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INHOMOGENEOUS MODEL OF METAL-AMMONIA SOLUTIONS (*)

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Résumé. — Les coefficients de pression et de température de la conductivité électrique des solutions M-NH₃ sont calculés à l'aide du modèle inhomogène de Cohen et Jortner, dans la gamme de concentrations comprise entre 1 et 9 moles pour cent de métal (MPM). L'absence de variations thermiques de l'effet Hall est aussi expliquée, ainsi que les variations du pouvoir thermoélectrique. Les effets de la pression et de la température sont essentiellement de modifier le volume des régions métalliques plus compressibles. Des résultats thermodynamiques montrent l'existence d'inhomogénéités ayant la taille requise par le modèle de Cohen et Jortner.

Abstract. — The inhomogeneous model of Cohen and Jortner is used to obtain the pressure *P* and temperature *T* coefficients of the electrical conductivity of M-NH₃ solutions in the 1-9 moles per cent metal (MPM) concentration range. The temperature independence of the Hall effect is explained as well as the variation of the thermoelectric power. The effects of *P* and *T* are primarily to alter the volumes of the more compressible metallic regions. Thermodynamic data show the existence of inhomogeneities of the required size for the Cohen-Jortner model.

1. Introduction. — Cohen and Jortner [1, 2] have recently proposed an inhomogeneous transport regime for several fluid systems that undergo a metal-non-metal transition. They applied this model to the calculation of the electrical conductivity of metal-ammonia solutions in the intermediate concentration range where these solutions undergo a metal-non-metal transition, i. e., between about 9 and 1.0 MPM (moles per cent metal). The suggestion that metal-ammonia solutions might be described as inhomogeneous fluids was previously made by Cohen and Thompson [3], who suggested the growth of associated complexes into large, metallic clusters 0.1 and 3 MPM. Optical evidence for the coexistence of both solvated (i. e., localized) and free electrons in a macroscopically homogeneous solution was reported by Somoano and Thompson [4]; Lelieur [5] has shown that the experimental results of magnetic susceptibility and Knight shift can be analyzed in an inhomogeneous model. However, the recent work by Cohen and Jortner gives a basis for quantitative calculations. In the present paper, it is shown that their model can be used to obtain the pressure and temperature coefficients of the electrical conductivity of metal-ammonia solutions, in the intermediate concentration

range. The temperature independence of the Hall effect is explained as well as the variations of the thermoelectric power.

2. Pressure dependence of the electrical conductivity. — The idea of the Cohen and Jortner model, applied to M-NH₃ solutions, is as follows: between about 1 and 9 MPM, the solutions are microscopically inho-

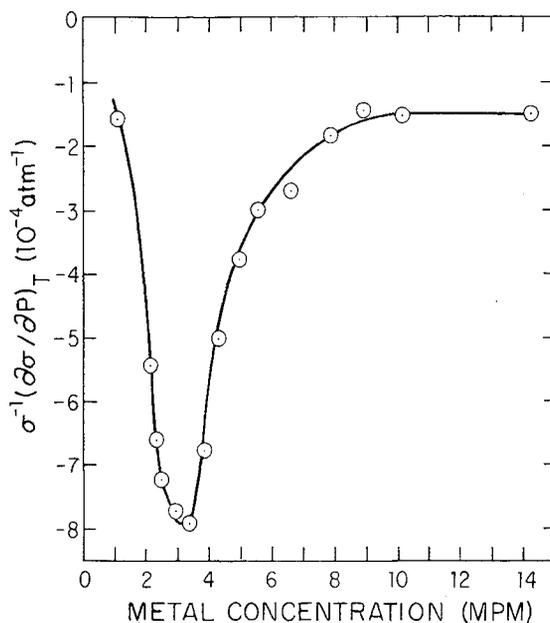


FIG. 1. — Experimental $(1/\sigma)(\partial\sigma/\partial P)_T$ for Na-NH₃ at -35 °C, from ref. [6] plotted versus the metal concentration expressed in MPM.

