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ION-MOLECULAR MODELS IN THE NEUTRALIZING BACKGROUND AS A REFERENCE SYSTEM FOR A METAL-POLAR LIQUID SOLUTIONS

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The ion-molecular models in the neutralizing background are proposed as a reference system for the description of the equilibrium properties of metal-polar liquid solutions. The analytic solution of the mean spherical approximation obtained by us previously for the ion-dipole system in a neutralizing background (¹⁰) is used to study the structure of sodium-ammonia solutions. It is shown that the structure of ammonia is close-packed and changes little with ion concentration. The shape of the ion-ion distribution function changes from solvation behaviour with Debye-like asymptotics at low ion concentration to density ordering in the metallic region.

The development of the statistical theory of ion-molecular system is stimulated by the necessity to develop the microscopic theory of electrolyte solutions. An explicit allowance for the molecular solvent results in new possibilities to describe and interpret on a quantitative level the solvation and other effects appearing due to the liquid polar solvent influence (¹⁻³).

Metal-polar liquid solutions (for example, solutions of alkali metals in liquid ammonia) are more complicated systems in contrast to electrolyte solutions (⁴). They can be considered as consisting of two subsystems, the quantum subsystem of conduction electrons and the classical ion-molecular subsystem (metal ions and solvent molecules). This approach has proved to be very

successful for the study of alkali metals (⁵⁻⁶) and solutions of alkali metals in their alkali halide melts (⁷⁻⁸), where classical subsystem was considered as ionic system in the neutralizing background. In our case of the metal-polar liquid solutions the ion-molecular system is also immersed in a uniform neutralizing background representing the metal conduction electrons and is considered as reference fluid which dominates the structure. Allowance for the electron subsystem, at least in the metallic region, similarly to the case of metals or metal-molten salt solution (⁹), can be means of perturbation theory through the pseudopotentials of the electron-ion and electron-molecule interactions and the dielectric function of the electron gas. In the nonmetal region the problem arises to provide consistency of the structure of the solution and the electron subsystem state.

The simplest ion-molecular model with neutralizing background is the ion-dipole system. We have obtained the analytical solution of the mean spherical approximation (MSA) for this model (¹⁰) and shall apply it here to study solutions of sodium in ammonia. The part of these results has been discussed in (¹¹).

The metal-polar liquid solution of the form $\text{Na}_x(\text{NH}_3)_{1-x}$ is composed of the cations, with density ρ_m , which we model by hard spheres with charge eZ_m and diameter σ_m , and the polar molecules with density ρ_s which we model by hard spheres with dipole moment p_s and diameter σ_s . The system is embedded in a uniform neutralizing background of density $\rho_\phi = \rho_m Z_m$, which models the metal electrons. The MSA reduces to the solution of the Ornstein-Zernike integral equations

$$h_{ij}(X_1, X_2) = c_{ij}(X_1, X_2) + \sum_{l=1}^2 \rho_l \int dX_3 h_{il}(X_1, X_3) c_{lj}(X_3, X_2) \quad (1)$$

supplement by the closure for the total correlation functions

$h_{ij}(X_1, X_2) = g_{ij}(X_1, X_2) - 1$ and the direct correlation functions $c_{ij}(X_1, X_2)$:

$$\begin{aligned} h_{ij}(X_1, X_2) &= -1 & \text{for} & & r_{12} < \sigma_{ij} = \frac{1}{2} (\sigma_i + \sigma_j) \\ c_{ij}(X_1, X_2) &= -\beta U_{ij}(X_1, X_2) & \text{for} & & r_{12} > \sigma_{ij} \end{aligned} \quad (2)$$

where $g_{ij}(X_1, X_2)$ are the pair distribution functions, $U_{ij}(X_1, X_2)$

are the electrostatic interaction between particles, $\beta = 1/K_B T$, $x_1 = (r_1, \Omega_1)$ denotes the set of coordinates of particle 1, Ω_1 is the set of Euler angles necessary to define the orientation of the molecule and r_{12} is the interparticle distance.

The results obtained in ⁽¹⁰⁻¹¹⁾ can be represented in the

form

$$g_{ij}(x_1, x_2) = g_{ij}^{HS}(r_{12}) + G_{ij}(x_1, x_2), \quad (3)$$

where $g_{ij}^{HS}(r_{12})$ are the pair distribution functions for a two-component mixture of hard spheres of diameters σ_m and σ_s . General expressions for electrostatic parts $G_{ij}(x_1, x_2)$ were presented in ⁽¹⁰⁾. They are expressed through the set of seven interaction parameters $M_m, \nu_m, M_s, \nu_s, \Gamma, B^{10}, b_2$ which couple with the parameters of the ion-ion $\alpha_0^2 = 4\pi\epsilon e^2 z_m^2$, ion-dipole

$\alpha_1^2 = \alpha_0 \alpha_2$ and dipole-dipole $\alpha_2^2 = \frac{4\pi}{3} \beta \rho_s^2$ interactions by the set of nonlinear equations.

