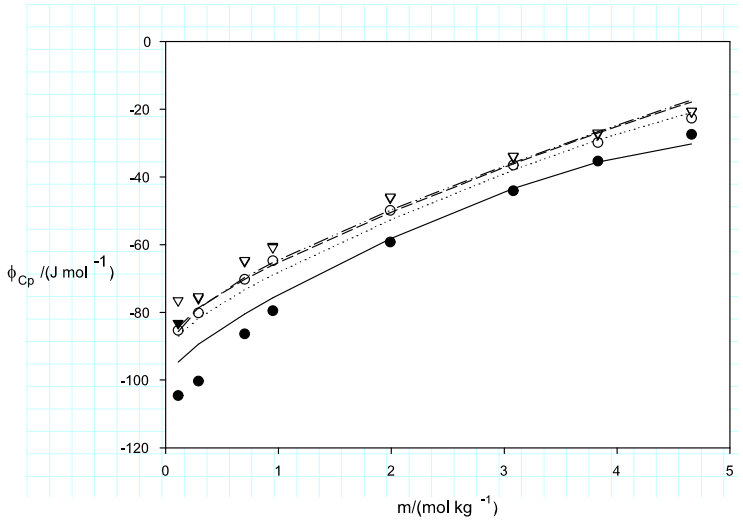

Figure 5.14: Molal heat capacity as a function of molality for aqueous KCl solution. Symbols are experimental data [31]: (●) 298 K, (○) 318 K, (▼) 338 K, (▽) 358 K

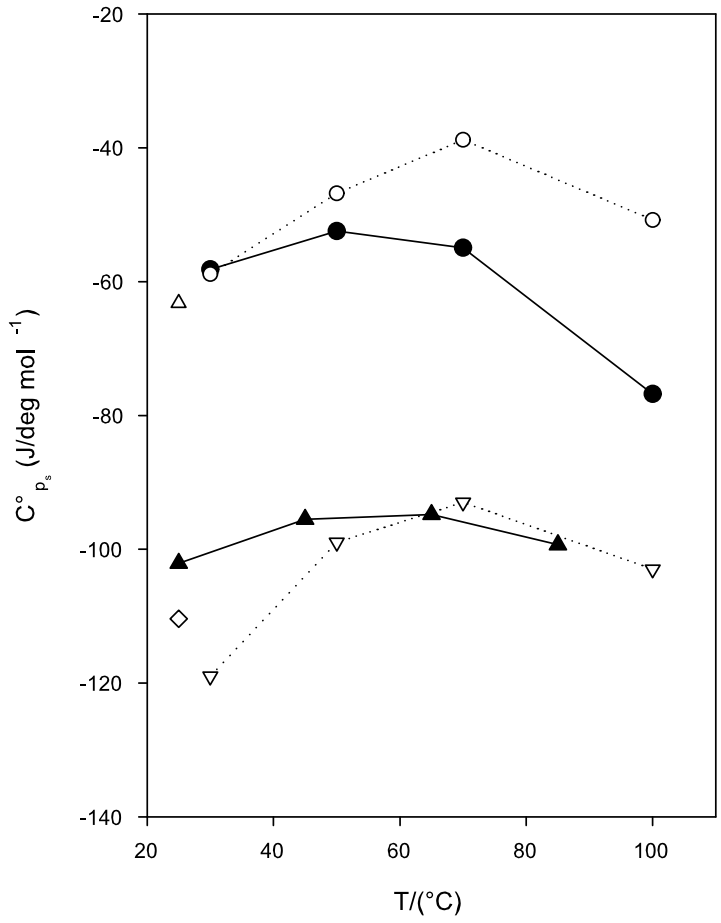

Figure 5.15: Partial heat capacity at infinite dilution $C_{p_s}^{\otimes}$. • LiCL and ▲ KCl (our work), ∘ LiCl and ▽ KCl [28], △ LiCl and KCl ◇ [33].

Table 4. Experimental values of $\bar{C}^{\otimes}_{p,s}$ calculated from Eq. 5.104 for LiCL

T (/K)	$\bar{C}^{\otimes exp}_{p_s}$	$\bar{C}^{\otimes fit}_{p_s}$
303.15	-68.16	-58.17
323.15	-56.26	-52.46
343.15	-51.47	-54.94
373.15	-58.1	-76.78

One also notices that this quantity for Li^+ is larger than for K^+. This fact, already observed by other authors [34, 35, 36] was interpreted by a stronger ionic hydration in the case of Li^+ as compared to K^+. Zwicky [35, 36] suggests two effects: *(i)* a physical effect of the ion on the solvent which is manifested as an internal pressure varying from point to point in the solution, and *(ii)* a chemical effect of the ion on the solvent which plays a part in determining the thermal properties of solutions, and for dilute solutions, increases linearly with the concentration. Webb [37] writes that the electrostriction effect is due to the pressures resulting from the attraction of the solvent dipoles by the ion. Authors [28, 34, 38, 25, 39] suggest that it might be interpreted in terms of structure breaking and structure making effect. Lynden-Bell [40] uses the solvation entropy which we have seen in a previous section, to describe the notion of structure breaking and structure making. This author proposes two alternative interpretations for these phenomena. In Figure 5.16 the solvation entropy becomes more negative as the solvent molecules become aligned in the electric field of the ion, this is the structure making effect. The increase in solvation entropy with charge is the result of the structure breaking by the ion. The double maximum occurs when the structure-making balances the structure-breaking.

Another point of view is to consider the uncharged solute, and we can remark a minimum for the solvation entropy. The low solvation entropy can be attributed to hydrophobic ordering. This effect has been known as the iceberg effect [41]. We can explain this effect with the micelle example and the monomers. Generally the internal energy U_1 for the micelle is higher that of the monomer. If we consider the solvation entropy we have the same trend, S_{solv_1} is higher than S_{solv_2}. Only the free energy F_1 of the system of the micelle and F_2 of the monomer has the opposite trend. Indeed $F = U - TS$

hence:

$$F_1 < F_2 \tag{5.116}$$

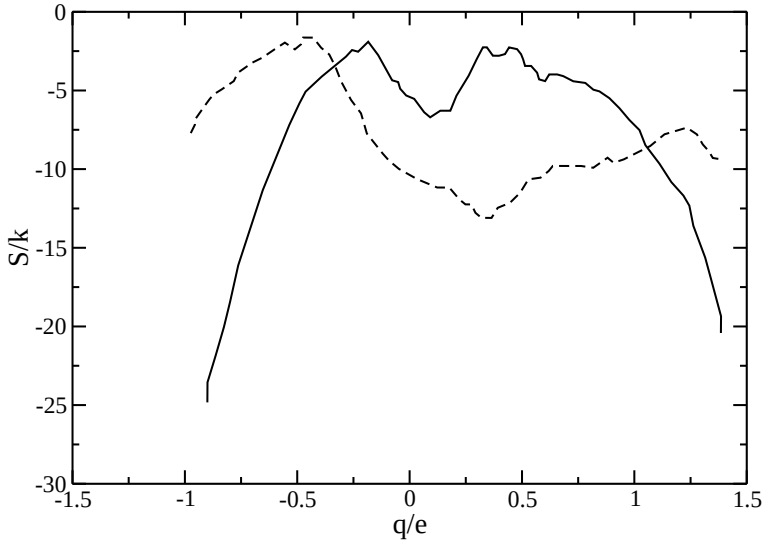

Figure 5.16: Variation of the solvation entropies of spheres of the size of sodium and chloride ions with ion charge at room temperature Solid line Na^{+q} and dotted line Cl^{+q}. Taken from [40].

The hydrophobic effect is attributed to the organization of the water molecules around ion. Water forms a cage around ion. If this manner is well-ordered we have the lower solvation entropy. The energy is very small and the solvation entropy is determined by the probability of finding a cavity in the liquid that is large enough to insert the sphere of solute. Thus the solvation entropy is negative and becomes more negative as the solute size increases. It has been shown [42] that the distribution of cavities in the neat liquid is sharpened by the network structure lowering the solvation entropy for larger solutes. The residence times of water molecules in the primary hydration shells of discharged sodium Na°, chloride Cl°, and iodide I° in SPC/E (water model) water are approximately 9, 18, and 24 picoseconds respectively at 298 K. The lifetimes of these cages are relatively long and they increase with the size of the non polar solute. The cage begins to break down when the solute is charged and the solvation entropy rises to a maximum. We have a structure-breaking effect. Further increases in the charge lower the entropy as the solvent molecules are ordered by the electric field of the solute. The residence times of water in the primary shells of the Na^{+}, Cl^{-}, I^{-} ions in Simple Point Charge - Extended (SPC/E) water are approximatively 20, 13, and 9 picoseconds at 298 K. They decrease with the size of the solute which the opposite trend of the uncharged solute.

However, these notions have recently been shown to be relatively ambiguous [43].

Frank and Evans [39] classified the ions on the basis of their partial solvation entropies because the entropy is an extensive property with a sound physical mean-

ing. Unfortunately, the present MSA-NRTL model with ion hydration cannot be used to compute values for the partial solvation entropy of ions at infinite dilution, because this model takes the hydrated ion as a reference (the species involved in the NRTL relation is the ion plus its hydration shell) and thus does not describe the interaction of the bare ion with water, which is what would be needed here.

Besides, Eq. 5.104 can be used to determine values for the $\bar{C}^{\otimes}_{p,s}$, by using experimental values for Φ_L and Φ_{C_p} as a function of T. This was done by first fitting the values for $\Phi_L(T)$ vs. T. This fit allowed us to calculate the derivative of Φ_L w.r.t. T, and introduce this value into Eq. 5.104. The calculation was made for two salt concentrations in the case of LiCl (for which sufficient data are available as a function of temperature, which is not the case of other salts), at 0.5 and 1 mol kg^{-1}. In principle, the resulting values for $\bar{C}^{\otimes}_{p,s}$ should not depend on the concentration used to compute it, and it should be a function of T alone for given salt.

The are given in Table 4. Figure 5.15 shows that displays negative values of $\bar{C}^{\otimes}_{p_s}$ over the entire temperature range of 10-80°C. This result is in accordance with Rüterjans et al. [28].

We also compared the "experimental" values of $\bar{C}^{\otimes}_{p_s}$ with our fitted values. Figure 5.17 shows that the "experimental" values at 0.5 and 1 mol kg^{-1} are quite close to each other, and differ appreciably from the fitted values at 300 and 373 K.

In Figure 5.13, we observe that, in the case of LiCl, Φ_{C_p} varies in a non-monotonous way as a function of T for any concentration. Initially, it increases up to 343 K, and then it decreases. The model renders this behavior rather satisfactorily in view of the difficulty of describing this second-order thermodynamic quantity (second derivative of G w.r.t. T). Figure 5.18 sums up the results for the molal heat capacities at different temperatures for several salts.

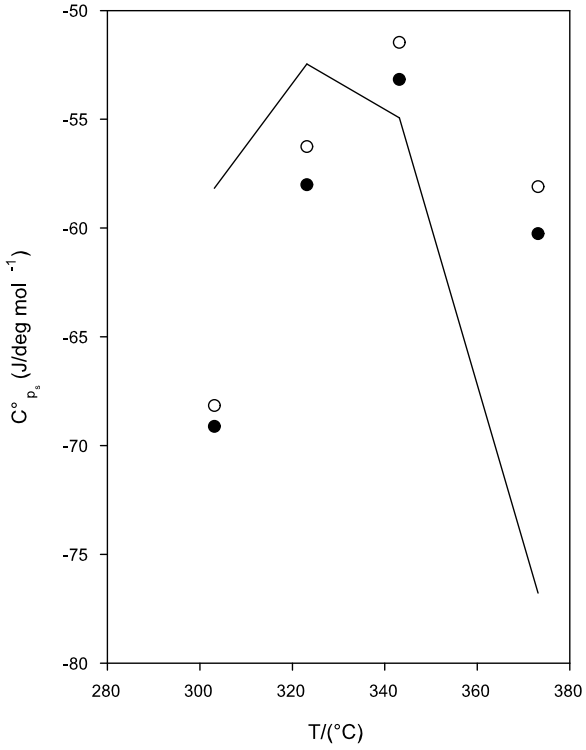

Figure 5.17: Molal heat capacity at infinite dilution $C_{p_s}^{\otimes}$. ∘ LiCL 0.5m experimental values, • LiCl 1m experimental values, solid line fit values

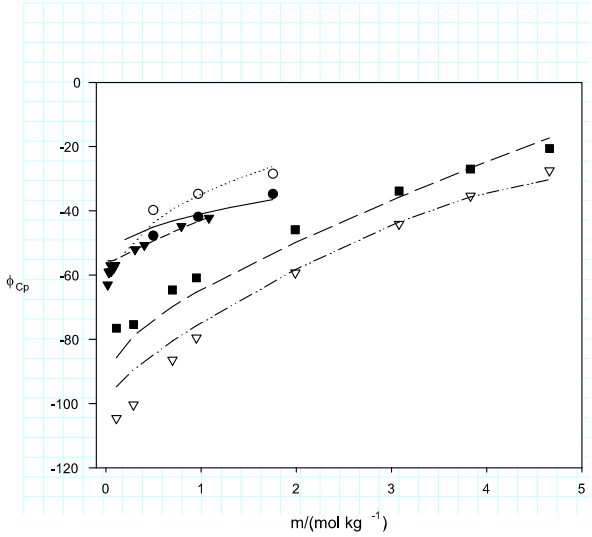

Figure 5.18: Recapitulation of molal heat capacities as a function of molality for aqueous solution at different temperatures. For LiCl: (•) 303 K, (∘) 373 K, for KCl: (▽) 298 K, (■) 358 K, for LiBr: (▼) 298 K.

Lastly, one notices that $\Phi_{C_p}(\text{LiCl}) > \Phi_{C_p}(\text{KCl})$ for given temperature. The same trend is found for $\bar{C}^{\otimes}_{p,s}$.

In Table 2 we also remark that the three $\tau^{(0)}_{WC,AC}$, $\tau^{(0)}_{CW}$, $\tau^{(0)}_{AW}$ have a little small values for the five salts of the order of a few kT, except for NaBr and LiBr which have $\tau^{(0)}_{WC,AC} \approx 4$. We also notice that $\tau^{(0)}_{AW}$ are close for the LiCl, KCl systems. The values are satisfactory.

On the contrary, $\tau^{(1)}_{WC,AC}$, $\tau^{(1)}_{CW}$ and $\tau^{(1)}_{AW}$ for NaCl are rather high and exhibit a pathological behavior. NaCl presents a peculiar behavior which is difficult to represent. The high values obtained reflect this difficulty.

If one looks at the mean ionic size we can see that it decreases by 69% for LiCl when it passes from 25°C to 100°C. It remains constant for NaCl. In the case of KCl, the mean ionic size increases by 56% for the same temperature variation. We observe the same trend for NaBr which passes from 0.446 nm at 298 K to 0.74 nm at 373 K, an increase of 60%. With regard to LiBr this size decreases a lot.

The third parameter which presents a good behavior as a function of the temperature is the hydration number. It decreases for the first three salts LiCl, NaCl and KCl, of 15%, 31% and 34% respectively.

For NaBr we observe an increase of the hydration number of 28% and finally for LiBr an important gap.

5.4.2 Mixed aqueous solvent electrolytes

We have studied the mixed aqueous solvent electrolytes (two solvents + one alkali salt) to calculate the activity coefficients of water and organic solvent at the temperature between 52°C and 72°C.

We verified numerically that the activity coefficients f_1 for water, f_2 for solvent and f_s for the salt accurately satisfy the Gibbs-Duhem relation.

The NRTL binary interaction parameters τ_{ij} obtained for the binary subsystems [16, 44] were used for the ternary systems. Two sets of binary parameters were determined earlier: those for the water/salt aqueous solution and those for the binary water (solvent 1)/solvent 2 mixture. The first set was calculated in the previous chapter [15].

As we have seen in the theoretical section, the activity coefficients of water and solvent, f_1 and f_2, can be computed from the vapor-liquid equilibrium data.

Data for the density of the water/methanol and water/ethanol mixtures were taken from refs. [45] and [46], respectively. Those for the virial coefficients were found in ref. [47] for methanol, from ref. [48] for ethanol, and from ref. [49, 50, 51] for water. The values of the dielectric constant of ethanol were taken from ref. [52] and from ref. [53] for methanol. Finally, the saturation pressures were obtained from refs. [54, 55] for water, ref. [56] for ethanol and from ref. [57] for methanol. The values of molar volumes were calculated from density values [58, 59].