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mogeneous with a volume fraction C occupied by metallic clusters of a mean concentration of about 9 MPM, the remaining volume consisting of small solvated electron-cation diamagnetic complexes. We assume that these dilute or electrolytic clusters have a 1 MPM concentration. The use of the effective medium theory (EMT) results in the following equations for the electrical conductivity σ [2]:

$$\begin{aligned} \sigma &= \sigma_0 f(C, x), \\ f(C, x) &= a + (a^2 + x/2)^{1/2}, \\ a &= \frac{1}{2} \left[\frac{3}{2} C - \frac{1}{2} (1-x) + x/2 \right], \\ x &= \sigma_1 / \sigma_0, \end{aligned} \quad (1)$$

where σ_0 and σ_1 are the conductivities in the metallic and electrolytic regions, respectively. Cohen and Jortner use Eggarter's theory to account for scattering from the boundaries of the metallic regions. The modified effective medium theory (EMTZ) thus obtained results in the following equations:

$$\begin{aligned} \sigma &= \sigma_0 D(C) \bar{f} \\ \bar{f} &= f(C, x(C)) \\ D(C) &= zC / (1 - C + zC) \\ x(C) &= \sigma_1 / \sigma_0 D(C) \\ z &= L / \Lambda \end{aligned} \quad (2)$$

where z corresponds to the ratio between the sampling length L for concentration fluctuations and the mean free path Λ at the lower limit of the propagation regime. It was interesting to apply this model to the calculation of various quantities which are experimentally well known in the intermediate concentration range of metal-ammonia solutions. For instance, the pressure coefficient of the electrical conductivity [6] (Fig. 1) is negative and has a minimum at about 3 MPM. The temperature coefficient is positive and has a maximum at about 2 MPM (Fig. 3). Let us determine first the expression of the pressure coefficient of the electrical conductivity. From the EMT equations, this pressure coefficient is given by [7]:

$$\begin{aligned} (1/\sigma) (\partial\sigma/\partial P)_T &= \\ &= (1/\sigma_0) (\partial\sigma_0/\partial P)_T + \frac{3}{4}(1-x) (a^2 + x/2)^{-1/2} (\partial C/\partial P)_T + \\ &+ [(2-3C) + 1/f] \frac{(a^2 + x/2)^{-1/2}}{4} (\partial x/\partial P)_T. \end{aligned} \quad (3)$$

The quantity C being defined by the ratio of the volume of the metallic clusters V_m to the total volume V of the solution, the quantity $(\partial C/\partial P)_T$ is related to the isothermal compressibility by:

$$\begin{aligned} (\partial C/\partial P)_T &= C \left\{ \frac{1}{V_m} (\partial V_m/\partial P)_T - \frac{1}{V} (\partial V/\partial P)_T \right\} = \\ &= C(\beta_T - \beta_T^m) \end{aligned} \quad (4)$$

where β_T is the isothermal compressibility at a given concentration and β_T^m is the isothermal compressibility

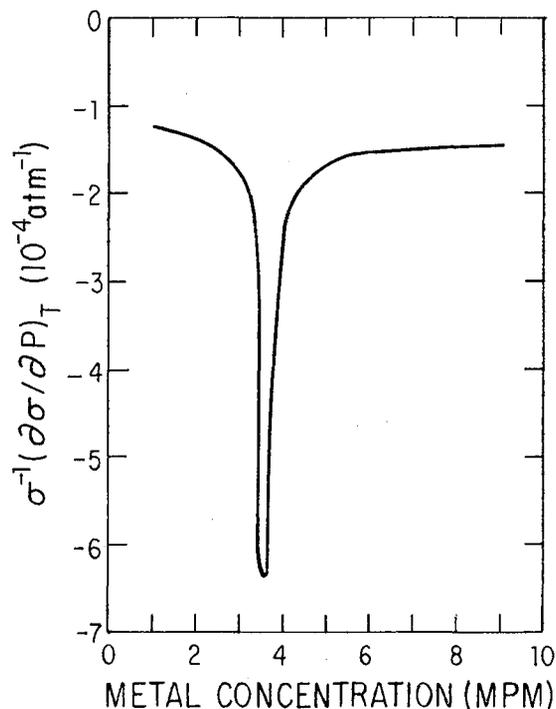


Fig. 2. — Calculated values of $(1/\sigma) (\partial\sigma/\partial P)_T$ from eq. (3) and (4) with $x = 1 \times 10^{-4}$.