Here we shall apply this results for the description solutions of sodium in liquid ammonia at 235°K. The diameter of the sodium ion is taken from data ionic melts ⁽¹²⁾, $\sigma_m = 2.6$ Å, and that of the ammonia molecule from the compressibility of pure ammonia ⁽⁴⁾, $\sigma_s = 3.0$ Å. The dipole moment of NH_3 is $p_s = 1.48$ D. The molar volume of the solution is assumed to be additive

$$V_\mu = xV_{\mu_m} + (1-x)V_{\mu_s} \quad (4)$$

where $x = \frac{\rho_m}{\rho_s + \rho_m}$ - the mole fraction of sodium. Instead of MSA we shall apply exp-like approximation ^(1,13)

$$g_{ij}(x_1, x_2) = g_{ij}^{HS}(r_{12}) e^{G_{ij}(x_1, x_2)} \quad (5)$$

which provides positive $g_{ij}(x_1, x_2)$ for all distances.

The expressions for $g_{ij}(x_1, x_2)$ are presented in the orientation-invariant form

$$g_{ms}(r, \vartheta_2) = g_{ms}^{000}(r) + g_{ms}^{011}(r) \cos \vartheta_2 + \dots$$

$$g_{ss}(r, \Omega_1, \Omega_2) = g_{ss}^{000}(r) + g_{ss}^{110}(r) \cos \vartheta_{12} + \quad (6)$$

$$g_{ss}^{112}(r) (3 \cos \vartheta_1 \cos \vartheta_2 - \cos \vartheta_{12}) + \dots$$

where ϑ_1, ϑ_2 are orientations of the dipole moment relative to r_{12} , ϑ_{12} is the angle between the dipole moments of the molecules. From definition $g_{ss}^{ooo}(r) = g_{NN}(r)$ is the ammonia-ammonia radial distribution function. The curve for pure ammonia is presented in

Figure 1.

Fig.1 The nitrogen-nitrogen pair distribution function $g_{ss}^{ooo}(r)$ for $x=0.0001$ as a function of the distance between molecules :
: experimental, : MD, : theory,
: uncorrected theory.

The curves from X-ray measurements (¹⁴) and molecular dynamics (MD) simulation (¹⁵) are also presented for comparison. Our theory deviates from the experiment only at small distances where it is necessary to allow for the softness of the intermolecular interactions. In order to do that, the procedure of Weeks, Chandler and Andersen (¹⁶) has been applied. The potential $U_{ss}(r, \Omega_1, \Omega_2)$ used in (¹⁵) has been decomposed as follows

$$\varphi_{NN}(r, \Omega_1, \Omega_2) = \begin{cases} U_{ss}(r, \Omega_1, \Omega_2) - U_{ss}(r_{\min}, \Omega_1, \Omega_2), & \text{for } r < r_{\min} \\ 0, & \text{for } r > r_{\min} \end{cases} \quad (8)$$

where the distance $r_{\min}$ corresponds to global minimum of the potential $U_{ss}(r, \Omega_1, \Omega_2)$.

The allowance of softness leads to the substitution of $g_{ss}(r)$ by $e^{-\beta\phi_{NN}(r, \hat{Q}, \hat{Q})} g_{ss}(r)$ and provides the correct first maximum of $g_{NN}(r)$. The theory and experiment show the first maximum at 3.4 Å. However, similarly to the MD data, we did not get the pronounced shoulder at ~ 3.7 Å, manifesting that the model is not so satisfactory. As already mentioned by Heinzinger et al (¹¹) the $g_{NN}(r)$ behaviour indicates a close-packed structure of ammonia. Our study shows a comparatively weak sensitivity of $g_{NN}(r)$ on the ionic concentration in a wide range. More sensitive are the harmonics $g_{ss}^{110}(r)$ and $g_{ss}^{112}(r)$. The function $g_{ss}^{112}(r)$ at two different concentrations corresponding to the nonmetallic and metallic regions is presented in figure 2.

Fig. 2 The orientation-invariant harmonics of pair distribution functions as a function of distance between particles for 1: $X = 0.05$ and 2: $X = 0.1$

As for the ion-molecular function $g_{ms}(r, \hat{\vartheta}_s)$ our calculations show that the function $g_{ms}^{000}(r) = g_{mN}(r)$ has also comparatively weak sensitivity on the ion concentrations. But the behaviour of $g_{ms}^{011}(r)$ leads for $g_{ms}(r, \hat{\vartheta}_s)$ to the strong first maximum, which corresponds to the orientation $\hat{\vartheta}_s = 0$, manifesting the presence of solvation shells. At increasing concentrations the structure becomes more smooth. However the dominating orientation

$\vartheta_s = 0$ preserves.

The ion-ion function $g_{mm}(r)$ is especially sensitive on the concentration. This can be seen in Fig. 2. Similarly to electrolyte solutions ⁽³⁾ at low ionic concentration (nonmetallic region) $g_{mm}(r)$ has Debye-like asymptotics. The allowance for solvent is manifested by the oscillations around the asymptotic behaviour due to solvation. At higher concentrations (metallic region) the asymptotic behaviour is absent and the oscillations are around the abscissa axis and their amplitude increases. The function $g_{mm}(r)$ becomes similar to the one in the case of liquid metals ^(5,6). One has to mention the more structured form of $g_{mm}(r)$ than the one for aforementioned system.

Thus we have shown that the ion-dipole model in the neutralizing background can be used as a reference system for the description of a metal-polar liquid solutions. Subsequent development of this approach can be connected with improvement of the description of the molecular model (taking into account the association and solvation effects, using site-site approach etc.) and taking into account electronic subsystem.

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