The results for the description of mixed aqueous solvent electrolytes at different temperatures, are collected in Table 5. Plots of the different thermodynamic properties are given in Figure 5.19-5.23.

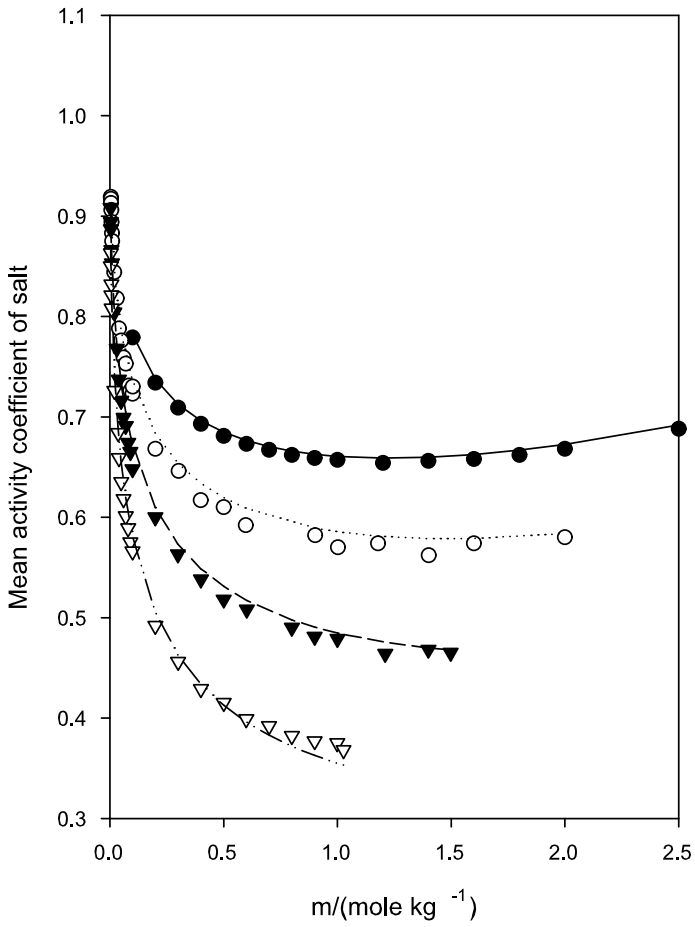

Figure 5.19: Results of fits for NaCl water-ethanol mixture at 25°. (•) 0 % ethanol, (∘) 20 % ethanol, (▼) 40 % ethanol, (▽) 60 % ethanol

These properties were represented using a total of 5 new adjustable parameters. Namely, these parameters were $p = \tau_{CZ}, \tau_{AZ}, \tau_{ZC,AC}, \sigma_2$ and h_2.The AARD value of 3.3% for the activity coefficient of water and ethanol in the salt-water-ethanol system obtained is much smaller than the value for water and methanol in the LiCl-water-methanol mixture. On the other hand, the AARD for NaBr-water-ethanol and KCL-water-methanol are with teh top of 10%. It is seen when one adds a little salt that the experimental activity coefficient of water changes much, this effect cannot be predicted by the model. This model does not account for this effect: the dramatic drop of experimental activity coefficient of water upon salt addition for small quantity of salt.

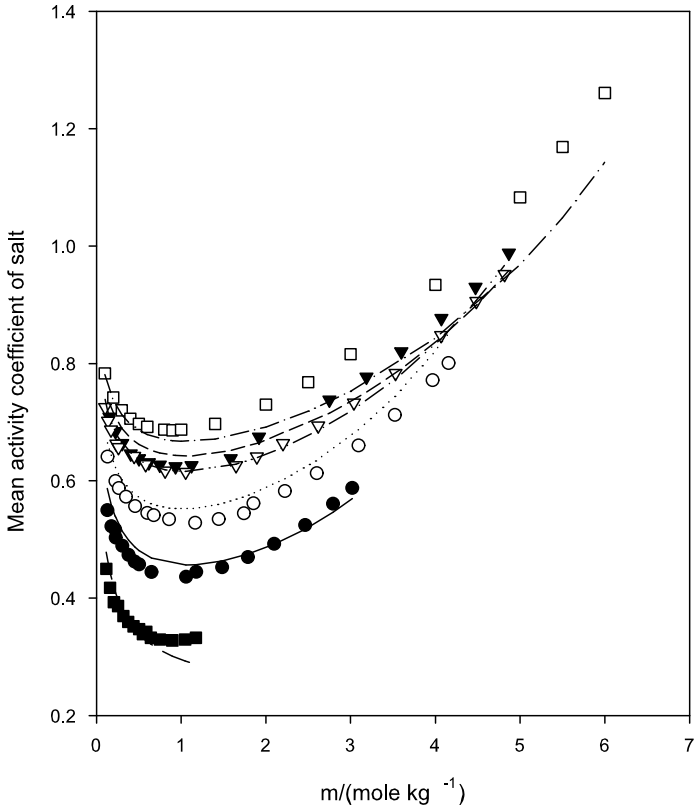

Figure 5.20: Results of fits for NaBr water-ethanol mixture at 25°. (□) refers 0 % ethanol, (■) 10 % ethanol, (▽) 20 % ethanol, (○) 40 % ethanol, (●) 60 % ethanol, (▼) 80 % ethanol

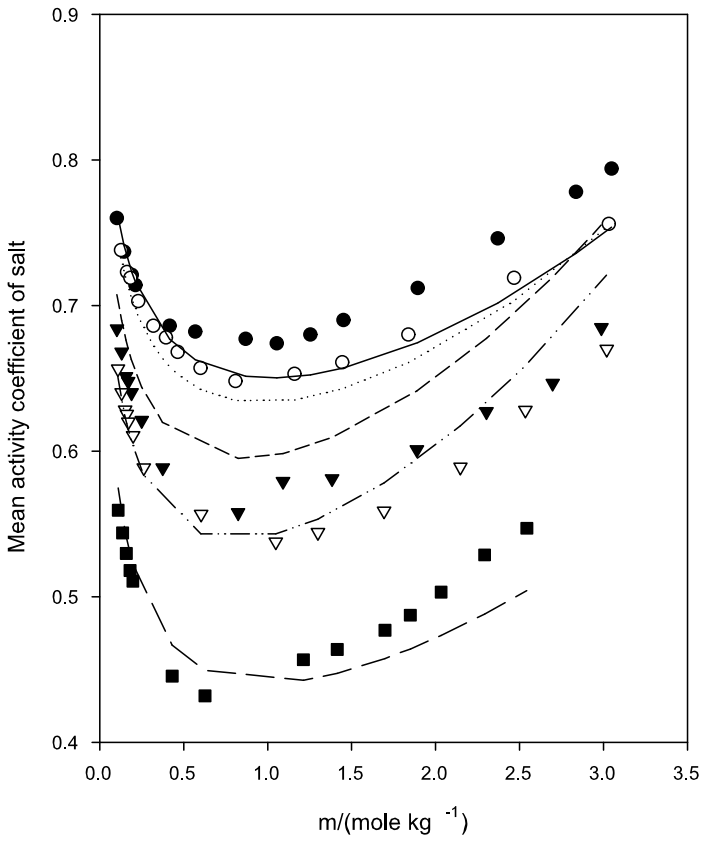

Figure 5.21: Results of fits for NaBr water-methanol mixture at 25°. (●) refers 10 % methanol, (○) 20 % methanol, (▼) 40 % methanol, (▽) 60 % methanol, (■) 80 % methanol

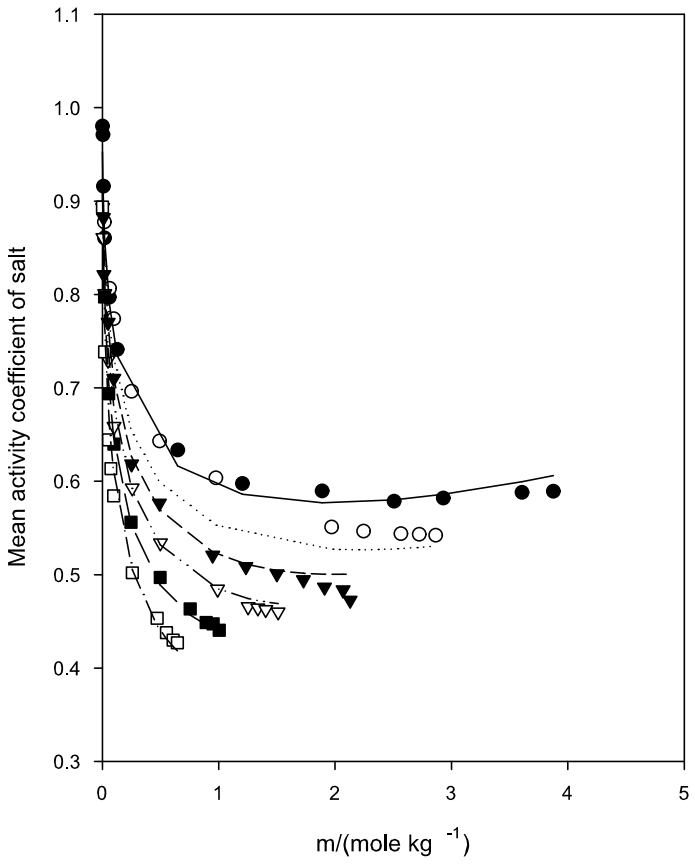

Figure 5.22: Results of fits for KCl water-methanol mixture at 25°. (●) 10 % methanol, (○) 20 % methanol, (▼) 30 % methanol, (▽) 40 % methanol, (■) 50 % methanol, (□) 60 % methanol

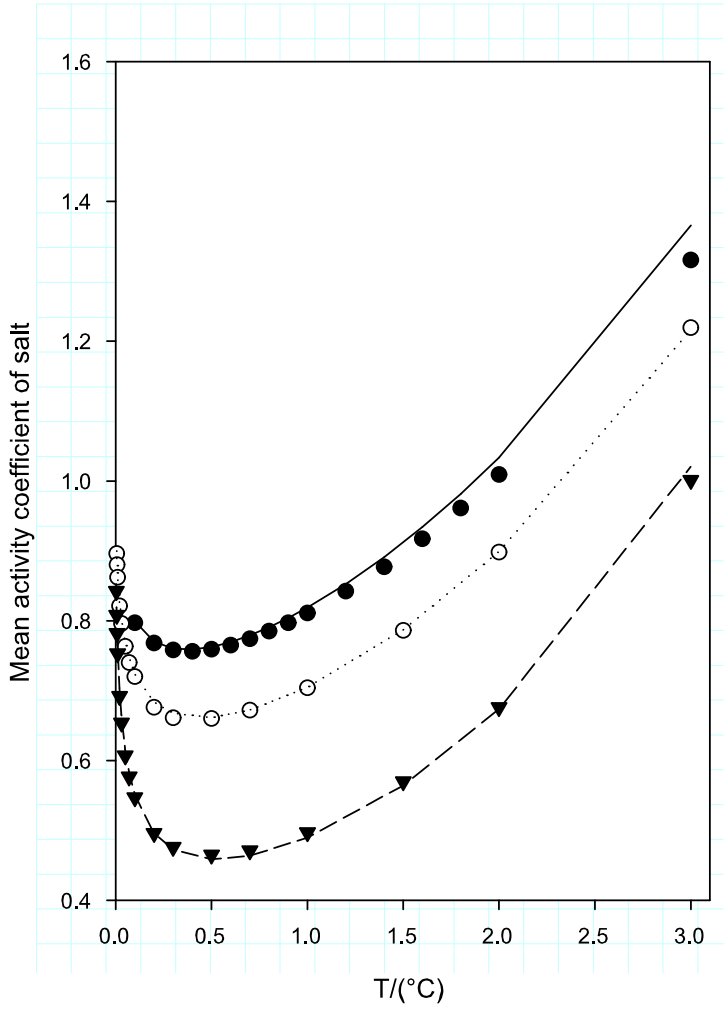

Figure 5.23: Results of fits for HCl water-dioxane mixture at 25°. (●) 0 % dioxane, (○) 20 % dioxane, (▼) 45 % dioxane

Table 5. Effective values of parameters for temperatures between 352-372 K.

Ref.	Mixture	T (/K)	x_{LiCl}	x_1	x_2	$AARD^a_{f_1}$	$AARD^b_{f_2}$
[60]	LiCl w-EtOH	352-366	0.005-0.034	0.282-0.936	0.03-0.713	4.4	2.2
[61, 62]	KCl w-EtOH	343-360	0.029-0.144	0.463-0.862	0.083-0.487	6.8	3.6
[63]	LiBr w-EtOH	352-356	0.029-0.144	0.463-0.862	0.083-0.487	2.1	1.1
[64]	NaBr w-EtOH	355-360	0.061-0.154	0.336-0.781	0.065-0.603	10.8	4
[60]	LiCl w-MeOH	342-372	0.005-0.065	0.281-0.499	0.032-0.714	3.4	9.5
[65]	KCl w-MeOH	351-365	0.005-0.065	0.281-0.499	0.032-0.714	5.1	10.6

[a] Average Absolute Relative Deviation (AARD) in % for f_1, [b] (AARD) in % for f_2

The results indicate that the LiCl-water ethanol system is more accurately described than the LiCl-water methanol system. It must be underlined that, in practice, the proportion of organic solvent in the mixed aqueous solvent solutions was limited to values allowing a satisfactory fit of the data. So, in the case of LiCl in water-ethanol mixtures the proportion of alcohol was limited to 70 weight-%. On the other hand, the treatment was applied to the maximum salt concentration to which data are available (maximum concentration of ca. 5 mol kg^{-1} for 1-1 salts in the water-ethanol mixture and ca. 2.5 mol kg^{-1} in the water-methanol mixture). We remark in Table 6 that the values of the interaction parameters τ are so little high but they remain of the order of a few k_BT, in agreement with those of previous work [19] presented in the next chapter.

Table 6. Results of fits for salt water-alcohol mixture at the temperature between 352 and 372 K: interaction parameters

Mixture	T (/K)	$\tau_{ZC,AC}$	τ_{CZ}	τ_{AZ}
LiCl w-EtOH	352-366	4.13	4.95	5.24
KCl w-EtOH	343-360	1.77	8.88	8.82
LiBr w-EtOH	343-360	0.85	13.9	15.56
NaBr w-EtOH	355-360	0.102	3.7	4.57
LiCl w-MeOH	342-372	6.37	6.67	5.33
KCl w-MeOH	342-372	3.31	4.67	4.66

The $\tau_{ZC,AC}$, τ_{CZ}, τ_{AZ} have a fine behavior. We find a high value of 13.9 for τ_{CZ} and 15.56 for τ_{AZ} for the LiBr-water ethanol system. For the other systems the interaction parameters τ have reasonable values.

All are positive. In particular τ_{CZ} and $\tau_{AZ}>0$, indicating a 'repulsion' between the ions and the solvent 2, as compared to the interaction between molecules of solvent 2.

Table 7. Results of fits for salt water-alcohol mixture as a function of the temperature : mean ionic size, hydration number

Mixture	T (/K)	$\sigma_2{}^a$	h_2
LiCl-w-EtOH	352-366	0.526	0
KCl-w-EtOH	343-360	0.427	3.22
LiBr-w-EtOH		0.722	0
NaBr-w-EtOH	355-360	0.684	0
LiCl-w-MeOH	342-372	0.774	0
KCl-w-MeOH		0.421	0

[a] In nm.

In Table 7, the mean ionic size remains constant for the temperature interval.

We remark that the solvation number h_2 is smaller than the hydration number h_1.

For electrolytes in solvent mixtures at 25°C, the model involves only binary system parameters. We took the binary parameters of Table 2. To describe the system we have 5 new parameters: the 3 interaction parameters τ, the mean ionic size and the hydration number, all as a function of temperature. The results of fits are satisfactory. Furthermore the interaction parameters τ again are of the order of a few k_BT's.

