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Concentration Dependence of the Viscosity of Aqueous Electrolytes. A Probe into Higher Concentration

S. Mahiuddin and K. Ismail*

Department of Chemistry, North-Eastern Hill University, Bijni Campus, Laitumkhrah, Shillong-793003, India *(Received: August 20, 1982; In Final Form: March 8, 1983)*

Densities and viscosities of the $Ca(NO_3)_2$–H_2O, $MgCl_2$–H_2O, and $NiCl_2$–H_2O systems were measured as functions of temperature and concentration (from dilute to the saturation point). An empirical equation of the form, $\eta = a_0 \exp(b_0 m + c_0 m^2)$ has been found to describe the concentration dependence of the viscosity (η) satisfactorily at all temperatures. In the above equation a_0, b_0, and c_0 are constants and m is the molality of the solution. Analysis of the temperature dependence of the viscosity in terms of the Vogel–Tammann–Fulcher (VTF) equation and also the empirical nature of the concentration dependences of the three parameters of the VTF equation has revealed the possibility of obtaining the above empirical equation from the Adam–Gibbs theoretical model. The viscosity B coefficients estimated from the parameters of this empirical equation were found to be comparable with literature values. The newly suggested equation is also shown to be reducible to both Vand type and Arrhenius type isothermal equations. In all three systems studied a structural transition has been found to occur over the concentration range ~2–3.5 m.

Introduction

Continuous efforts have been going on to obtain a feasible expression for describing the concentration dependence of the viscosity, and transport properties in general, of binary solutions. The importance of this kind of study has been highlighted very recently by Pitzer.[1] Several empirical as well as theoretical equations are available in the literature[2-5] for this purpose but, unfortunately, they fail to be applicable when the concentration becomes considerably high, except for the Vand equation[6] and others[7-11] essentially based on the Vand equation. Although the Vand equation empirically describes the experimental data at higher concentrations, the theoretical concept on which the Vand equation was developed cannot be valid at these high concentrations. Therefore, the reason for the applicability of the Vand equation at high concentrations must be of a different theoretical origin.

In recent years one of the approaches being used to obtain an isothermal equation for explaining the concentration dependence of transport properties in glass-forming molten mixtures[12-14] is substituting the concentration dependence of the three parameters involved into the VTF equation,[15] an expression generally employed for describing the temperature dependence of transport properties. The VTF equation for the viscosity, η, is written as

$$\eta = A_0 T^{1/2} \exp[B_0/(T - T_0)] \quad (1)$$

A_0, B_0, and T_0 are the three parameters cited above. T_0 is a significant parameter known as the ideal glass transition temperature.

Since aqueous solutions also have a greater tendency to form glass especially at high concentrations, Angell and Bressel[16] made an attempt to derive an isothermal expression from eq 1 for the $Ca(NO_3)_2$–H_2O system by employing the above-mentioned approach used in glass-forming molten systems. Interestingly, they found that the isothermal equation thus obtained could be reduced to the form of the Vand equation[6] thereby providing an explanation for the success of the Vand equation at high concentrations. However, while deriving the isothermal equation from eq 1 Angell and Bressel neglected the dependence of the A_0 parameter on the concentration and that of B_0 was taken into account only partly. Therefore, there is room for improving Angell and Bressels' isothermal equation (AB equation) by making more appropriate substitutions for the concentration dependences of the three parameters of the VTF equation. Moreover, in a conductance study[16] of the $Ca(NO_3)_2$–H_2O system the computed value of the ideal glass transition composition, the key parameter of the AB equation, was found to differ from the value expected from the plot of T_0 vs. mole fraction. Another limitation of the AB equation is that the temperature range over which this equation may be applied falls between the T_0 values of the solvent and solute. Accordingly, the AB equation cannot be employed meaningfully at temperatures lying outside this range. In this paper we have therefore made an attempt to employ an alternative expression for describing the concentration dependence of the viscosity by measuring the viscosities of three electrolytic solutions, viz., $Ca(NO_3)_2$–H_2O, $MgCl_2$–H_2O, and $NiCl_2$–H_2O, as functions of temperature and concentration.