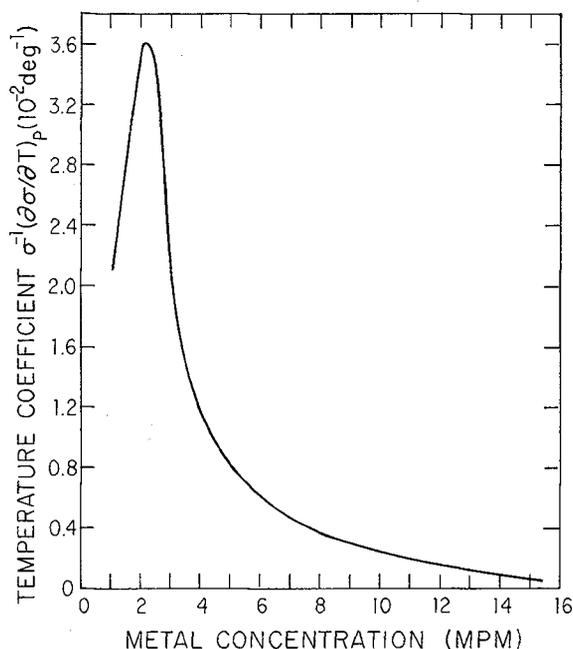


Fig. 3. — Experimental values of $(1/\sigma) (\partial\sigma/\partial T)_P$ from ref. [17] for Na-NH₃ at. — 33 °C.

of a metallic cluster, i. e., of a 9 MPM solution. The isothermal compressibility of Na-NH₃ solutions has been measured by Bøddeker and Vogelgesang [8]. Their results have been used to obtain $(\partial C/\partial P)_T$. The calculation of $(1/\sigma) (\partial\sigma/\partial P)_T$ also requires values of $(1/\sigma_1) (\partial\sigma_0/\partial P)_T$ and $(1/\sigma_1) (\partial\sigma_1/\partial P)_T$. These

quantities are taken to be equal to their experimental values: $-1.46 \times 10^{-4} \text{ atm}^{-1}$ (9 MPM) and $-1.26 \times 10^{-4} \text{ atm}^{-1}$ (1 MPM) respectively. The relation proposed by Jortner and Cohen [2] between C and the metal concentration was also used. The overall trend of $(1/\sigma) (\partial\sigma/\partial P)_T$ is given by the second term of the right hand side member of eq. (3). See [7] for a more detailed discussion. The calculated $1/\sigma(\partial\sigma/\partial P)_T$ (Fig. 2) has a minimum at 3.67 MPM (i. e., for $C = \frac{1}{3}$ for which $a \approx 0$). The minimum of the calculated values has approximately the experimental value for $x = 1 \times 10^{-4}$. However the dip around this minimum is much narrower than the experimental one. With the EMP equations, changing x modifies $(1/\sigma) (\partial\sigma/\partial P)_T$ only around the minimum between 3 and 4 MPM, and the minimum varies as $x^{-1/2}$.