Table 8. Results of fits for salt water-alcohol mixture at 25°C

Ref.	Mixture	$\tau_{ZC,AC}^{(0)}$	$\tau_{CZ}^{(0)}$	$\tau_{AZ}^{(0)}$	$h_1^{(0)}$	$h_2^{(0)}$	$\sigma_1^{(0)a}$	$\sigma_2^{(0)}$	$AARD_\gamma{}^b$
[66]	NaCl w-EtOH 60[c]	2.35	11.97	11.98	2.39	5.2	0.469	0.208	1.4
[67]	NaBr w-EtOH 80	0.16	-1.71	2.85	4.39	0	0.446	0.497	3.7
[67]	NaBr w-MeOH 80	1.29	-3.23	0.48	4.39	0	0.446	0.471	3.4
[68]	KCl w-MeOH 60	3.09	5.26	3.28	4.85	0	0.403	0.241	2.59
[69, 70]	HCl w-$C_4H_8O_2$ 45	-1.02	-0.331	-2.15	4.32	0	0.439	0.0	0.96

[a] In nm, [b] AARD in %, c max w-% of solvent 2.

In Table 8, the interaction parameters have a satisfactory behavior.

If we compare the mean ionic size $\sigma_2^{(0)}$=0.208 nm in the NaCl-water ethanol and KCl water-methanol respect to NaCl and KCl in pure water we find smaller values.

We notice on the contrary a different behavior for NaBr-water-ethanol and methanol.

For HCl the size in the mixture is of the order of HCl in water like [19], $\sigma_1^{(0)}$=0.473 nm.

We have the solvation number $h_2^{(0)} = 0$ for NaBr water-ethanol, NaBr and KCl water-methanol and HCl water-dioxane except for NaCl water-ethanol. It was mentionned above that NaCl is a system which presents a difficult behavior.

5.5 Conclusion

The above results show that the MSA-NRTL model is improved when taking into account the process of solvation. It has been possible to fit the model so as to describe the heats of dilution and the heat capacities of aqueous solutions. The interpretation of the variations of these quantities in terms of entropy provides the physical meaning of the models allowing the calculation of the partial molal heat capacity at infinite dilution $\bar{C}^{\otimes}_{p,s}$, namely the structure breaking/structure making effect in the liquid. This can be compared to experimental results such as those of Omta et al. [71] who showed by means of femtosecond pump-probe spectroscopy that the structure of water around the ions is not really modified beyond the first solvation shell. The presence of the ions would have no influence on the hydrogen-bond network in liquid water. The ion plus its hydration sphere should be regarded as a rigid spherical solute on a picosecond time scale. Pursuing future improvements, hydration will be treated as a function of concentration of solute.

List of symbols

a_i	activity of species i
A	anion
A_H	Debye-Hückel coefficient for enthalpy
A_Φ	Debye-Hückel coefficient for the osmotic function
b	Universal parameter equal to 1.2 $kg^{1/2}mol^{-1/2}$
C	cation
C$'$	cation hydrated
C^Φ_{CA}	The third virial coefficient
C_P	heat capacity
D	The static dielectric constant
d_i	density of solvent i
e	charge of proton
f_i	activity coefficient of i on stoichiometric mole fraction scale
g_i	activity coefficient of i on "true" mole fraction scale
G	Gibbs energy of solution
$\bar{G}$	partial molal excess Gibbs energy
$\mathcal{G}$	specific Gibbs energy
$\bar{G}_i$	Gibbs energy per particle of i
H	Total enthalpy of the solution
h_i	hydration number of cation by solvent i
I	ionic strength
J	Total relative heat capacity
k_B	Boltzmann constant
L	Relative enthalpy
m	molality
M_i	molar mass of solvent i
n_w	number of kilograms of solvent
n	mole number
N_{av}	Avogadro number
N_i	number of particles of i
P_{ik}, $P_{ik,jk}$	defined by eqs 6.61 and 6.62

q_i	Constant parameters of Pitzer
S	entropy
S_{model}	set of particle numbers within the model (eq 6.19)
S_{LR}	set of particle numbers at LR level (eq 6.20)
T	temperature
V	volume of solution
W	water
x_i	stoichiometric mole fraction
y_i	"true" mole fraction scale
z	Electronic charge
z_i	valence of ion i
Z	coordination number

Greek letters

α	NRTL random parameter, Universal parameter equal to $2.0^{1/2} mol^{-1/2}$
β	$= 1/k_B T$
$\beta_{CA}^{(0)}$,	$\beta_{CA}^{(1)}$ The second virial coefficients
$\gamma_{\pm}$	mean salt activity coefficient on molal scale
Γ	MSA screening parameter
ε_i	relative permittivity of solvent i
ε_0	permittivity of a vacuum
κ	Debye screening parameter
λ	Bjerrum length
μ_i	chemical potential of species i
ν	$= \nu_C + \nu_A$
ν_i	stoichiometric number of species i in salt
ϕ	osmotic coefficient
Φ_{C_p}	molal heat capacity
Φ_L	molal heat enthalpy
ρ_i	number density of species i
σ_i	diameter of species i

Subscripts

1	total water
2	total solvent
W	free water
Z	free solvent
sol	Solution

Superscripts

$\otimes$	reference state
(0)	value at T=298.15 K
el	electrostatic contribution
ex	Excess
hyd	contribution from hydration
id	ideal contribution
MSA	contribution within mean spherical approximation
SR	contribution of short range forces

Bibliography

[1] H.L. Friedman, J. Chem. Phys. 32 (1960) 1351-1362.

[2] K.S. Pitzer, G. Mayorga, J. Phys. Chem. 77 (1973) 2300.

[3] K.K. Kelley, U. S. Bur. Mines, Bull. 477 (1950)

[4] J.R. Loehe, M.D. Donohue, AIChE J. 43 (1997) 180-195.

[5] J.M. Prausnitz, Adv. Chem. Eng. 16 (1991) 155-168.

[6] J.M. Prausnitz, F.W. Tavares, AIChE J. 50 (2004) 739-761.

[7] Y. Liu, S. Watanasiri, Chem. Eng. Prog. (October 1999) 25-42.

[8] H. Ohtaki, T. Radnai, Chem. Rev. 93 (1993) 1157-1204.

[9] A.L. Capparelli, D.S. Gill, H.G. Hertz, R. Tutsch, J. Chem. Soc. Faraday Trans. 74 (1978) 1849-60.

[10] E. Hawlicka, D. Swiatla-Wojcik, J. Phys. Chem. A, 2002, 106, 1336-45.

[11] H. Schneider, in: J.F. Coetzee, C.D. Ritchie (Eds.), Solute-Solvent Interactions, Marcel Dekker, New York-London, 1969, pp. 301-342.

[12] D. Feakins, in: F. Franks (Ed.), Physico-Chemical Processes in Mixed Aqueous Solvents, Heinemann Educational Books Ltd., London, 1969, pp. 71-90.

[13] A.J. Stace, A.K. Shukla, J. Am. Chem. Soc. 104 (1982) 5314-18.

[14] A. Fratiello, D.C. Douglass, J. Chem. Phys. 39 (1963) 2017-22.

[15] J.P. Simonin, S. Krebs, W. Kunz, Ind. Eng. Chem. Res. 45 (2006) 4345-4354.

[16] N. Papaiconomou, J.P. Simonin, O. Bernard, W. Kunz, Phys. Chem. Chem. Phys. 4 (2002) 4435-4443.

[17] R.A. Robinson, R.H. Stokes, Electrolyte Solutions, Second ed., London, 1965.

[18] C.C. Chen, P.M. Mathias, H. Orbey, AIChE J. 45 (1999) 1576-86.

[19] J.P. Simonin, S. Krebs, O. Bernard, W. Kunz, Fluid Phase Equilib. 242 (2006) 176-188.

[20] L. Blum, J.S. Hoye, J. Phys Chem. 81 (1977) 1311-1316.

[21] J.M. Prausnitz, R.N. Lichtenthaler, E.G. de Azevedo, third ed., Prentice Hall PTR, New Jersey, 1999.

[22] S. Quist, W.L. Marshall, J. Phys. Chem. 72 (1968) 684-703.

[23] L.F. Silvester, K.S. Pitzer, J. Phys. Chem. 81 (1977) 1822-1828.

[24] Landolt-Börnstein, Heats of Mixing and Solution, New Series, Springer-Verlag, New York, 1976.

[25] C.T. Liu, W.T. Lindsay, J. Sol. Chem. 1 (1972) 45-69.

[26] W.J. Hamer, Y.C. Wu, J. Phys. Chem. 1 (1972) 1047-1099.

[27] H.F. Gibbard, G. Scatchard, J. Chem. Eng. Data 18 (1973) 293-298.

[28] H. Rüterjans, F. Schreiner, U. Sage, Th. Ackermann, J. Phys. Chem. 73 (1969) 986-994.

[29] H.F. Gibbard, G. Scatchard, R.A. Rousseau, J. Chem. Eng. Data 19 (1974) 281-288.

[30] H.P. Snipes, C. Manly, D. Ensor, J. Chem. Eng. Data 20 (1975) 287-291.

[31] J.E. Tanner, F.W. Lamb, J. Sol. Chem. 7 (1978) 303-.

[32] J.L. Fortier, P.A. Leduc, J. E. Desnoyers, J. Sol. Chem. 3 (1974) 323-349.

[33] C.M. Criss, F.J. Millero, J. Phys. Chem. 100 (1996) 1288-1294.

[34] H.S. Franck, W.Y. Wen, Disc. Faraday Soc. 24 (1957) 133-.

[35] H.M. Evjen, F. Zwicky, Phys. Rev. 33 (1929) 860-868.

[36] F. Zwicky, Proc. Nat. Acad. Sci. 12 (1926) 86-92.

[37] T.J. Webb, J. Am. Chem. Soc. 48 (1926) 2589-2603.

[38] C.M. Criss, J.W. Cobble, J. Am. Chem. Soc. 86 (1964) 5390-5393.

[39] H.S. Franck, M.W. Evans, J. Chem. Phys. 13 (1945) 507-532.

[40] R.M. Lynden-Bell, J.C. Rasaiah, J.P. Noworyta, Pure Appl. Chem. 73 (2001) 1721-1731.

[41] R.W. Gurney, Ionic Processes in Solution, New-York, 1962.

[42] L.R. Pratt, A. Pohorille, Proc. Natl. Acad. Sci. 89 (1992) 2995.

[43] J.F. Griffith, H.A. Scheraga, J. Molecular Struct. (Theochem) 711 (2004) 33-48.

[44] H. Renon, J.M. Prausnitz, AICHE J. 14 (1968) 135-144.

[45] H. Yokogama, M. Vematsu, J. Chem. Thermodyn. 35 (2003) 813-823.

[46] Y. Takiguchi, O. Osada, M. Uematsu, J. Chem. Thermodyn. 28 (1996) 1375-1385.

[47] K. Kerl, H. Varchmin, Int. J. Thermophys. 12 (1991) 171-189.

[48] C.B. Kretschmer, R. Wiebe, J. Am. Chem. Soc. 76 (1954) 2579-2583.

[49] H.S. Wu, W.E. Locke, S.I. Sandler, J. Chem. Eng. Data 36 (1991) 127-130.

[50] H.S. Wu, W.E. Locke, S.I. Sandler, J. Chem. Eng. Data 35 (1990) 169-172.

[51] H.S. Wu, S.I. Sandler, J. Chem. Eng. Data 34 (1989) 209-213.

[52] G. Akerlöf, J. Am. Chem. Soc. 54 (1932) 4125-4139.

[53] A.M. Shkodim, P.Y. Galushkov, I.N. V'Yunnik, Vestn. Khar'k. Univ. 84 (1972) 20-22.

[54] Z. Cai, R. Xie, Z. Wu, J. Chem. Eng. Data 41 (1996) 1101-1103.

[55] L. Lee, C. Lee, J. Chem. Eng. Data 43 (1998) 17-20.

[56] L.A. Watts, B. Louie, Int. J. Thermophys. 21 (2000) 1139-1151.

[57] M. Autosik, Z. Fras, S.K. Malonowski, J. Chem. Eng. Data 44 (1999) 368-372.

[58] F.M. Jaeger, Z. Anorg. Allgem. Chem. 101 (1917) 1-214.

[59] O.R. Howel, Proc. Roy. Soc. London Ser. A, 137 (1932) 418-433.

[60] J.E. Boone, PhD Thesis, USA (1976).

[61] A.I. Johnson, W.F. Furter, Can. J. Chem. Eng. 38 (1960) 78-87.

[62] R. Sun, Huagong Xuebao 25 (1996) 13-17.

[63] R. Sun, Hua Hsueh Kung Yeh Yu Kung Cheng 47 (1996) 401-409.

[64] D. Meranda, W.F. Furter, AIChE J. 18 (1972) 111-116.

[65] H. Nishi, E. Nagao, Kenkyu Kiyo Wakayama Kogyo Koto Senmon Gakko, 25 (1990) 71-74.

[66] M.A. Esteso, O.M. González-Diaz, F.F. Hernández-Luis, L. Fernández-Merida, J. Sol. Chem. 18 (1989) 277-288.

[67] S. Han, S.H. Pan, Fluid Phase Equilib. 83 (1993) 261-270.

[68] L. Malahias, O. Popovych, J. Chem. Eng. Data 27 (1982) 105-109.

[69] H.S. Harned, J.G. Donelson, J. Am. Chem. Soc. 60 (1938) 336-339.

[70] H.S. Harned, J.G. Donelson, C. Calmon, J. Am. Chem. Soc. 60 (1938) 2133-2135.

[71] A.W. Omta, M.F. Kropman, S. Woutersen, H.J. Bakker, Science 301 (2003) 347-349.

Chapter 6

Stepwise solvation-equilibrium model associated to the MSA-NRTL model

The previous model of assigning to the ions a fixed hydration number independent of concentration is clearly an over simplification (though a convenient one). This inevitably results in failure of the equations at high concentrations. For example, if the lithium ion is assumed to exist as tetrahydrate, all the water in the solutions is bound at a molality of 55.51/4, i.e., 13.9 m, and the water activity should then be zero. In fact, lithium chloride is soluble beyond 20 m, and the water activity in the 20 m solution is still 0.11. Clearly, one need a model in which the hydration phenomenon is treated as an equilibrium of various stages of hydration. The essential validity of this idea is strongly supported by impportant mass-spectrometric studies of the enthalpy and free-energy changes for stepwise hydration processes in the gas phase, reported in recent years by Kebarke [1] and associates.

We now present aa model accounting for the decrease of hydration number with salt concentration, based on the work of Stokes and Robinson.

6.1 Modelling of the thermodynamic properties of ionic solutions using a stepwise solvation-equilibrium model

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Abstract The stepwise solvation-equilibrium model of Stokes and Robinson is used for a description of departures from ideality in ionic solutions. It is shown how to construct a thermodynamically consistent model including solvation effects. Simple expressions are derived for the mean ion solvation number. The model is applied to strong electrolyte solutions (pure water+salt and mixed aqueous solvent+salt) by taking the mean spherical approximation (MSA) for the long-range contribution to the Gibbs energy and a local composition model, the nonrandom two-liquid (NRTL) model, for the short-range contribution.

6.1.1 Introduction

The modelling of the thermodynamic properties of ionic solutions can have various applications in solution chemistry, in geochemistry and for the design and control of industrial processes. In the latter domain, it may be useful for liquid-liquid extraction, distillation, hydrometallurgy, seawater desalination, absorption refrigeration,

crystallisation and synthesis of drugs and chemicals, with not only water as the solvent but also organic solvents and aqueous solvent mixtures.

Various models have been proposed in the literature, among which one may distinguish two types: *(i)* models based on a statistical mechanical treatment of the system, pictured as a collection of objects of definite shape and size, interacting through elementary known pair potentials, and *(ii)* semi-empirical or phenomenological models, comprising a contribution from electrostatic interactions (generally a Debye-Hückel term) that is generally decoupled from other interactions.

Models of type *(i)* are constructed at the McMillan-Mayer (MM) level of solutions [2] where the solvent is regarded as a continuum (primitive level), as in the primitive mean spherical approximation (MSA) [3, 4, 5, 6, 7, 8], or at the Born-Oppenheimer level where all species are considered on an equal footing, as in the nonprimitive ion-dipole mixture MSA [9]. Examples of models of type *(ii)* include the Pitzer model [10] and representations using a local composition term such as the nonrandom two liquid (NRTL) model [11, 12, 13]. In principle, models of type *(i)* are appealing because they are expressed in terms of basic microscopic interactions. However, the equations are analytically tractable only for simplified systems, such as a collection of charged hard spheres in a dielectric continuum. They rapidly become highly complicated as more realistic systems and interactions are considered, requiring the use of numerical techniques in order to solve them. Descriptions at the MM level, which can give satisfactory descriptions of osmotic and activity coefficients [4, 5, 6, 7, 8], do not seem to be well suited to the description of enthalpies and heat capacities because they do not account explicitly for the properties of the solvent. Therefore, this route seems difficult for practical applications in which analytical working equations are desired. Such expressions can be obtained more easily within models of type *(ii)*. In this case however, each parameter may account for several elementary phenomena. An unpleasant consequence of this fact is that the variations of these lumped parameters cannot be correlated with the characteristics of the salt. Nevertheless, since it is nearly hopeless to include all effects separately in the equations, one has to distinguish which interactions are predominant and introduce them in the formulation of the model. Other (minor) interactions may be hoped to have only a small perturbative effect on the values of the main parameters.