Experimental Section

Calcium nitrate tetrahydrate (EM, R grade), magnesium chloride hexahydrate (BDH, AR grade), and recrystallized nickel chloride hexahydrate (SD, AR grade) were used in preparing the three systems. The water used was doubly distilled in a quartz distilling unit. Different aqueous solutions of each system were prepared by varying the

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(1) K. S. Pitzer, *J. Am. Chem. Soc.*, **102**, 2902 (1980).
(2) A. Einstein, *Ann. Phys.*, **19**, 289 (1906); **34**, 591 (1911).
(3) G. Jones and M. Dole, *J. Am. Chem. Soc.*, **51**, 2950 (1929).
(4) S. P. Moulink, *J. Phys. Chem.*, **72**, 4682 (1968).
(5) D. E. Goldsack and R. Franchetto, *Can. J. Chem.*, **55**, 1062 (1977).
(6) V. Vand, *J. Phys. Colloid Chem.*, **52**, 277, 300, 314 (1948).
(7) E. Mooney, *J. Colloid Chem.*, **6**, 163 (1951).
(8) J. Padova, *J. Chem. Phys.*, **38**, 2635 (1963).
(9) D. G. Thomas, *J. Colloid Sci.*, **20**, 267 (1965).
(10) B. Breslau and I. Miller, *J. Phys. Chem.*, **74**, 1056 (1970).
(11) F. H. Spedding and M. J. Pikal, *J. Phys. Chem.*, **70**, 2430 (1966).
(12) C. A. Angell, *J. Phys. Chem.*, **70**, 3988 (1966).
(13) N. Islam and K. Ismail, *J. Phys. Chem.*, **80**, 1929 (1976).
(14) N. Islam, K. P. Singh, and S. Kumar, *J. Chem. Soc., Faraday Trans. 1*, **75**, 1312 (1979), and references therein.
(15) (a) H. Vogel, *Phys. Z.*, **22**, 645 (1921); (b) V. G. Tammann and W. Hesse, *Z. Anorg. Allgem. Chem.*, **156**, 245 (1926); (c) G. S. Fulcher, *J. Am. Ceram. Soc.*, **8**, 339 (1925).
(16) C. A. Angell and R. D. Bressel, *J. Phys. Chem.*, **76**, 3244 (1972).

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TABLE III: Least-Squares Fitted Values of the Parameters of Eq 2 for the Viscosities of the $Ca(NO_3)_2$-H_2O, $MgCl_2$-H_2O, and $NiCl_2$-H_2O Systems

T, K	concn range, m	a_0	b_0	10^3c_0	ln η std dev
		$Ca(NO_3)_2$-H_2O			
273.0	0.1305-13.635	1.5235	0.2769	21.503	0.047
298.0	0.1305-12.79	0.8611	0.2813	11.5559	0.037
	0.1305-20.251	0.8711	0.2770	11.4870	0.058
308.0	0.1305-12.79	0.7001	0.2898	8.2131	0.036
343.0	0.1305-12.79	0.4127	0.3035	1.2603	0.041
		$MgCl_2$-H_2O			
293.0	0.1145-5.3787	1.0480	0.3210	22.3947	0.018
298.0	0.1145-5.3787	0.9356	0.3184	21.3237	0.017
308.0	0.1145-5.9872	0.7609	0.3126	20.2845	0.017
323.0	0.1145-5.9872	0.5831	0.3163	16.3528	0.018
		$NiCl_2$-H_2O			
288.0	0.1736-4.9901	1.1617	0.3506	18.6401	0.020
298.0	0.1736-5.6853	0.9108	0.3574	14.3925	0.020
308.0	0.1736-5.6853	0.7408	0.3581	10.8796	0.020
323.0	0.1736-5.6853	0.5596	0.3751	3.8780	0.018

concentration from dilute to the saturation point (at room temperature, ~20 °C). For the $Ca(NO_3)_2$–H_2O, $MgCl_2$–H_2O, and $NiCl_2$–H_2O systems the concentrations of the solutions studied varied from 0.1305 to 12.79 m, from 0.1145 to 5.9872 m, and from 0.1736 to 5.6853 m, respectively. The exact concentration of each solution was determined volumetrically at 25 °C by the EDTA titration method.

The viscosity measurements were made with a Hoppler BH-2 falling ball viscometer with an accuracy of 0.5%. For measuring the densities a calibrated glass pycnometer was used. These measurements were made in a NBE Type ultrathermostat which maintained the temperature to ±0.02 °C.