The same calculation has been made with the EMTZ equations (eq. (2)). If it is assumed that z is pressure independent, $(1/\sigma) (\partial\sigma/\partial P)_T$ can be computed using the same values of $(1/\sigma_0) (\partial\sigma_0/\partial P)_T$, $(1/\sigma_1) (\partial\sigma_1/\partial P)_T$, and $(\partial C/\partial P)_T$. The calculated values are essentially similar to those calculated from eq. (3). The experimental value of the minimum is approximately obtained for $x = 3 \times 10^{-5}$ and $z = 2$, but it is impossible to ascertain only one value for the x and z . Considering the EMTZ equations (eq. (2)), the calculated values of $(1/\sigma) (\partial\sigma/\partial P)_T$ can be changed if it is considered that z is pressure dependent, which is realistic if z is viewed as a cluster size. It has been shown [7] that a $(\partial z/\partial P)_T$ value of, for instance, $2 \times 10^{-3} \text{ atm}^{-1}$, has a quite significant effect on the calculated values of pressure coefficient for concentrations greater than the minimum, and decreases the calculated values in this range toward the experimental values quite significantly. Other factors could also affect the calculated values of the pressure coefficient such as a modification of the relation between C and M or a concentration dependent z . These factors should account for the difference between calculated and experimental values.

In conclusion, it must be emphasized that the pressure coefficient of the electrical conductivity can be explained on the basis that the metallic regions are more compressible than the dilute regions whatever values are assigned to the various parameters of the calculation.

3. Temperature coefficient of the electrical conductivity. — The calculation of the temperature coefficient can also be done from the EMT and the EMTZ equations. First of all, it must be noted that such a calculation will give the temperature coefficient at constant volume, while the experimental determination of the electrical conductivity has always been done in presence of the ammonia vapor pressure, and therefore for temperatures less than about 240 K, the experimental temperature coefficient of the electrical conductivity can be considered as obtained at

constant pressure. Both quantities are related by the following equation:

$$\frac{1}{\sigma} (\partial\sigma/\partial T)_P = \frac{1}{\sigma} (\partial\sigma/\partial T)_V + \frac{1}{\sigma} (\partial\sigma/\partial P)_T \frac{1}{\beta_T} \frac{1}{\rho} (\partial\rho/\partial T)_P \quad (5)$$

where β_T is the isothermal compressibility and $(1/\rho) (\partial\rho/\partial T)_P$ the thermal expansion coefficient at constant

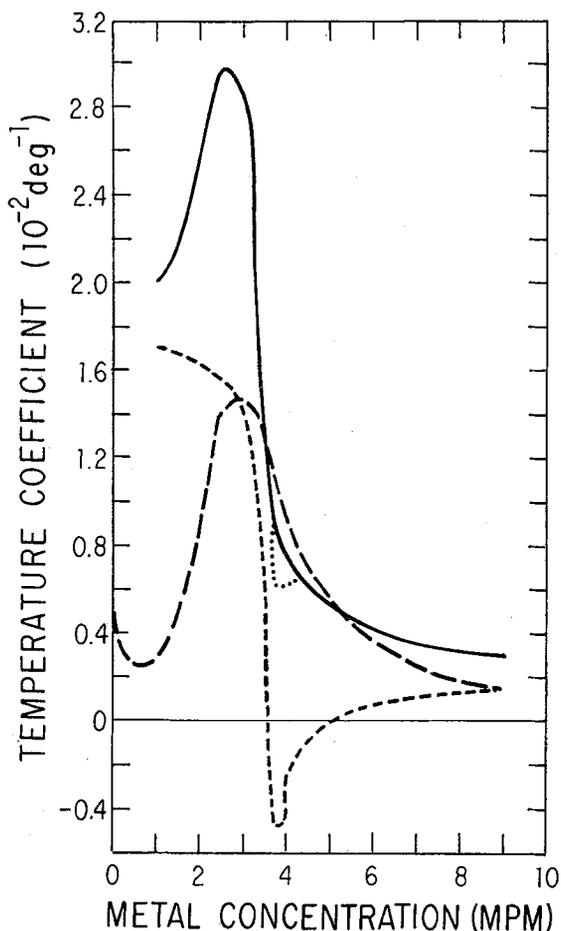


FIG. 4. — Calculated $(1/\sigma) (\partial\sigma/\partial T)_V$ (— — —), $(1/\sigma) (\partial\sigma/\partial P)_T$ (— — —), and the thermal expansion term

$$(1/\sigma) (\partial\sigma/\partial P)_T \frac{1}{\beta_T} \frac{1}{\rho} (\partial\rho/\partial T)_P$$