For a strong electrolyte in water, ion-ion electrostatic interactions are one such major effect. Their influence on departures from ideality can be expressed using a suitable model such as the MSA. This effect is dominant at low salt concentration. As salt concentration becomes higher, ion-ion interactions become progressively screened while the contribution of other forces becomes relatively increasingly important. These other forces are short-ranged (SR) as opposed to long-ranged

ion-ion electrostatic forces. SR forces between particles have various origins and their effect is much more difficult to estimate than that of electrostatic forces. This difficulty can be circumvented at the MM level where only the solvent-averaged potentials between ions need be considered [2], without having to account for ion-solvent and solvent-solvent interactions. Clearly, one needs to account for SR forces if one wishes to construct a model including the solvent explicitly.

At this stage, it is necessary to distinguish between strong and weak attractive SR forces. Strong SR attractions lead to association in solution, namely solvation, chemical association and ion-pairing. Weak SR attractions may alternatively be termed van der Waals forces.

The importance of association has long been recognised [14] and it has been the subject of many studies in the literature. Association has been introduced using chemical models (*e.g.* that of Dolezalek [14]), or physical models based on the thermodynamic perturbation theory (*e.g.* the sticky point interaction model of Wertheim [15] or the therefrom derived SAFT formalism [16]). The effect of weak SR interactions has been described by a van der Waals perturbation term [17, 18, 19], a virial expansion term in the Pitzer model [10] or a contribution corresponding to interactions with nearest neighbours, as in Guggenheim lattice model [20] or local composition models like NRTL [21] or UNIQUAC [14].

Although hydration is known to be a crucial process in aqueous ionic solutions, the thermodynamic models taking it explicitly into account are rather scarce. The simplest way of accounting for this effect is to suppose a *constant* salt hydration number, independent of salt concentration. This simplification was introduced by Robinson and Stokes [22], and subsequently utilised in the literature, *e.g.* in combination with NRTL by Chen *et al.* [23]. However, if a more realistic picture is desired, it must be noticed that it is not possible to impose an arbitrary, empirical, dependence for the hydration number vs. salt concentration. On the other hand, such a variation may be obtained by using the stepwise hydration-equilibrium model of Stokes and Robinson [24] in which a cation can possess various discrete degrees of hydration, related by stepwise hydration/dehydration equilibria.

In the present paper, hydration effects are introduced by utilising the basic assumptions of the latter model [24], which was used subsequently by Schönert [25] for nonelectrolytes and by Zerres and Prausnitz [26] for mixed-solvent electrolytes.

We make here the approximation that simple anions are not solvated, meaning that no solvent molecules are firmly attached to this type of anion on a sufficiently long time scale (this notion is distinguished from the notion of coordination, the former having a more dynamical meaning than the latter [27]). The reason for this simplification is twofold. Firstly, various experimental [28] and theoretical [29] stud-

ies point to weak hydration for simple anions, such as halides (except F^-). A water molecule is known to interact with a halide anion in much the same way as it interacts with another water molecule, i.e. through hydrogen bonding. Consequently, the mean residence time of a water molecule in the vicinity of such an anion is believed to be comparable with the its residence time in the vicinity of a bulk water molecule (a few ps) [27]. Secondly, calculations were made in this work in which the anion was also supposed to be hydrated. Because the stepwise hydration model certainly is not adapted to this type of ion, a constant hydration number [22], h_A, was ascribed to a given anion. It was found that the best results with this procedure were obtained for $h_A = 0$.

This simplification is besides very common. It was used in the original work of Stokes and Robinson [24], as well as in many models at the MM level [7, 8, 26].

In contrast, some water molecules are tightly bound to small and/or plurivalent cations. This view is confirmed by recent *ab initio* molecular dynamics simulations, for Li^+ [30], Na^+ [31], K^+ [32], Mg^{2+} [33] and Ca^{2+} [34]. It is known that cation hydration may be conveniently modelled as a process in which water can bind to a finite number of sites [25, 26, 35]. We use this model below in section 6.1.2.

In the present work, it is shown how the various hydration equilibria can be handled in a thermodynamically consistent way, for a given Gibbs energy that is assumed to be split into short-range and long-range (electrostatic) contributions. The further assumption of independent hydration sites on cation allows one to account for all stepwise hydration equilibria in a compact way. Finally, the method is applied by taking particular forms for the electrostatic and SR contributions to the Gibbs energy of solution, namely the MSA and NRTL expressions, respectively.

The theoretical aspects of this work are developed in the next section of this paper. The third section is devoted to the presentation of the results and to their discussion.

Most of the calculations of this work were done using the symbolic calculation device Maple$^{\mathrm{R}}$.

6.1.2 Theoretical

Model for stepwise hydration.

We first consider an aqueous solution containing one strong electrolyte, $C_{\nu_C}A_{\nu_A}$, with C the cation of stoichiometric number ν_C and valence z_C, and A the anion of stoichiometric number ν_A and valence z_A.

Hereafter we use the subscripts 1 and W to distinguish the total water and the *free* water (not bound to a cation), respectively. We adopt the basic view of Stokes

and Robinson [24], who proposed that hydration may be modelled as a succession of the following equilibria

$$\mathrm{C}(i-1) + \mathrm{W} \rightleftharpoons \mathrm{C}(i)$$

with C(i) the hydrate containing i water molecules. The number of hydration water molecules per cation is assumed to be bound by an integer n, representing the number of "sites" on a cation: $i \leq n$.

These equilibria imply the following relation between the chemical potentials of the species

$$\mu_{C(i-1)} + \mu_W = \mu_{C(i)} \tag{6.1}$$

defining the equilibrium constants

$$K_i \equiv \frac{a_{C(i)}}{a_{C(i-1)}} a_W^{-1} \tag{6.2}$$

with $a_{C(i)}$ being the activity of C(i) and a_W that of free water.

Then, considering the various hydrates C(i) as independent species with chemical potentials $\mu_{C(i)}$, the total Gibbs energy of solution may be written as

$$G = N_W \mu_W + \sum_{i=0}^{n} N_{C(i)} \mu_{C(i)} + N_A \mu_A \tag{6.3}$$

where N_k is the number of particles of species k. Now, one gets from eq 6.1

$$\mu_{C(i)} = \mu_{C(0)} + i\,\mu_W \tag{6.4}$$

Inserting this equation into eq 6.3 leads to

$$G = N_1 \mu_W + N_C \mu_{C(0)} + N_A \mu_A \tag{6.5}$$

because the total number of water molecules is

$$N_1 = N_W + \sum_{i=0}^{n} i N_{C(i)} \tag{6.6}$$

each cation C(i) possessing i bound water molecules and the total number of cations is

$$N_C = \sum_{i=0}^{n} N_{C(i)} \tag{6.7}$$

Besides, the Gibbs energy written at the Lewis-Randall (LR) level (the level of the experimentalist)

$$G = N_1 \mu_1 + N_C \mu_C + N_A \mu_A \tag{6.8}$$

It follows from eqs 6.5 and 6.8 that

$$\mu_1 = \mu_W \tag{6.9}$$

and

$$\mu_C = \mu_{C(0)} \tag{6.10}$$

Eq 6.10 indicates that the deviation from ideality for the cation C is related to that for the unhydrated cation, C(0). Eq 6.9 entails that

$$a_1 = a_W \tag{6.11}$$

because the standard chemical potentials of 1 and W are identical.

Relations similar to eqs 6.9 and 6.10 for associating solutions have been known for a long time [36]. They were previously used by Schönert [25] for nonelectrolytes.

We now present a new method to treat hydration equilibria and departures from ideality in closed form as follows.

For each hydrated cation C(i) one has

$$a_{C(i)} \equiv y_{C(i)}\, g_{C(i)} \tag{6.12}$$

with y_k the so-called 'true' mole fraction of species k defined as

$$y_k \equiv \frac{N_k}{N_W + N_C + N_A} \tag{6.13}$$

because the total number of independent species in solution is $N_W + N_C + N_A$, as opposed to the stoichiometric mole fraction, x_k, defined for the experimentalist (at the LR level) as

$$x_k \equiv \frac{N_k}{N_1 + N_C + N_A} \tag{6.14}$$

In eq 6.12, $g_{C(i)}$ is the activity coefficient of C(i) on the 'true' mole fraction scale. Therefore by using eqs 6.12-6.14 in eq 6.2 one gets

$$K_i \equiv \frac{x_{C(i)}}{x_{C(i-1)}} \frac{g_{C(i)}}{g_{C(i-1)}}\, a_W^{-1} \tag{6.15}$$

We now make the common assumption that the Gibbs energy of the system may be split into two parts [14] as

$$G = G^{el} + G^{SR} \tag{6.16}$$

in which G^{el} is the long-range electrostatic contribution for ion-ion interactions and G^{SR} is the short-range contribution. This (convenient) assumption may be expected to be less satisfactory mainly at intermediate salt concentrations, because at low concentration the behaviour of the system is governed by electrostatic interactions

and, at high concentration, it is dominated by SR interactions (when electrostatic forces are screened). Eq 6.16 implies that any activity coefficient g_i, defined by

$$\ln g_i \equiv \partial \beta G / \partial N_i \tag{6.17}$$

may be decomposed as

$$g_i = g_i^{el}\, g_i^{SR} \tag{6.18}$$

At constant pressure and temperature, the relevant set of variables for the present model is

$$S_{\text{model}} = \{N_W, N_{C(0)}, N_{C(1)}, ..., N_{C(n)}, N_A\} \tag{6.19}$$

leading to the definition of 'true' mole fractions (eq 6.13) while the relevant set for the experimentalist (at the LR level) is

$$S_{\text{LR}} = \{N_1, N_C, N_A\} \tag{6.20}$$

to which stoichiometric mole fractions (eq 6.14) are associated. We will denote by f an activity coefficient on this LR mole fraction scale.

We now turn to the calculation of the electrostatic and SR activity coefficients appearing in eq 6.18, which are required for solving the hydration equilibria (eq 6.15) and assessing the deviations from ideality (eqs 6.9 and 6.10).

In this paper, we make the simplification that the different forms of the hydrated cation, the C(i)'s, are energetically equivalent (identical SR and electrostatic interactions for all hydrates). This hypothesis permits the development of a first reference model with a minimum number of parameters. In future work, it will be possible to relax this hypothesis by introducing suitable phenomenological dependencies for the parameters.

Simplification of hydration equilibrium constants.

The electrostatic contribution to the Gibbs energy of solution, G^{el}, provided by any reasonable model (at least at the primitive level where the solvent is regarded as a continuum, which entails that G^{el} is not a function of N_W explicitly) is expected to have an expression of the form

$$G^{el} = G^{el}(\{N_{C(j)}, 0 \leq j \leq n\}, N_A, V) \tag{6.21}$$

as it is the case for the the Debye-Hückel [37], or for the MSA expression (the latter is given in section 6.1.2). In this equation, V is the volume of solution, which is known from experiment at the LR level, as a function of S_{LR}, that is $V = V(N_1, N_C, N_A)$.

Therefore, if we assume that all cation hydrates are eneregetically equivalent, one obtains from eq 6.21

$$G^{el} = G^{el}(N_1, N_C, N_A) \tag{6.22}$$

The electrostatic contribution to the activity coefficients of C(j) is defined as

$$\ln g^{el}_{C(j)} \equiv \left[\frac{\partial \beta G^{el}}{\partial N_{C(j)}}\right]_{N_W,\{N_{C(k)},k\neq j\},N_A} \tag{6.23}$$

a partial derivative performed in particular at constant N_W.

The form of G^{el} given in eq 6.22 leads one to use the chain rule to pass from the set of variables S_{model} to S_{LR}. Using eqs 6.6 and 6.7, one gets

$$\left[\frac{\partial G^{el}}{\partial N_{C(j)}}\right]_{N_W,\{N_{C(k)},k\neq j\},N_A} = \left[\frac{\partial G^{el}}{\partial N_C}\right]_{N_1,N_A} + j\left[\frac{\partial G^{el}}{\partial N_1}\right]_{N_C,N_A} \tag{6.24}$$

Furthermore, by using the chain rule and eq 6.6, one finds

$$\ln g^{el}_{W} \equiv \left[\frac{\partial \beta G^{el}}{\partial N_{W}}\right]_{\{N_{C(k)}\},N_A} = \left[\frac{\partial G^{el}}{\partial N_1}\right]_{N_C,N_A} \tag{6.25}$$

Therefore, by combining eqs 6.23-6.25 and taking eq 6.24 for $j = 0$, we obtain

$$\ln g^{el}_{C(j)} = \ln g^{el}_{C(0)} + j \ln g^{el}_{W} \tag{6.26}$$

from which it results that

$$\frac{g^{el}_{C(j)}}{g^{el}_{C(j-1)}} = g^{el}_{W} \tag{6.27}$$

Besides, the SR contribution to the Gibbs energy is naturally constructed in terms of the variables contained in S_{model}. Assuming that the various cation hydrates have identical SR interaction parameters it stems that G^{SR} must have the form

$$G^{SR} = G^{SR}(N_W, N_C, N_A)$$

It is noticed that this contribution is a function of N_W instead of N_1 for G^{el} in eq 6.22.

By applying eq 6.23, in which differentiation is made at constant N_W, one thus arrives at the relation

$$g^{SR}_{C(j)} = g^{SR}_{C(j-1)} \tag{6.28}$$

Therefore, the combination of eqs 6.18, 6.27 and 6.28 leads to

$$\frac{g_{C(j)}}{g_{C(j-1)}} = g^{el}_{W} \tag{6.29}$$

which, by insertion into eq 6.15 and using the relation $a_W \equiv y_W g_W$, gives

$$K_i \equiv \frac{x_{C(i)}}{x_{C(i-1)}} \left(y_W\, g^{SR}_{W}\right)^{-1} \tag{6.30}$$

Hydration sites on cation.

We assume that the cation possesses n independent similar sites for solvent binding. This model is well known in inorganic chemistry [35, 38]. It has been used previously by Schönert [25] and Zerres and Prausnitz [26] for cation hydration.

It can be shown using statistical considerations at infinite dilution that the equilibrium constants K_i of eq 6.2 satisfy the following relation [35]

$$K_i = \frac{\mathsf{C}_n^i}{\mathsf{C}_n^{i-1}}\, k_1 \tag{6.31}$$

with

$$\mathsf{C}_n^i \equiv \frac{n!}{i!\,(n-i)!}$$

being the number of arrangements of i water molecules on the n independent sites.

In particular, for $i = 1$, eq 6.31 gives

$$K_1 = nk_1$$

meaning that k_1 represents the equilibrium constant for the attachment of a water molecule to an individual site.

Thus, it stems from eqs 6.30 and 6.31 that

$$x_{C(i)} = x_{C(0)}\, \mathsf{C}_n^i \left(k_1 y_W\, g_W^{SR}\right)^i \tag{6.32}$$

By using this equation into eq 6.7 (written for x_C), we get from the binomial formula

$$x_C = x_{C(0)}\, \left(1 + k_1 y_W\, g_W^{SR}\right)^n \tag{6.33}$$

Moreover, for each solution composition, the average hydration number of cation is given by

$$h_1 \equiv \sum_{j=1}^{n} j x_{C(j)}/x_C \tag{6.34}$$

By using eqs 6.32 and 6.33 into eq 6.34, we obtain after simplification the remarkably simple result

$$h_1 = n\, \frac{k_1 y_W\, g_W^{SR}}{1 + k_1 y_W\, g_W^{SR}} \tag{6.35}$$

This equation extends a relation given by Schönert [39] for semi-ideal nonelectrolyte solutions.

At infinite dilution of salt ($y_W = 1$ and $g_W^{SR} = 1$ in eq 6.35) the value of h_1 is

$$h_1^{(\otimes)} = n\, \frac{k_1}{1 + k_1} \tag{6.36}$$

showing that $h_1^{(\otimes)} \leq n$, and $h_1^{(\otimes)} \simeq n$ if $k_1 \gg 1$.

The amount of free water is determined by calculating the mole fraction x_W which satisfies the relation

$$x_W + h_1 x_C = x_1 \tag{6.37}$$

as deduced from eqs 6.6 and 6.34, in which h_1 is given by eq 6.35. In eq 6.37, x_C and x_1 are known for a given composition of solution. Moreover, h_1 is a function of x_W, x_C and x_A because of eqs 6.13, 6.14 and 6.35. This equation may be solved numerically for x_W, by using a simple iterative procedure of the form $x_W(j+1) = x_1 - h_1(j)x_C$ and iterating on j, or by using a Newton-Raphson algorithm.

Calculation of the thermodynamic quantities.

The mean activity coefficient of salt in the LR system is

$$\ln f_\pm \equiv \frac{\nu_C}{\nu} \ln f_C + \frac{\nu_A}{\nu} \ln f_A \tag{6.38}$$

where $\nu \equiv \nu_C + \nu_A$. In this equation, the activity coefficient of cation, f_C, is calculated using eq 6.10, from which we have

$$\beta\mu_C^\otimes + \ln(f_C x_C) = \beta\mu_{C(0)}^\otimes + \ln(g_{C(0)} y_{C(0)})$$

in which $\mu_X^\otimes$ designates the standard chemical potential of X.

This conversion from the set of variables S_{model} to the set S_{LR} can be handled according to the classic procedure [22] by calculating the quantity $\mu_{C(0)}^{(\otimes)} - \mu_C^{(\otimes)}$ at infinite dilution, which by virtue of eq 6.33 leads to

$$\beta\left(\mu_{C(0)}^\otimes - \mu_C^\otimes\right) = n \ln(1 + k_1)$$

and hence

$$f_C = \frac{y_C}{x_C} \left(\frac{1 + k_1}{1 + k_1 y_W \, g_W^{SR}}\right)^n g_{C(0)} \tag{6.39}$$

For the anion, one has

$$f_A = \frac{y_A}{x_A} \, g_A \tag{6.40}$$

In these relations, the activity coefficients $g_{C(0)}$ and g_A are obtained using eq 6.18, the SR parts being computed with infinite dilution as the reference state, according to

$$\ln g_i^{SR} \equiv \frac{\partial \beta \Delta G^{SR}}{\partial N_i} - \frac{\partial \beta \Delta G^{SR}}{\partial N_i}(N_C \to 0, N_A \to 0) \tag{6.41}$$

Finally, the mean activity coefficient of salt on the molality scale, $\gamma_\pm$, is obtained using the classic conversion formula [22]

$$\gamma_\pm = x_1 \, f_\pm \tag{6.42}$$

By virtue of eq 6.11, the osmotic coefficient is calculated according to

$$\phi \equiv -\frac{x_1}{1-x_1} \ln a_W \tag{6.43}$$

with

$$x_1 = 1/(1 + \nu m M_1)$$

m being the molality of salt and M_1 the molar mass of solvent, and

$$a_W = y_W g_W \tag{6.44}$$

in which g_W is obtained from eqs 6.17 and 6.18.

In eq 6.43, by virtue of eq 6.44, we may decompose $\ln a_W$ as

$$\ln a_W = \ln x_1 + \ln\left(\frac{y_W}{x_1}\right) + \ln g_W^{el} + \ln g_W^{SR}$$

and therefore we may write

$$\phi = \phi^{id} + \phi^{hyd} + \phi^{el} + \phi^{SR} \tag{6.45}$$

with the contributions

$$\phi^X \equiv -\frac{x_1}{1-x_1} \ln H^X$$

and $H^{id} = x_1$ for the ideal contribution, $H^{hyd} = y_W/x_1$, $H^{el} = g_W^{el}$ and $H^{SR} = g_W^{SR}$.

In eq 6.45, ϕ^{hyd} may be regarded as the first contribution to ϕ resulting from hydration ($\phi^{hyd} = 0$ in the absence of hydration).

In the present model, all solvation equilibria are accounted for consistently, with all intermediate activity coefficients calculated from the Gibbs energy of the system. This guarantees that the mean salt activity coefficient $\gamma_\pm$ and the osmotic coefficient ϕ automatically satisfy the Gibbs-Duhem relation.

Case of solutions of acids.

In the case of strong acids (such as HCl) in water, it may be preferable to consider that the state of minimum hydration for the proton is the hydronium ion, H_3O^+, not H^+.

In that case, one may utilise eq 6.30 for the reaction

$$H^+ + W \rightleftharpoons H_3O^+$$

with the equilibrium constant K_0, and eq 6.33 with n the number of sites on the H_3O^+ ion. Then, the use of the same conversion procedure as in the preceding subsection and taking the limit $K_0 \to \infty$ leads to

$$f_{H^+} = \frac{y_{H^+}}{x_{H^+}} \left(\frac{1+k_1}{1+k_1 y_W\, g_W^{SR}}\right)^n \left(y_W\, g_W^{SR}\right)^{-1}\, g_{H_3O^+} \tag{6.46}$$

The average hydration number (eq 6.35) is modified as

$$h_H = 1 + n\,\frac{k_1 y_W\, g_W^{SR}}{1 + k_1 y_W\, g_W^{SR}} \tag{6.47}$$

Contributions to Gibbs energy of solution.

For the practical calculation of activity coefficients used in the Results section, the particular forms taken for the contributions to the Gibbs energy of solution were as follows.

Expression for G^{el}

For the electrostatic contribution, we adopted the restricted primitive MSA expression [3], as in our previous work [13], which reads

$$G^{el} = A_v^{MSA}\, V \tag{6.48}$$

with V the volume of solution and A_v^{MSA} the Helmholtz energy per unit volume, expressed as

$$\beta A_v^{MSA} = -\lambda \frac{\Gamma}{1 + \Gamma\sigma_1} \left(\rho_C z_C^2 + \rho_A z_A^2\right) + \frac{\Gamma^3}{3\pi} \tag{6.49}$$

in which σ_1 is the mean ionic diameter in water, taken to be the same for the various hydrates and the anion,

$$\rho_k = N_k/V$$

is the number density of species k, λ is the Bjerrum distance,

$$\lambda = \beta e^2/4\pi\varepsilon_0\varepsilon \tag{6.50}$$

with $\beta = 1/k_B T$, e the charge of the proton, ε_0 the permittivity of a vacuum and ε the relative permittivity of solution. The value of λ is *ca.* 7×10^{-10} m for water at 25°C.

In eq 6.49, Γ is the MSA screening parameter, which satisfies the relation [40]

$$\frac{\partial A_v^{MSA}}{\partial \Gamma} = 0 \tag{6.51}$$

so giving

$$\Gamma = \frac{1}{2\sigma_1}\left(\sqrt{1 + 2\kappa\sigma_1} - 1\right) \tag{6.52}$$

with κ the Debye screening parameter

$$\kappa = \sqrt{4\pi\lambda(\rho_C z_C^2 + \rho_A z_A^2)}$$

Thus it results from eqs 6.48 and 6.49 that

$$\beta G^{el} = -\lambda \frac{\Gamma}{1+\Gamma\sigma_1}\left(N_C z_C^2 + N_A z_A^2\right) + \frac{\Gamma^3}{3\pi} V \tag{6.53}$$

which has the form of eq 6.21.

Using eq 6.51 in the chain rule for partial derivatives, which allows to differentiate G^{el} at constant Γ, and eq 6.7, differentiation of G^{el} w.r.t. $N_{C(0)}$ leads to

$$\ln g_{C(0)}^{el} = -\lambda \frac{\Gamma}{1+\Gamma\sigma_1} z_C^2 + \frac{\Gamma^3}{3\pi}\left[\frac{\partial V}{\partial N_{C(0)}}\right]_{N_W,\{N_{C(k)},k\neq 0\}} \tag{6.54}$$

By applying eq 6.24 to V instead of G^{el}, and taking it for $j = 0$, one finds that eq 6.54 may be rewritten as

$$\ln g_{C(0)}^{el} = -\lambda \frac{\Gamma}{1+\Gamma\sigma_1} z_C^2 + \frac{\Gamma^3}{3\pi}\left[\frac{\partial V}{\partial N_C}\right]_{N_1,N_A} \tag{6.55}$$

Moreover, differentiating eq 6.53 w.r.t. N_A yields

$$\ln g_A^{el} = -\lambda \frac{\Gamma}{1+\Gamma\sigma_1} z_A^2 + \frac{\Gamma^3}{3\pi}\left[\frac{\partial V}{\partial N_A}\right]_{N_1,N_C} \tag{6.56}$$

Lastly, by applying eq 6.25 to G^{el} of eq 6.53 at constant Γ, one has that

$$\ln g_W^{el} = \frac{\Gamma^3}{3\pi}\left[\frac{\partial V}{\partial N_1}\right]_{N_C,N_A} \tag{6.57}$$

These expressions can easily be extended to the case of a solvent mixture by taking the relative permittivity of the mixture in eq 6.50. Then, the MSA activity coefficients of the solvents are given by expressions similar to eq 6.57.

Expression for G^{SR}

For the SR contribution, we took the NRTL expression for the system composed of the species: the free water W, the "dressed" cations C(i) and the anion A.

The NRTL model, proposed by Renon and Prausnitz [21], is a local composition model that is related [41] to Guggenheim's quasi-chemical lattice theory [20]. Its use in the case of electrolyte solutions has been described elsewhere [11, 12, 13], so that we will only give the main results here.

In this framework and assuming that all cations are characterised by the same NRTL parameters, the Gibbs energies per particle for one salt in water are respectively given by [11, 12, 13]

$$\bar{G}_W^{SR} = \frac{N_C P_{CW}}{N_W + N_C P_{CW} + N_A P_{AW}} \tau_{CW} + \frac{N_A P_{AW}}{N_W + N_C P_{CW} + N_A P_{AW}} \tau_{AW} \tag{6.58}$$

$$\bar{G}_C^{SR} = \frac{N_W P_{WC,AC}}{N_W P_{WC,AC} + N_A} \tau_{WC,AC} \tag{6.59}$$

$$\bar{G}_A^{SR} = \frac{N_W P_{WA,CA}}{N_W P_{WA,CA} + N_C} \tau_{WA,CA} \tag{6.60}$$

in which no CC or AA term is present because of electrostatic exclusion effects (ions of the same charge sign cannot be close to each other).

In the above formulae, the P's, responsible for nonrandom local distributions, are defined by

$$P_{ik} = p_{ik}/p_{kk} \tag{6.61}$$

and

$$P_{ik,jk} = p_{ik}/p_{jk} \tag{6.62}$$

where p_{ik} is proportional to the "probability" of finding a particle of type i in the close vicinity of a particle of type k,

$$p_{ik} \equiv \exp(-\alpha\beta w_{ik}) \tag{6.63}$$

where w_{ik} is the $i-k$ interaction energy and $\beta \equiv 1/k_B T$ (k_B being the Boltzmann constant and T the temperature). The lattice model of Guggenheim for the description of nonrandom mixtures [20] suggests that the parameter α be related to the mean coordination number, Z, as [21, 41]

$$\alpha = \frac{2}{Z} \tag{6.64}$$

Here we take $\alpha = 0.3$, corresponding to *ca.* 6 closest neighbours for each species.

Moreover, one has in eqs 6.58-6.60

$$\tau_{ik} \equiv \beta(w_{ik} - w_{kk}) \tag{6.65}$$

$$\tau_{ik,jk} \equiv \beta(w_{ik} - w_{jk}) \tag{6.66}$$

Using eq 6.63, eqs 6.61 and 6.62 may therefore be rewritten as

$$P_{ik} = \exp(-\alpha\tau_{ik}) \tag{6.67}$$

$$P_{ik,jk} = \exp(-\alpha\tau_{ik,jk}) \tag{6.68}$$

The SR Gibbs energies (eqs 6.58-6.60) are thus expressed as a function of the three interaction parameters: τ_{CW}, τ_{AW} and $\tau_{WC,AC}$. Because of eqs 6.65 and 6.66 and the relation $w_{ik} = w_{ki}$, the parameter $\tau_{WA,CA}$ is related to the other parameters by

$$\tau_{WA,CA} = \tau_{WC,AC} + \tau_{AW} - \tau_{CW} \tag{6.69}$$

The total SR Gibbs energy is given by

$$G^{SR} = N_W \bar{G}_W^{SR} + N_C \bar{G}_C^{SR} + N_A \bar{G}_A^{SR} \tag{6.70}$$

These NRTL relations can be easily generalised to the case of multisolvent electrolyte mixtures [11, 12, 13], as needed in the next section for binary solvent mixtures.

Salt in a two-solvent mixture.

This model can be applied to the case of salts in solvent mixtures [26]. The generalisation of eq 6.32 for a mixture of solvents 1 and 2 is

$$x_{C(i,j)} = x_{C(0,0)} \left[\mathsf{C}_n^i \left(k_1 y_W \, g_W^{SR} \right)^i \right] \left[\mathsf{C}_{n-i}^j \left(k_2 y_Z \, g_Z^{SR} \right)^j \right] \tag{6.71}$$

with Z designating free solvent 2, i and j being the numbers of molecules of W and Z, respectively, on the cation and k_2 being the analogue of k_1 for solvent 2. This relation can be shown by successively taking off j molecules of 2 ($n-i$ sites available for molecules of type Z) and then i molecules of 1, from C(i,j), and using eq 6.32. In eq 6.71, it is supposed that n is the maximum number of binding sites accessible to both solvents 1 and 2.

Because

$$x_C = \sum_{i=0}^{n} \sum_{j=0}^{n-i} x_{C(i,j)}$$

one finds

$$x_C = x_{C(0,0)} \left(1 + k_1 y_W \, g_W^{SR} + k_2 y_Z \, g_Z^{SR} \right)^n \tag{6.72}$$

The two mean solvation numbers h_1 and h_2 of C by the two solvents W and Z, respectively, are

$$h_1 \equiv \sum_{i=1}^{n} i \sum_{j=0}^{n-i} x_{C(i,j)} / x_C$$

$$h_2 \equiv \sum_{j=1}^{n} j \sum_{i=0}^{n-j} x_{C(i,j)} / x_C$$

for which we get from eq 6.71 the following simple relations after simplification

$$h_1 = n \, \frac{k_1 y_W g_W^{SR}}{1 + k_1 y_W g_W^{SR} + k_2 y_Z g_Z^{SR}} \tag{6.73}$$

$$h_2 = n \, \frac{k_2 y_Z g_Z^{SR}}{1 + k_1 y_W g_W^{SR} + k_2 y_Z g_Z^{SR}} \tag{6.74}$$

with the analogues of eq 6.37 for the conservation of molecules of solvents 1 and 2,

$$x_W + h_1 x_C = x_1 \tag{6.75}$$

$$x_Z + h_2 x_C = x_2 \tag{6.76}$$

Eq 6.39 becomes

$$f_C = \frac{y_C}{x_C} \left(\frac{1 + k_1 x_1^{(\circ)} g_1^{SR,(\circ))} + k_2 x_2^{(\circ))} g_2^{SR,(\circ))}}{1 + k_1 y_W g_W^{SR} + y_Z g_Z^{SR}} \right)^n g_{C(\circ))} \tag{6.77}$$

for the reference state being infinite dilution of salt in the solvent mixture, which is the usual convention in the literature. In eq 6.77, $x_k^{(\circ))}$ and $g_k^{SR,(\circ))}$ $(k = 1, 2)$ refer to quantities in the salt-free solvent mixture, containing the same amounts of solvents as in the ionic solution (salt-free basis).

It may be shown that the expression for the mean activity coefficient of salt (eq 6.38) is

$$\gamma_\pm = (x_1 + x_2)\, f_\pm \tag{6.78}$$

which replaces eq 6.42 in the case of solvent mixtures.

In eqs 6.39 and 6.40, the activity coefficients $g_{C(0)}$ and g_A were computed by using eqs 6.55 and 6.56 for the electrostatic part (with a mean ionic diameter σ in the mixture instead of σ_1 in water and with ε in eq 6.50 being the relative permittivity of the solvent mixture), and the analogue of eq 6.70 for ions in solvent mixtures as given elsewhere [13].

6.1.3 Results and discussion

Binary aqueous ionic solutions.

First, it was verified numerically that, as stated above at the end of Section 6.1.2, the osmotic and mean activity coefficients, ϕ and $\gamma_\pm$ given by eqs 6.43 and 6.42, respectively, accurately satisfy the Gibbs-Duhem relation. The free water mole fraction, x_W, was computed numerically by solving eq 6.37, using a simple iterative and rapidly converging algorithm with the initial value $y_W = x_1$.