The $(1/\sigma) (\partial\sigma/\partial T)_P$ curve has to be compared to the experimental curve in figure 3. The kink (....) in the $(1/\sigma) (\partial\sigma/\partial T)_P$ curve results from the addition of the short and long dashed curves. Such a kink has been observed in the temperature coefficient of the electrical conductivity of Li-NH_3 by Nasby and Thompson [9].

pressure. These terms and $(1/\sigma) (\partial\sigma/\partial P)_T$ are known experimentally, and the correction term due to the thermal expansion (i. e., the second term of the right hand side member of eq. (5)) can be computed, and the corresponding values are reported in figure 4.

The temperature coefficient at constant volume is

immediately obtained from the EMT equations and is given by [7]:

$$\begin{aligned} \frac{1}{\sigma} (\partial\sigma/\partial T)_V &= \frac{1}{\sigma_0} (\partial\sigma_0/\partial T)_V + \\ &+ \frac{3}{4} (1-x) \left(a^2 + \frac{x}{2}\right)^{-1/2} (\partial C/\partial T)_V \\ &+ [(2-3C) + 1/f] \frac{(a^2 + x/2)^{-1/2}}{f} (\partial x/\partial T)_V. \quad (6) \end{aligned}$$

The thermal variations $(\partial C/\partial T)_V$ are deduced from density measurements. From the definitions of C , one obtains:

$$(\partial C/\partial T)_P = C \left[\frac{1}{\rho} (\partial\rho/\partial T)_P - \frac{1}{\rho_m} (\partial\rho_m/\partial T)_P \right] \quad (7)$$

where ρ is the density of a given solution and ρ_m the density of a 9 MPM solution. $(\partial C/\partial T)_P$ can therefore be deduced from experimental quantities following eq. (7), and $(\partial C/\partial T)_V$ is then deduced from $(\partial C/\partial T)_P$ by a relation similar to eq. (5) [7]. The calculation of $(1/\sigma) (\partial\sigma/\partial T)_V$ by eq. (6) requires also values of $(1/\sigma_0) (\partial\sigma_0/\partial T)_V$ and $(1/\sigma) (\partial\sigma_1/\partial T)$. These quantities have been taken equal to their experimental values, that is $0.15 \times 10^{-2} \text{ deg}^{-1}$ and $1.71 \times 10^{-2} \text{ deg}^{-1}$, respectively. Figure 4 shows the values of $(1/\sigma) (\partial\sigma/\partial T)_V$ along with the correction term of eq. (5), and $(1/\sigma) (\partial\sigma/\partial T)_P$. It is shown that the trends of the experimental values of $(1/\sigma) (\partial\sigma/\partial T)_P$ are obtained. The maximum of the calculated $(1/\sigma) (\partial\sigma/\partial T)_P$ values is at 2.5 MPM compared to the observed values of 2.1 MPM for Na-NH₃, 2.4 MPM for Li-NH₃, 2.7 MPM for K-NH₃. The calculated maximum is equal to $3 \times 10^{-2} \text{ deg}^{-1}$ compared to $3.6 \times 10^{-2} \text{ deg}^{-1}$ for Na-NH₃ solutions. The calculated values reproduce well the fast decrease of $(1/\sigma) (\partial\sigma/\partial T)_P$ between 3 and 4 MPM. It must be recognized that the maximum in $(1/\sigma) (\partial\sigma/\partial T)_P$ is not due to the variations of $(1/\sigma) (\partial\sigma/\partial T)_V$, but is rather a consequence of the maximum in the correction term

$$(1/\sigma) (\partial\sigma/\partial P)_T \frac{1}{\beta_T} \frac{1}{\rho} (\partial\rho/\partial T)_P.$$

The modified effective medium theory equations ((eq. (2)) can also give an expression of $(1/\sigma) (\partial\sigma/\partial T)_V$ and a similar calculation has been made using the same values of $(\partial C/\partial T)_V$, $(1/\sigma_1) (\partial\sigma_1/\partial T)_V$, $(1/\sigma_0) (\partial\sigma_0/\partial T)_V$. This calculation gives almost the same results as eq. (6). Only values close to $C = \frac{1}{3}$ are somewhat sensitive to the values of z and x [7].