In this work, parameter values were adjusted by simultaneously fitting the experimental osmotic and activity coefficients for strong electrolytes [42] at 25°C. The numerical values for these thermodynamic quantities were obtained from the NIST databank [43], in which primary data for uni-univalent salts are taken from the compilation of Hamer and Wu [44]. In the fits, the maximum concentration of solution was limited to 6 mol kg^{-1} for 1-1 salts and to 4 mol kg^{-1} for 2-1 salts, because of the simplifying assumptions made in the model that all cation hydrates are energetically equivalent (same sizes and same SR parameters for all cations C(k)). The fits

of $\gamma_\pm$ and ϕ were performed by using a least-square minimisation algorithm of the Marquardt type.

In the calculation of the osmotic and activity coefficients, it was noted that the terms containing derivatives of volume V, in eqs 6.55 and 6.56, were much smaller than the other MSA term. Therefore, as previously [13], it was assumed that the volume of solution does not vary when salt is added, that is

$$\frac{\partial V}{\partial N_C} = \frac{\partial V}{\partial N_A} = 0 \tag{6.79}$$

and, therefore

$$\frac{\partial V}{\partial N_1} = \frac{M_1}{N_{Av} d_1}$$

where N_{Av} is Avogadro's number and d_1 the density of pure water. This simplification was found to have a very small effect on the parameter values as compared to fits in which the variation of V with added salt is accounted for. It offers the clear advantage of not requiring solution density data.

The values for the number of sites on a given cation, n, were chosen on the basis of recent works using classic [45, 46] and *ab initio* [30, 31, 32, 33, 34] numerical simulations together with a six-parameter adjustment of n, k_1, τ_{CW}, τ_{AW}, $\tau_{WC,AC}$ and σ_1. The latter was found to result in average values that were in reasonable agreement with the former. Namely, a value of 4 was taken for monovalent cations Li^+, Na^+ and K^+, and of 8 for divalent cations Mg^{2+}, Ca^{2+} and Sr^{2+}. In the case of H^+, the maximum number of bound water molecules was taken to be of 4 [47, 48], the minimum number being either 0 or 1 (depending on whether $n = 4$ or 3, respectively) as explained in section 6.1.2. In the case of the uranyle ion, the fit yielded a value of $n = 10$.

Next, an 'optimum' value for k_1 was determined for Li^+ by fitting the thermodynamic quantities, $\gamma_\pm$ and ϕ, for LiCl, LiBr and LiI at the same time. This resulted in the value $k_1(Li^+) \simeq 14.3$. Let us notice that the uncertainty upon the determination of the optimum value of k_1 is not small, on the order of $\pm 20\%$, because of the high flexibility of the NRTL formulae that can accommodate values in a relatively wide range. Then, a common value for the parameter τ_{Li^+W} was obtained by averaging the values for the 3 salts and 3-parameter adjustments of τ_{AW}, $\tau_{WC,AC}$ and σ_1 were made separately for each salt. The so obtained values for τ_{AW}, with A= Cl^-, Br^- and I^-, were taken as optimum values and they were used for other salts comprising these anions. For other cations, the remaining parameters were determined by fitting the experimental data for the three corresponding halides. The best value for $\tau_{ClO_4^- W}$ was computed by considering lithium and sodium perchlorates. This value was then used for uranyle perchlorate together with $n = 10$.

The procedure of determining common parameter values for the alkali halides decreases the effective number of adjusted parameters to a mean value of 3 per salt.

The results for the parameters are presented in Table 1. The values for τ_{CW} and k_1 are identical for all salts containing the cation C and, similarly, τ_{AW} is the same for all salts containing the anion A. On the other hand, the parameters $\tau_{WC,AC}$ and σ_1 are characteristic of the salt.

The results of Table 1 exhibit a few noteworthy features and trends as follows. For alkali cations, the value of k_1 decreases in the series $Li^+ > Na^+ > K^+$, as expected. In contrast, k_1 is nearly identical for the three alkali earth cations studied here. All τ values are of the order of unity, corresponding to interaction energies of the order of a few k_BT's, as for interactions between solvent molecules (see for instance values given in Table 3). This satisfying result contrasts with a previous work [13] in which hydration was not included. Besides, it is seen in Table 1 that generally, for a given cation C, the average diameter σ_1 satisfies the relation $\sigma_1(CCl) < \sigma_1(CBr) < \sigma_1(CI)$, as expected since the anion sizes are in this order. However, this is not the case for acids and lithium salts for which the diameters for the chloride and the bromide are inverted.

Other comments about the τ's are that *(i)* the more negative values of τ_{CW} ($=w_{CW} - w_{WW}$) are for Li^+ and Mg^{2+}, suggesting a stronger interaction for small and/or divalent (hydrated) cations with the surrounding water in the second hydration shell, and *(ii)* the τ_{AW}'s are such that $\tau_{I^-W} < \tau_{Br^-W} < \tau_{Cl^-W} < 0$. However, the τ parameters involved in the NRTL model do not have a sufficiently precise microscopic physical meaning allowing direct interpretation of their dependencies upon cation and anion identities.

Typical plots of the osmotic coefficient are shown in Figures 6.1 and 6.2, for 1-1 and 2-1 salts, respectively. In Figure 6.2, results for $CaBr_2$ are not shown because they are very close to those for $MgCl_2$.

Figure 6.3 presents the plots of the quantity h_1/n for the electrolytes LiCl and NaCl ($n = 4$), and $MgCl_2$ and $CaCl_2$ ($n = 8$). The value of h_1/n in the case of KCl varies from 0.645 at infinite dilution to 0.597 at 5 mol kg^{-1} (plot not shown). One observes that $h_1(Li^+) > h_1(Na^+) > h_1(K^+)$, in agreement with common notions about ion hydration. Besides, h_1 decreases faster for 2-1 salts than for 1-1 salts, with variations of the order of 2 % for the latter and 7% for the former in the concentration range 0-4 mol kg^{-1}.

Table 1

Results for parameters with $n = 4$ for 1-1 electrolytes and $n = 8$ for 2-1 electrolytes.

Salt	m range[a]	k_1	τ_{CW}	τ_{AW}	$\tau_{WC,AC}$	σ_1[b]	AARD$_\phi$[c] (%)	σ_ϕ[d]
LiCl	0.001-6	14.3	-0.820	-1.29	0.337	0.489	0.23	0.003
LiBr	0.1-6	14.3	-0.820	-1.64	0.159	0.443	0.19	0.003
LiI	0.1-3	14.3	-0.820	-1.80	0.316	0.668	0.43	0.007
$LiNO_3$	0.001-6	14.3	-0.820	-2.22	3.30	0.527	0.35	0.006
$LiClO_4$	0.001-4.5	14.3	-0.820	-2.05	1.53	0.615	0.05	0.001
NaCl	0.001-6.14	8.00	0.75	-1.29	1.56	0.437	0.08	0.001
NaBr	0.005-6	8.00	0.75	-1.64	1.73	0.460	0.10	0.002
NaI	0.1-6	8.00	0.75	-1.80	1.49	0.519	0.22	0.003
$NaClO_4$	0.2-6	8.00	0.75	-2.05	3.58	0.496	0.26	0.003
KCl	0.001-5	1.82	1.47	-1.29	1.71	0.392	0.09	0.001
KBr	0.001-5.5	1.82	1.47	-1.64	2.24	0.418	0.05	0.0006
KI	0.002-4.5	1.82	1.47	-1.80	2.40	0.477	0.18	0.002
HCl	0.001-6	11.4	-1.20	-1.29	0.321	0.520	0.18	0.003
HBr	0.001-6	11.4	-1.20	-1.64	-0.589	0.472	0.18	0.004
HI	0.02-6	11.4	-1.20	-1.80	-0.243	0.656	0.24	0.005
$MgCl_2$	0.1-4	10.0	-2.10	-1.29	-0.231	0.505	0.50	0.006
$MgBr_2$	0.1-4	10.0	-2.10	-1.64	-0.355	0.562	0.17	0.003
MgI_2	0.1-4	10.0	-2.10	-1.80	-3.79	0.610	0.28	0.008
$CaCl_2$	0.1-4	8.89	-1.20	-1.29	0.175	0.526	0.20	0.005
$CaBr_2$	0.1-4	8.89	-1.20	-1.64	-0.272	0.561	0.44	0.008
CaI_2	0.1-4	8.89	-1.20	-1.80	-3.21	0.626	0.37	0.005
$SrCl_2$	0.1-4	13.3	-1.00	-1.29	1.13	0.520	0.38	0.006
$SrBr_2$	0.1-4	13.3	-1.00	-1.64	1.14	0.560	0.45	0.006
SrI_2	0.1-4	13.3	-1.00	-1.80	-0.159	0.626	0.22	0.003
$UO_2(ClO_4)_2$	0.1-4	10.3	-2.80	-2.05	0.285	0.651	0.24	0.005

[a]In mol kg^{-1}, [b]in nm, [c]Average Absolute Relative Deviation for ϕ, [d]Standard deviation for fit of ϕ.

Table 2

Results for parameters in the case of acids, with 3 sites ($n = 3$) on the H_3O^+ ion (section 6.1.2).

Salt	m range[a]	k_1	τ_{CW}	τ_{AW}	$\tau_{WC,AC}$	σ_1[b]	AARD$_\phi$ (%)	σ_ϕ
HCl	0.001-6	6.00	-1.1	-1.289	-0.0346	0.522	0.19	0.004
HBr	0.001-6	6.00	-1.1	-1.64	-1.50	0.477	0.16	0.003
HI	0.02-6	6.00	-1.10	-1.80	-0.993	0.662	0.24	0.004

[a]In mol kg^{-1}, [b]in nm, [c]Average Absolute Relative Deviation for ϕ, [d]Standard deviation of fit of ϕ.

Table 3

Values of parameters for mixed aqueous solvent mixtures.

Solvent mixture (W-Z)	τ_{WZ}	τ_{ZW}
Water-Methanol	0.711	-0.139
Water-Ethanol	1.47	0.0542
Water-Dioxane	0.818	1.16

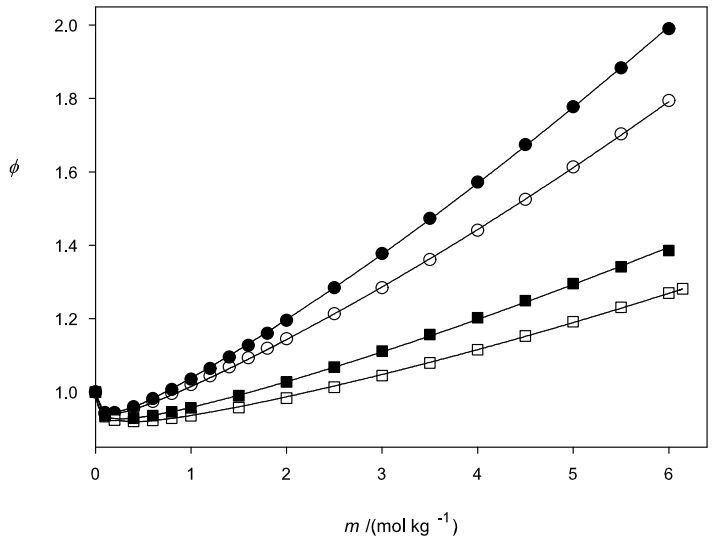

Figure 6.1: Osmotic coefficient as a function of molality. Symbols: experimental data for LiCl (○), LiBr (●), NaCl (□) and NaBr (black square). Solid lines: results of least-square fit.

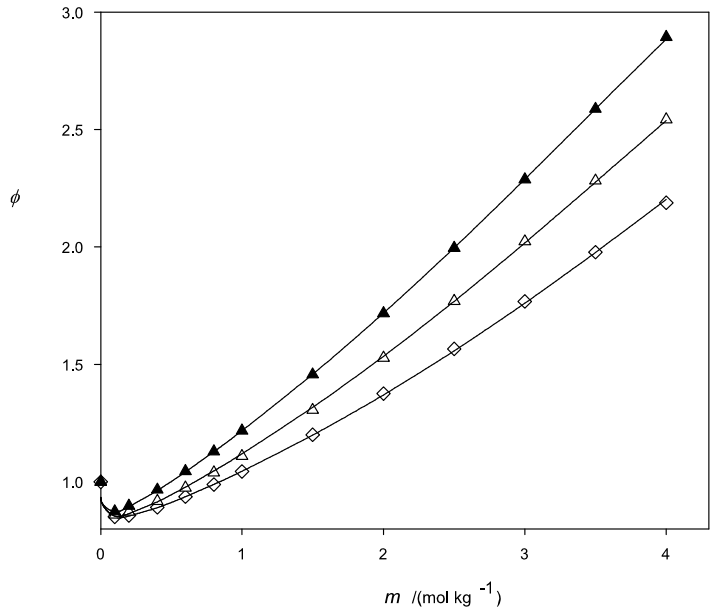

Figure 6.2: Osmotic coefficient as a function of molality. Symbols: experimental data for aqueous solutions of $MgCl_2$ ($\triangle$), $MgBr_2$ (black triangle) and $CaCl_2$ ($\diamond$). Solid lines: results of least-square fit.

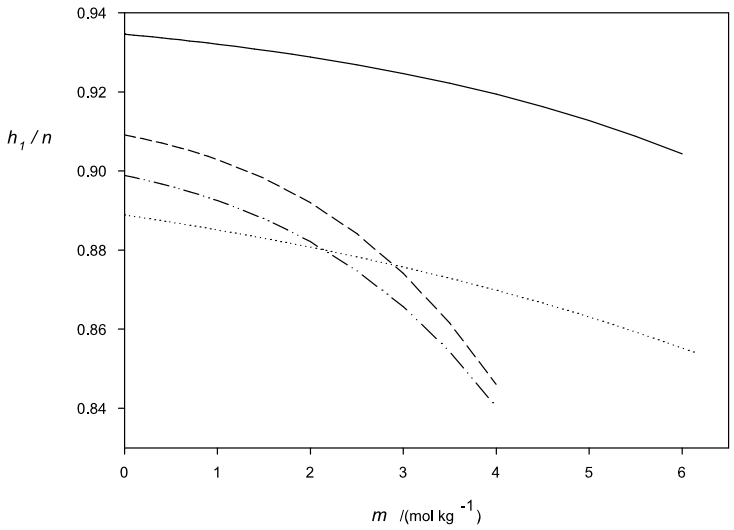

Figure 6.3: Quantity h_1/n as a function of molality, for LiCl, NaCl, $MgCl_2$ and $CaCl_2$ aqueous solutions.

Lastly, the contributions to the osmotic coefficient, defined by eq 6.45, are studied by plotting the quantity

$$R^X \equiv \phi^X/\phi^{id} \tag{6.80}$$

for $X = hyd$, el or SR ($R^{id} = 1$) and where ϕ^{id} is the ideal osmotic coefficient. In Figure 6.4 are plotted these functions for LiCl, and in Figure 6.5 for KCl. In the case of LiCl, the hydration and SR contributions are nearly equal and amount to more than half the ideal contribution at 6 mol kg^{-1}; the MSA contribution is negative (-R^{MSA} is plotted in the figure) and rapidly reaches a plateau value of *ca.* 0.1. In contrast, in the case of KCl, the SR contribution is very small (with a value of *ca.* -0.005 at 5 mol kg^{-1}) and $-R^{MSA}$ is larger than in the case of LiCl because the average diameter is smaller (see Table 1); R^{hyd} increases almost linearly to a value of *ca.* 0.25 at 5 mol kg^{-1}. In the case of $MgCl_2$ (plot not shown), the maximum values of R^{hyd} and R^{SR} (at 4 mol kg^{-1}) are *ca.* 0.8 and 1.2, and the plateau value of $-R^{el}$ is 0.2.

Thus, an important conclusion that can be drawn from these results is that the influence of hydration on the osmotic coefficient is important at moderate and high concentration, even though the variation of h_1 is rather slow (less than 7 % in the range 0-4 mol kg^{-1}, as mentioned above).

Mixed aqueous solvent electrolytes.

Mean activity coefficients of salts in binary water-organic solvent mixtures at 25°C were fitted by using eqs 6.38, 6.40, 6.77 and 6.78. Experimental data were taken from the literature [49, 50, 51, 52, 53, 54], for alkali halides in water-alcohol mixtures and HCl in the water-dioxane mixture, with maximum salt concentrations between 2 and 4.9 mol kg^{-1}.

In all cases, the present description (for strong electrolytes) could not be applied to the case of high proportions of organic solvent because of important ion pairing in such media. Therefore, in practice, the proportion of organic solvent in the mixed aqueous solvent solutions was limited to values allowing a satisfactory fit of the data or to values known to ensure complete dissociation of salt, as in the case of NaCl in water-ethanol mixtures containing less than 70 weight-% of ethanol [51, 55]. On the other hand, the treatment was applied to the maximum salt concentrations to which data are available.

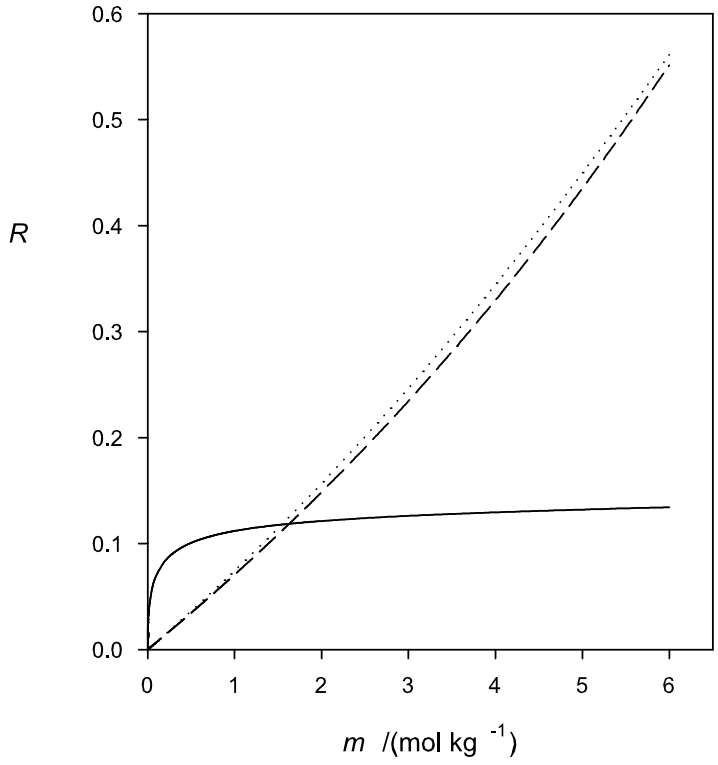

Figure 6.4: Functions $-R^{el}$ (solid line), R^{hyd} (dashed line) and R^{SR} (dotted line) in the case of LiCl aqueous solution.

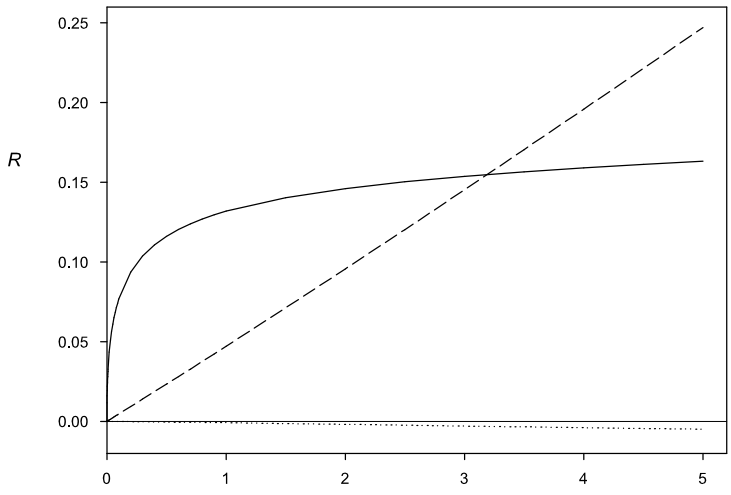

Figure 6.5: Functions $-R^{el}$ (solid line), R^{hyd} (dashed line) and R^{SR} (dotted line) in the case of KCl aqueous solution.

Figure 6.3 presents the plots of the quantity h_1/n for the electrolytes LiCl and NaCl ($n = 4$), and $MgCl_2$ and $CaCl_2$ ($n = 8$). The value of h_1/n in the case of KCl varies from 0.645 at infinite dilution to 0.597 at 5 mol kg^{-1} (plot not shown). One observes that $h_1(Li^+) > h_1(Na^+) > h_1(K^+)$, in agreement with common notions about ion hydration. Besides, h_1 decreases faster for 2-1 salts than for 1-1 salts, with variations of the order of 2 % for the latter and 7% for the former in the concentration range 0-4 mol kg^{-1}.

Lastly, the contributions to the osmotic coefficient, defined by eq 6.45, are studied by plotting the quantity

$$R^X \equiv \phi^X/\phi^{id} \tag{6.81}$$

for $X = hyd$, el or SR ($R^{id} = 1$) and where ϕ^{id} is the ideal osmotic coefficient. In Figure 6.4 are plotted these functions for LiCl, and in Figure 6.5 for KCl. In the case of LiCl, the hydration and SR contributions are nearly equal and amount to more than half the ideal contribution at 6 mol kg^{-1}; the MSA contribution is negative (-R^{MSA} is plotted in the figure) and rapidly reaches a plateau value of *ca.* 0.1. In contrast, in the case of KCl, the SR contribution is very small (with a value of *ca.* -0.005 at 5 mol kg^{-1}) and $-R^{MSA}$ is larger than in the case of LiCl because the average diameter is smaller (see Table 1); R^{hyd} increases almost linearly to a value of *ca.* 0.25 at 5 mol kg^{-1}. In the case of $MgCl_2$ (plot not shown), the maximum values of R^{hyd} and R^{SR} (at 4 mol kg^{-1}) are *ca.* 0.8 and 1.2, and the plateau value of $-R^{el}$ is 0.2.

Thus, an important conclusion that can be drawn from these results is that the influence of hydration on the osmotic coefficient is important at moderate and high concentration, even though the variation of h_1 is rather slow (less than 7 % in the range 0-4 mol kg^{-1}, as mentioned above).

Mixed aqueous solvent electrolytes.

Mean activity coefficients of salts in binary water-organic solvent mixtures at 25°C were fitted by using eqs 6.38, 6.40, 6.77 and 6.78. Experimental data were taken from the literature [49, 50, 51, 52, 53, 54], for alkali halides in water-alcohol mixtures and HCl in the water-dioxane mixture, with maximum salt concentrations between 2 and 4.9 mol kg^{-1}.

In all cases, the present description (for strong electrolytes) could not be applied to the case of high proportions of organic solvent because of important ion pairing in such media. Therefore, in practice, the proportion of organic solvent in the mixed aqueous solvent solutions was limited to values allowing a satisfactory fit of the data or to values known to ensure complete dissociation of salt, as in the case of NaCl in water-ethanol mixtures containing less than 70 weight-% of ethanol [51, 55]. On

the other hand, the treatment was applied to the maximum salt concentrations to which data are available.

Values for the parameters τ_{WZ} and τ_{ZW} in the case of water-methanol and water-ethanol mixtures can be found in the literature [56]. However, they were recalculated here by fitting vapour pressure experimental data [57, 58]. The corresponding results and the values for the water-dioxane mixture [56] are given in Table 3.

For computing the electrostatic contributions to the activity coefficients, it was assumed that the mean ionic diameter is given by the following relation

$$\sigma = x_1^{(\circ))}\sigma_1 + x_2^{(\circ))}\sigma_2 \tag{6.82}$$

with $x_k^{(\circ))}$ being the mole fraction of solvent k on a salt-free basis and σ_2 an average ion size for solvent 2. Moreover, for use in eq 6.50, the relative permittivities of the solvent mixtures were found to be well reproduced by the relation

$$\varepsilon = x_1^{(w,0)}\varepsilon_1 + x_2^{(w,0)}\varepsilon_2$$

where $x_k^{(w,0)}$ is the weight mole fraction of solvent k on a salt-free basis and ε_k is the relative permittivity of solvent k. Experimental values for the ε_k's of the various solvents were found in the literature [59, 60]. The approximation expressed by eq 6.79 was used and the derivatives of V with respect to N_1 and N_2 were calculated by assuming that the density of solution is the average of the two solvent densities.

The number of additional unknown parameters is of five, namely k_2, τ_{CZ}, τ_{AZ}, $\tau_{ZC,AC}$ and σ_2 (the parameters for aqueous solutions being taken from the preceding section). The data for water-methanol electrolytes were described by assuming that $k_2 = k_1$, thus following NMR experimental observations for the K^+ cation [61] and recent simulation results for the Na^+ cation [62], where no preferential solvation was found for these ions. In contrast, data for other solvent mixtures were fitted by taking $k_2 = 0$, in accordance with the principle of preferential hydration in these solvent mixtures [63, 64, 65, 66]. However, we note that the precise physical cause for the seemingly different behaviour between methanol and ethanol in the solvation of cations is not clearly established.

With these assumptions about the values of k_2, and assuming that the parameters τ_{CW} and $\tau_{WC,AC}$ for water-methanol solutions are identical to those determined for purely aqueous solutions (although methanol is now also attached to the cation since $k_2 = k_1$), the four remaining parameters τ_{CZ}, τ_{AZ}, $\tau_{ZC,AC}$ and σ_2 were regressed for each system. The results of parameter fits are collected in Table 4 and three typical plots of the mean salt activity coefficient vs. salt concentration are shown in Figures 6.6, 6.7 and 6.8.

In the case of NaBr in water-methanol and water-ethanol mixtures, recommended experimental data [44] for the binary aqueous solutions (indicated by empty squares

Table 4

Results for parameters for salts in mixed aqueous solvent: water + solvent Z.

Z	Salt	m_{max} [a]	$x_{2,max}^{(w,0)}$ [b]	k_2	τ_{CZ}	τ_{AZ}	$\tau_{ZC,AC}$	σ_2 [c]	AARD$_{\gamma_\pm}$ [d] (%)	$\sigma_{\gamma_\pm}$ [e]
MeOH	NaBr	3.05	0.4	8.00	5.05	-1.55	0.851	0.105	0.76	0.006
MeOH	KCl	3.9	0.6	1.82	3.47	-1.20	0.531	0.174	1.9	0.02
EtOH	NaCl	2	0.7	0	-0.213	-1.96	-2.10	0.0592	1.1	0.009
EtOH	NaBr	4.9	0.4	0	-0.213	-1.98	-1.55	0.0290	1.2	0.01
$C_4H_8O_2$	HCl	3	0.45	0	-2.83	-2.92	-3.65	0.103	0.76	0.007

[a]Maximum molality in mol kg^{-1}, [b]maximum weight fraction of solvent 2 on a salt-free basis, [c]in nm, [d]Average Absolute Relative Deviation for $\gamma_\pm$, [e]Standard deviation of fit of $\gamma_\pm$.

in Figures 6.6 and 8) suggest appreciable experimental errors of the order of 2-3 % for the measurements in the water-alcohol mixtures.

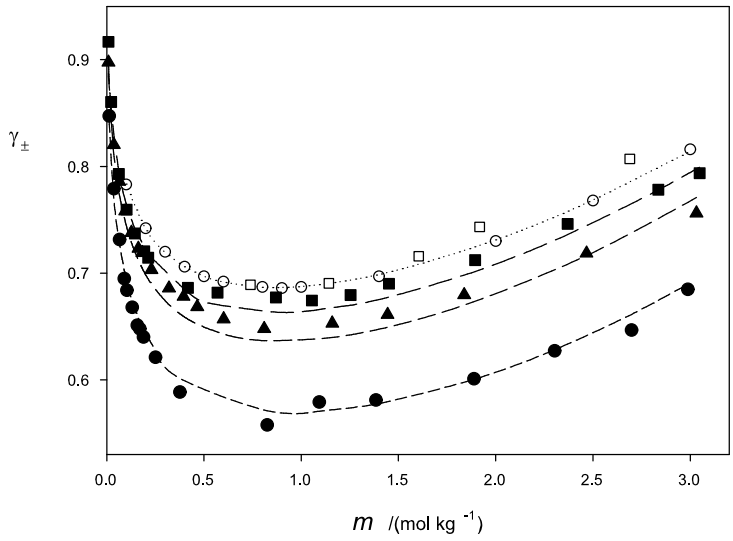

Figure 6.6: Mean activity coefficient of NaBr in water-methanol mixtures for various methanol weight fractions, $x_2^{(w,0)}$ (on a salt-free basis). Symbols are experimental data. The symbol (○) refers to data from ref. [44] for NaBr in pure water. Other data are from ref. [49]: NaBr in pure water (□), $x_2^{(w,0)}$=0.1 (black square), $x_2^{(w,0)}$=0.2 (black triangle), $x_2^{(w,0)}$=0.4 (●). Lines are the results of fits.

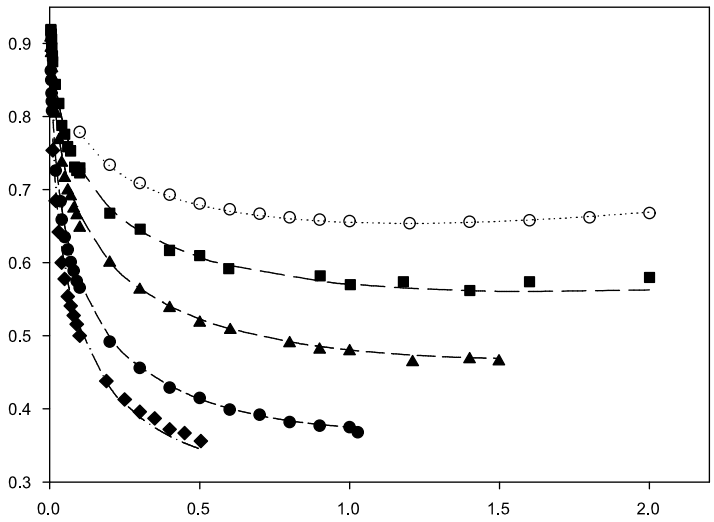

Figure 6.7: Mean activity coefficient of NaCl in water-ethanol mixtures for various ethanol weight fractions, $x_2^{(w,0)}$ (on a salt-free basis). Symbols are experimental data. The symbol (∘) refers to data from ref. [44] for NaCl in pure water. Other data are from ref. [51]: $x_2^{(w,0)}$=0.2 (black square), $x_2^{(w,0)}$=0.4 (black triangle), $x_2^{(w,0)}$=0.6 (•), $x_2^{(w,0)}$=0.7 (black diamond). Lines are the results of fits.

As shown by the AARD's of fits in Table 4 and Figures 6.6-6.8, the representation of the mean salt activity coefficient $\gamma_\pm$ is satisfactory. The small values found for the closest approach distance σ_2 mean that σ, expressed by eq 6.82, needs to decrease appreciably with the organic solvent mole fraction in order to reproduce the behaviour of $\gamma_\pm$ at low salt concentration where the electrostatic contribution dominates. The minimum values of σ obtained in the fits are between 2.6×10^{-10} m and 3.7×10^{-10} m for the salts in the water-alcohol mixtures, and it is 4.7×10^{-10} m for HCl in the water-dioxane mixture. The values of the parameters τ_{CZ} and τ_{AZ} for the alkali halides in the alcohols show opposite trends as compared to water: for NaBr and KCl in the water-methanol mixture, $\tau_{CZ} > \tau_{CW}$ and $\tau_{AZ} > \tau_{AW}$, while $\tau_{CZ} < \tau_{CW}$ and $\tau_{AZ} < \tau_{AW}$ for NaCl and NaBr in the water-ethanol mixture. The latter systems were described with a common value of -0.213 for the parameter τ_{Na^+Z} (Z=ethanol). The HCl-water-dioxane system was treated by taking 4 sites on the H^+ ion ($n = 4$) and the parameter values of Table 1 for HCl in water.