It must be emphasized that negative values of $(1/\sigma) (\partial\sigma/\partial P)_T$ have been obtained, in our calculation, from negative values of $(\partial C/\partial P)_T$, while positive values of $(1/\sigma) (\partial\sigma/\partial T)_P$ are obtained from negative values of $(\partial C/\partial T)_V$. This is a consequence of the importance of the correction term which intervenes in $(1/\sigma) (\partial\sigma/\partial T)_P$, and of the difference in sign and in order of

magnitude of $(1/\sigma_1) (\partial\sigma_1/\partial P)_T$ and $(1/\sigma_1) (\partial\sigma_1/\partial T)_V$. In the calculation of $(1/\sigma) (\partial\sigma/\partial T)_V$, one may alternatively deduce $(\partial C/\partial T)_V$ from the magnetic susceptibility. In this case, $(\partial C/\partial T)_V$ would be positive, but would lead to calculated values of $(1/\sigma) (\partial\sigma/\partial T)_V$ about five times too large at the maximum, this maximum being located at $C = \frac{1}{3}$ (i. e., 3.67 MPM). Finally, it must be noted that a satisfactory calculation of the temperature coefficient is obtained (i) on using the EMT or the EMTZ equations, (ii) by taking into account the correction term due to the thermal expansion, which turns out to be quite important and responsible for the maximum of $(1/\sigma) (\partial\sigma/\partial T)_P$ and (iii) by deducing the thermal variations $(\partial C/\partial T)_V$ from the density measurements. It must also be recognized that the rather similar trends in $(1/\sigma) (\partial\sigma/\partial T)_P$ and $(1/\sigma) (\partial\sigma/\partial P)_T$ is now clearly a consequence of the compressibility of the metallic regions.

4. Hall effect. — The Hall effect measurements in M-NH₃ solutions have been the source of many efforts and discussions. For concentrations larger than about 9 MPM, the Hall effect coefficient has the free electron value. For concentrations less than 9 MPM the ratio of the free electron Hall coefficient R_0 to the experimental Hall coefficient R_H decreases and shows a minimum around 3 MPM [9]. It has been shown [5, 10] that this minimum is compatible with the expected variation of the Hall coefficient for concentrations less than 1 MPM. Another puzzling aspect of the Hall effect data in the M-NH₃ solutions is the absence of temperature dependence, even in the intermediate concentration range where the other properties display an important temperature dependence. Recently Cohen and Jortner [11] derived an expression for the Hall constant R_H in the effective medium theory. This equation does not explain the minimum observed in R_0/R_H . However, when this equation is modified to account for the scattering by the boundaries of the metallic clusters (to obtain the equivalent of eq. (2) for the electrical conductivity), more satisfactory results are obtained (*). Our calculation has shown that the interpretation of the temperature coefficient of the electrical conductivity does not need any thermal carrier excitation. Therefore, it is concluded that $(1/R_H) (\partial R_H/\partial T)_V$ must be negligible. However, the experimental temperature coefficient will be obtained at constant pressure. It is easy to show [7] that, since $(1/R_H) (\partial R_H/\partial T)_V$ is negligible, $(1/R_H) (\partial R_H/\partial T)_P$ will be of the order of $(1/\rho) (\partial\rho/\partial T)_P$, which is what has been observed [9].

5. Thermoelectric power. — The inhomogeneous model has also been used for the calculation of the thermoelectric power (**), using an effective medium theory expression obtained by Airapetiants [12]. It is found that this calculation reproduces fairly well

(*) Jortner, J., private communication.

(**) Damay, P. and Lelieur, J. P., to be published.

the experimental thermoelectric power in the intermediate concentration range [13].

In conclusion, the inhomogeneous model applied to metal-ammonia solutions in the intermediate concentration range gives satisfactory interpretation of the transport properties.

6. Thermodynamics. — The inhomogeneous model proposed by Cohen and Jortner assume clusters of, say, 25 Å. Such an assumption has been criticized, since the origin of these clusters is unclear. A thermodynamical analysis by Turner [14] suggests that such clusters do not exist in alloys such as Mg-Bi and Tl-Te. We now show that the same analysis suggests that they could exist in metal-ammonia solutions. It is known [15] that the concentration fluctuations $\langle (\Delta C)^2 \rangle$ in a binary mixture is related to the thermodynamic activity by the equation :

$$N \langle (\Delta C)^2 \rangle \equiv S_{cc}(0) = C_2 \left\{ \frac{1}{a_1} (\partial a_1 / \partial C_1)_{T,P} \right\}^{-1} \quad (8)$$

where a_i and C_i are the activity and the mean concentration of species i respectively, N is the mean number of atoms in the volume of interest V , and ΔC is the departure from the mean of the concentration of species 1 in this volume. Turner derives an expression for $S_{cc}(0)$, valid only for a low density of clusters, in terms of the mean number η of atoms in a cluster, assuming the clusters exist. This expression is given by :

$$S_{cc}(0) \equiv N \langle (\Delta C)^2 \rangle = \eta(C_1 - C_4)(C_3 - C_4). \quad (9)$$

where C_3 and C_4 are the average concentration of species 1 in the clusters and in the matrix respectively. Consider for instance the lower limit of the intermediate concentration range, i. e., between, say, 1 and 4 MPM. It is assumed in the inhomogeneous model that there is a low density of metallic clusters of 9 MPM concentration in a matrix of 1 MPM. The quantity $S_{cc}(0)$ has been determined by Ichikawa and Thompson [16]. Therefore, the relation [8] can be used to evaluate η . For a 2 MPM Na-NH₃ solution at 238 K, $S_{cc}(0) \simeq 0.1$, $C_1 = 0.02$, $C_3 = 0.09$, $C_4 = 0.01$ lead to $\eta \simeq 125$. For a 3 MPM Na-NH₃ solution $S_{cc}(0) \simeq 0.2$, $C_1 = 0.03$, $C_3 = 0.09$, $C_4 = 0.01$ lead also to $\eta \simeq 125$ because $S_{cc}(0)$ has approximately doubled between 2 and 3 MPM, as $(C_1 - C_4)$. Close to the critical concentration (~ 4 MPM), $S_{cc}(0) \simeq 0.55$, $C_1 = 0.04$, $C_3 = 0.09$, $C_4 = 0.01$ lead to $\eta \simeq 230$. At the upper limit of the intermediate concentration range, it can be considered that the solution is a 9 MPM metallic matrix in which 1 MPM dilute clusters are embedded. For instance, for a 8 MPM Na-NH₃ solution, $S_{cc}(0) \simeq 0.05$, $C_1 = 0.08$, $C_3 = 0.01$, $C_4 = 0.09$ lead to $\eta \simeq 60$ where η now refers to the non-metallic clusters. For a 7 MPM Na-NH₃ solution $S_{cc}(0) \simeq 0.1$, $C_1 = 0.07$, $C_3 = 0.01$, $C_4 = 0.09$ lead to $\eta \simeq 60$. Similarly for a 6 MPM solution, $S_{cc}(0) \simeq 0.2$ lead to $\eta \simeq 85$. The present estimation of η , derived from the Turner relation, suggests that the inhomogeneous model is relevant in the whole intermediate concentration range and not only close to the consolute point.

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