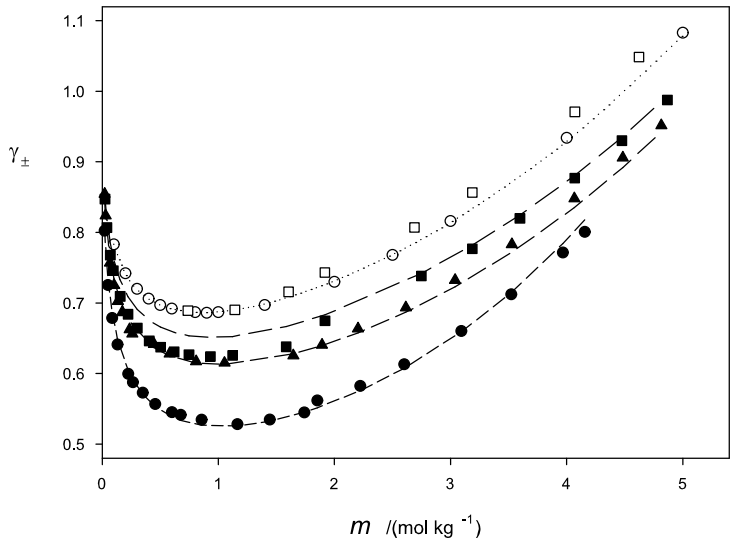

Figure 6.8: Mean activity coefficient of NaBr in water-ethanol mixtures for various ethanol weight fractions, $x_2^{(w,0)}$ (on a salt-free basis). Symbols are experimental data. The symbol (○) refers to data from ref. [44] for NaBr in pure water. Other data are from ref. [49]: NaBr in pure water (□), $x_2^{(w,0)}$=0.1 (black square), $x_2^{(w,0)}$=0.2 (black triangle), $x_2^{(w,0)}$=0.4 (●). Lines are the results of fits.

6.1.4 Conclusion

The formalism developed in this work provides a compact and thermodynamically consistent framework to account for stepwise hydration effects on the departures from ideality in ionic solutions. It may be used with other expressions for the contributions to the Gibbs energy, G^{el} and G^{SR}.

In future work, the present model will be extended to the case of highly concentrated ionic solutions and associating electrolytes.

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List of symbols

a_i	activity of species i
A	anion
A_v	Helmholtz energy per volume unit
C	cation
C$'$	cation hydrated
C(k)	cation hydrated with k water molecules
C(k, p)	cation solvated with k water molecules and p solvent molecules
d_i	density of solvent i
e	charge of proton
f_i	activity coefficient of i on stoichiometric mole fraction scale
g_i	activity coefficient of i on "true" mole fraction scale
G	Gibbs energy of solution
$\bar{G}_i$	Gibbs energy per particle of i
h_i	hydration number of cation by solvent i
k_B	Boltzmann constant
k_i	equilibrium constant for attachment of a molecule of i
K_i	equilibrium constant
L	Relative enthalpy
m	molality
M_i	molar mass of solvent i
n	number of sites on cation
N_{Av}	Avogadro number
N_i	number of particles of i
P_{ik}, $P_{ik,jk}$	defined by eqs 6.61 and 6.62
S_{model}	set of particle numbers within the model (eq 6.19)
S_{LR}	set of particle numbers at LR level (eq 6.20)
T	temperature
V	volume of solution
w_{ij}	$i-j$ interaction energy
W	water
x_i	stoichiometric mole fraction
y_i	"true" mole fraction scale
z_i	valence of ion i
Z	coordination number

Greek letters

α	NRTL random parameter
β	$= 1/k_B T$
$\gamma_\pm$	mean salt activity coefficient on molal scale
Γ	MSA screening parameter
ε_i	relative permittivity of solvent i
ε_0	permittivity of a vacuum
κ	Debye screening parameter
λ	Bjerrum length
μ_i	chemical potential of species i
ν	$= \nu_C + \nu_A$
ν_i	stoichiometric number of species i in salt
ϕ	osmotic coefficient
ρ_i	number density of species i
σ_i	diameter of species i

Subscripts

1	total water
2	total solvent
W	free water
Z	free solvent

Superscripts

$(\otimes)$	reference state
el	electrostatic contribution
hyd	contribution from hydration
id	ideal contribution
MSA	contribution within mean spherical approximation
SR	contribution of short range forces

Bibliography

[1] M. Arshadi, R. Yamdagni, P. Kebarle, J. Phys. Chem. 74 (1970) 1475.

[2] W.G. McMillan, J.E. Mayer, J. Chem. Phys. 13 (1945) 276-305.

[3] L. Blum, J.S. Høye, J. Phys. Chem. 81 (1977) 1311-16.

[4] R. Triolo, J.R. Grigera, L. Blum, J. Phys. Chem. 80 (1976) 1858-61.

[5] R. Triolo, L. Blum, M.A. Floriano, J. Phys. Chem. 82 (1978) 1368-70.

[6] R. Triolo, L. Blum, M.A. Floriano, J. Chem. Phys. 67 (1977) 5956-59.

[7] J.P. Simonin, L. Blum, P. Turq, J. Phys. Chem. 100 (1996) 7704-09.

[8] J.P. Simonin, J. Phys. Chem. 101 (1997) 4313-20.

[9] L. Blum, F. Vericat, W.R. Fawcett, J. Chem. Phys. 96 (1992) 3039-44.

[10] K.S. Pitzer, G. Mayorga, J. Phys. Chem. 77 (1973) 2300-08.

[11] C.C. Chen, H.I. Britt, J.F. Boston, L.B. Evans, AIChE J. 28 (1982) 588-96.

[12] C.C. Chen, L.B. Evans, AIChE J. 32 (1986) 444-54.

[13] N. Papaiconomou, J.P. Simonin, O. Bernard, W. Kunz, Phys. Chem. Chem. Phys. 4 (2002) 4435-43.

[14] J.M. Prausnitz, R.N. Lichtenthaler, E. Gomez de Azevedo, Molecular Thermodynamics of Fluid-Phase Equilibria, Prentice Hall, Upper Saddle River, New Jersey, USA, 1999.

[15] M.S. Wertheim, J. Stat. Phys. 35 (1984) 19-34.

[16] G. Jackson, W.G. Chapman, K.E. Gubbins, Mol. Phys. 65 (1988) 1-31.

[17] J.P. Hansen, I.R. McDonald, Theory of simple liquids, Academic Press, New York, 1986.

[18] J.P. Simonin, Fluid Phase Equilib. 165 (1999) 41-58.

[19] W. Kunz, L. Belloni, O. Bernard, B.W. Ninham, J. Phys. Chem. B 108 (2004) 2398-2404.

[20] E.A. Guggenheim, Mixtures, Clarendon Press, Oxford, 1952.

[21] H. Renon, J.M. Prausnitz, AIChE J. 14 (1968) 135-44.

[22] R.A. Robinson, R.H. Stokes, Electrolyte Solutions, 2nd ed., Butterworths, London, 1959.

[23] C.C. Chen, P.M. Mathias, H. Orbey, AIChE J. 45 (1999) 1576-86.

[24] R.H. Stokes, R.A. Robinson, J. Solution Chem. 2 (1973) 173-84.

[25] H. Schönert, Z. Phys. Chem. 150 (1986) 163-79.

[26] H. Zerres, J.M. Prausnitz, AIChE J. 40 (1994) 676-91.

[27] R.W. Impey, P.A. Madden, I.R. McDonald, J. Phys. Chem. 87 (1983) 5071-83.

[28] H. Ohtaki, T. Radnai, Chem. Rev. 93 (1993) 1157-1204.

[29] A. Grossfield, J. Chem. Phys. 122 (2005) 024506 1-10.

[30] A.P. Lyubartsev, K. Laasonen, A. Laaksonen, J. Chem. Phys. 114 (2001) 3120-26.

[31] S.R. Rempe, L.R. Pratt, Fluid Phase Equilib. 183-184 (2001) 121-32.

[32] L.M. Ramaniah, M. Bernasconi, M. Parrinello, J. Chem. Phys. 111 (1999) 1587-91.

[33] F.C. Lightstone, E. Schwegler, R.Q. Hood, F. Gygi, G. Galli, Chem. Phys. Lett. 343 (2001) 549-55.

[34] M.M. Naor, K. van Nostrand, C. Dellago, Chem. Phys. Lett. 369 (2003) 159-64.

[35] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, 5^{th} edition, Wiley, Sons, New York, 1988.

[36] I. Prigogine, R. Defay, Thermodynamique Chimique, Dunod, Paris, 1950.

[37] R.H. Fowler, E.A. Guggenheim, Statistical Thermodynamics, Cambridge University Press, 1949.

[38] R. Pitzer, Inorg. Chem. 23 (1984) 3027-28.

[39] H. Schönert, Z. Phys. Chem. 150 (1986) 181-99.

[40] H.C. Andersen, D. Chandler, J. Chem. Phys. 57 (1972) 1918-29.

[41] H. Renon, J.M. Prausnitz, AIChE J. 15 (1969) 785-785.

[42] L.G. Sillen, A.E. Martell, Stability Constants of Metal-Ion Complexes, and Supplement no. 1, The Chemical Society, London, 1964.

[43] R.N. Goldberg, J.L. Manley, R.L. Nuttal, Program Gamphi for Calculating Activity, Osmotic Coefficients of Aqueous Electrolyte Solutions at 298.15 K, National Bureau of Standards, Chemical Thermodynamics Division, 1984.

[44] W.J. Hamer, Y.C. Wu, J. Phys. Chem. Ref. Data 1 (1972) 1047-99.

[45] S.H. Lee, J.C. Rasaiah, J. Phys. Chem. 100 (1996) 1420-25.

[46] S. Koneshan, J.C. Rasaiah, R.M. Lynden-Bell, S.H. Lee, J. Phys. Chem. B 102 (1998) 4193-4204.

[47] M. Tuckerman, K. Laasonen, M. Sprik, M. Parrinello, J. Phys. Chem. 99 (1995) 5749-52.

[48] A. Botti, F. Bruni, S. Imberti, M.A. Ricci, A.K. Soper, J. Chem. Phys. 121 (2004) 7840-48.

[49] S. Han, S.H. Pan, Fluid Phase Equilib. 83 (1993) 261-70.

[50] L. Malahias, O. Popovych, J. Chem. Eng. Data 27 (1982) 105-09.

[51] M.A. Esteso, O.M. Gonzalez-Diaz, F.F. Hernandez-Luis, L. Fernandez-Merida, J. Solution Chem. 18 (1989) 277-88.

[52] H.S. Harned, J.G. Donelson, J. Am. Chem. Soc. 60 (1938) 339-41.

[53] H.S. Harned, J.G. Donelson, J. Am. Chem. Soc. 60 (1938) 2128-30.

[54] H.S. Harned, J.G. Donelson, C. Calmon, J. Am. Chem. Soc. 60 (1938) 2133-35.

[55] H.O. Spivey, T. Shedlovsky, J. Phys. Chem. 71 (1967) 2165-71.

[56] B. Mock, L.B. Evans, C.C. Chen, AIChE J. 32 (1986) 1655-64.

[57] R.C. Phutela, Z.S. Kooner, D.V. Fenby, Aust. J. Chem. 32 (1979) 235-59.

[58] Z.S. Kooner, R.C. Phutela, D.V. Fenby, Aust. J. Chem. 33 (1980) 9-13.

[59] G. Åkerlöf, J. Am. Chem. Soc. 54 (1932) 4125-39.

[60] G. Åkerlöf, O.A. Short, ibid. 58 (1936) 1241-43.

[61] A.L. Capparelli, D.S. Gill, H.G. Hertz, R. Tutsch, J. Chem. Soc. Faraday Trans. 74 (1978) 1849-60.

[62] E. Hawlicka, D. Swiatla-Wojcik, J. Phys. Chem. A, 2002, 106, 1336-45.

[63] H. Schneider, in: J.F. Coetzee, C.D. Ritchie (Eds.), Solute-Solvent Interactions, Marcel Dekker, New York-London, 1969, pp. 301-342.

[64] D. Feakins, in: F. Franks (Ed.), Physico-Chemical Processes in Mixed Aqueous Solvents, Heinemann Educational Books Ltd., London, 1969, pp. 71-90.

[65] A.J. Stace, A.K. Shukla, J. Am. Chem. Soc. 104 (1982) 5314-18.

[66] A. Fratiello, D.C. Douglass, J. Chem. Phys. 39 (1963) 2017-22.

Chapter 7

Conclusion

This PhD thesis was conducted in the context of a collaboration between two laboratories belonging to the universities of Regensburg (Germany) and Paris VI (France). It was supported by a grant from the AiF (Germany). The orientations of the work and the results were discussed periodically with the DECHEMA (Germany). The final aim of this research is the development of a software program for the assessment of departures from ideality observed in mixed solvent electrolytes.

The present work constitutes a stage on that way, with the inclusion of solvation effects in chemical engineering thermodynamic models. Here, this method has been used in conjunction with the MSA-NRTL model of Papaiconomou et al. (2002). If necessary, it will be possible to introduce it into other models for the short range part of the Gibbs energy.

In this thesis, solvation has been described in two ways as follows.

- By using the classic simple model of Robinson and Stokes, in which a *constant* solvation number (i.e., constant w.r.t. salt concentration) is attributed to each ion.

  It has been shown that the introduction of a hydration number on the ions improves the capability of the MSA-NRTL model to fit experimental osmotic and activity coefficients of aqueous ionic solutions (Table 1 of Chapter 4). A consistent set of NRTL parameter values has been proposed for simple 1-1 and 1-2 salts in water. The case of associating electrolytes (e.g., associating acids HNO3 and H2SO4) has been approached.

- By using the more complex, and more realistic, stepwise solvation-equilibrium model of Stokes and Robinson, which assumes that ions have various discrete degrees of solvation that are connected through elementary chemical reactions involving one solvent molecule at each step. It has been shown here how to

combine this effect with those of other interactions in a thermodynamically consistent way.

A consistent set of NRTL parameter values has also been proposed for this model.

Both methods have been applied to the representation of activity coefficients in two-solvent mixtures at 25°C. However only in the first case has the model been used for a description of "real world" electrolyte solutions, that is to say to solutions in a wide range of temperatures, between 25 and 100°C.

It is well known that it is much more difficult to describe thermodynamic quantities of the "first kind" (enthalpy and entropy), that are first derivatives of the Gibbs energy w.r.t. temperature, and quantities of the "second kind" (heat capacities), that are second derivatives of the Gibbs energy w.r.t. temperature, than to represent activity coefficients.

The capability of the MSA-NRTL model including constant hydration numbers to represent dilution enthalpies and heat capacities has been investigated in the case of binary aqueous solutions. Values for the hydration, MSA and NRTL temperature-dependent parameters have been optimised. Generally, satisfactory representations of the quantities could be obtained. It must be underlined that, when the corresponding data were available, the quantities of the various kinds were refined *simultaneously*. This was the case for LiCl and KCl in water between 25 and 100°C.

The model has also been used in the case of ternary mixed aqueous solvent electrolytes. It was possible to describe the activity coefficients of the solvents in a narrower temperature range (typically 70-100°C) and, separately, the mean salt activity coefficient in the mixture at 25°C. It was not possible to fit the two types of quantities simultaneously in these two different temperature ranges. The origin of this result has not been elucidated.

The prospects for this work are as follows.

- The effect of temperature and ion association could be introduced in the stepwise solvation-equilibrium model. This could be done by introducing a temperature-dependent equilibrium constant. Ion association could be modelled at the same level than the hydration reaction. For electrolytes that are known to be strong in aqueous solution, cation-anion pairing is expected to be relevant in the case of solvent mixtures containing a high proportion of nonaqueous solvent(s).

As stated in the second paragraph below eq 6.20, it would be possible to relax the hypothesis of hydrated cations, the C(i)s, being energetically equivalent. This would introduce additional parameters (which in principle is not desirable) but this would lead to a more realistic picture of cation hydrates interactions with other species in solution.

- For the model with constant solvation numbers, it would also be interesting to study the case of solvent mixtures containing a high proportion of nonaqueous solvent. This would then allow representations in the whole range of solvent compositions.

- Here, only aqueous solutions of sulfuric acid have been treated. It will be important to also consider solutions of this acid in mixed solvents, which is a system of great importance for the industry.

- Finally, it might be desirable to try to replace the NRTL model by another more satisfactory model to account for short-range interactions. Actually, the NRTL model of Renon and Prausnitz is a very popular tool in the field of chemical engineering thermodynamics. However, some of its theoretical weaknesses have been reported in the literature 30 years ago (e.g., V. Flemr, Coll. Czech. Chem. Comm. 41 (1976) 3347-9). Moreover, there is a continuous effort for finding better models, as shown by the work of Aranovich and Donohue (e.g., J. Chem. Phys. 105 (1996) 7059-63, for binary systems on a lattice) and that of a Chinese group (J. Hu and Z. Duan, J. Chem. Phys. 123 (2005) 244505). The application of such alternative tracks have not been explored in the literature.

This discussion shows that this topic, which lies at the frontier between fundamental and applied thermodynamics, will require appreciable further work for the development of a "complete model".