Results and Discussion

The densities of all the solutions are found to be linear functions of both temperature (Table I) and molarity, c (Figure 1) within the experimental ranges of temperature and concentration. (Figure 1 and Table I are available as supplementary material. See paragraph at end of text regarding supplementary material.) The dependence of the density on molality, however, does not exhibit such a linear relationship (Figure 1). From Figure 1 it may be realized that the present density values of the $Ca(NO_3)_2$–H_2O, $MgCl_2$–H_2O, and $NiCl_2$–H_2O systems are in good agreement with the literature data.[17-20]

The measured viscosities of the three solutions at different temperatures and concentrations are given in Table II (supplementary material). In Figure 2 (supplementary material) a comparison of the present viscosity data of the three systems is made with the reported values[16,18,20,21] by plotting the viscosity isotherms. From these isotherms it is apparent that initially at low m there is a gradual increase in η with concentration and the variation in η becomes rapid at high molalities. An attempt has been made to describe such a concentration dependence of η in terms of an empirical equation of the form

$$\eta = a_0 \exp(b_0m + c_0m^2) \tag{2}$$

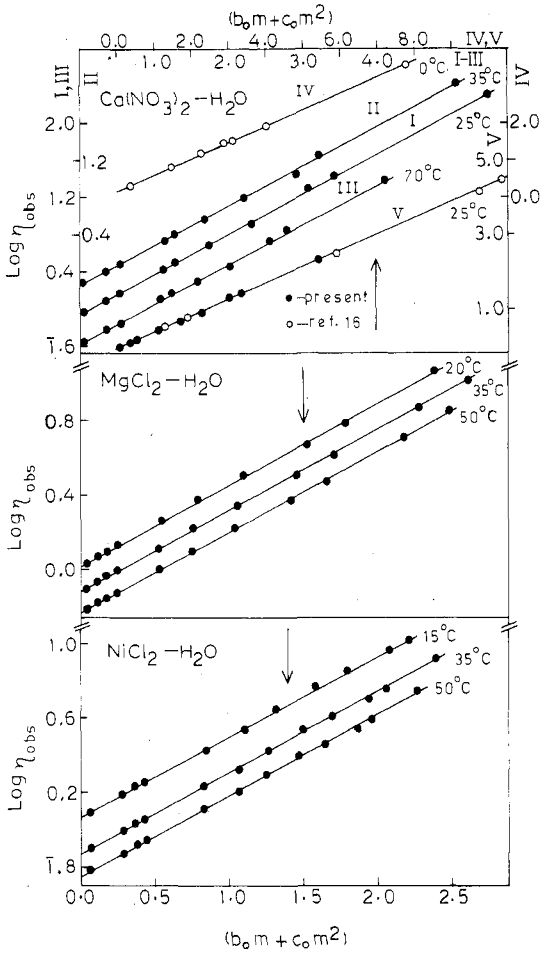

Figure 3. Plots of log η vs. $b_0m + c_0m^2$ for the $Ca(NO_3)_2$–H_2O, $MgCl_2$–H_2O, and $NiCl_2$–H_2O systems.

where a_0, b_0, and c_0 are constant parameters for a particular system. This isothermal equation has been adopted with a view that it may probably be derived from the VTF equation. A least-squares fitting of the viscosity data to eq 2 has been made and a surprisingly good fit has been obtained for all of the systems under study as is apparent from Table III. In order to verify further the suitability of eq 2 in describing the concentration dependence of the viscosity we extended for the $Ca(NO_3)_2$–H_2O system the upper limit of the concentration range of the data fitting at 25 °C from 12.79 to 20.25 m by incorporating the viscosity data reported by Angell and Bressel.[16] Interestingly, eq 2 has been found to fit well within this extended concentration range also (Table III). The applicability of eq 2 has also been examined at a relatively lower temperature by least-squares fitting (Table III) to this equation the reported[16] viscosity data of the $Ca(NO_3)_2$–H_2O system at 0 °C in the concentration range 1.12 to 13.63 m. The success of eq 2 in describing the concentration dependence of η with a respectable accuracy is also envisaged by the linearity of the plot of log η vs. $b_0m + c_0m^2$ (Figure 3).

After examining the ability of eq 2 to explain the dependence of η on the concentration, it is now essential to provide a probable theoretical basis to this empirical equation. For this we first made an analysis of the temperature dependence of the viscosity by plotting log η vs. $1/T$ (Figures 4–6 (supplementary material)). From these plots it is apparent that the viscosities of all the solutions under investigation show a non-Arrhenius temperature dependence and are therefore least-squares fitted to the VTF eq 1. However, it may be noted from Figures 4–6 that the non-Arrhenius behavior is not very pronounced in the

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[17] W. W. Ewing and R. J. Mikovsky, J. Am. Chem. Soc., 72, 1390 (1950).

[18] R. C. Weast, Ed., "Handbook of Chemistry and Physics", 58th ed, CRC Press, Cleveland, Ohio, 1977.

[19] J. N. Pearce and H. C. Eckstrom, J. Phys. Chem., 41, 563 (1937).

[20] S. Phang, Aust. J. Chem., 32, 1149 (1979).

[21] G. Maisano, P. Migliardo, F. Wanderlingh, and M. P. Fontana, J. Chem. Phys., 68, 5594 (1978).

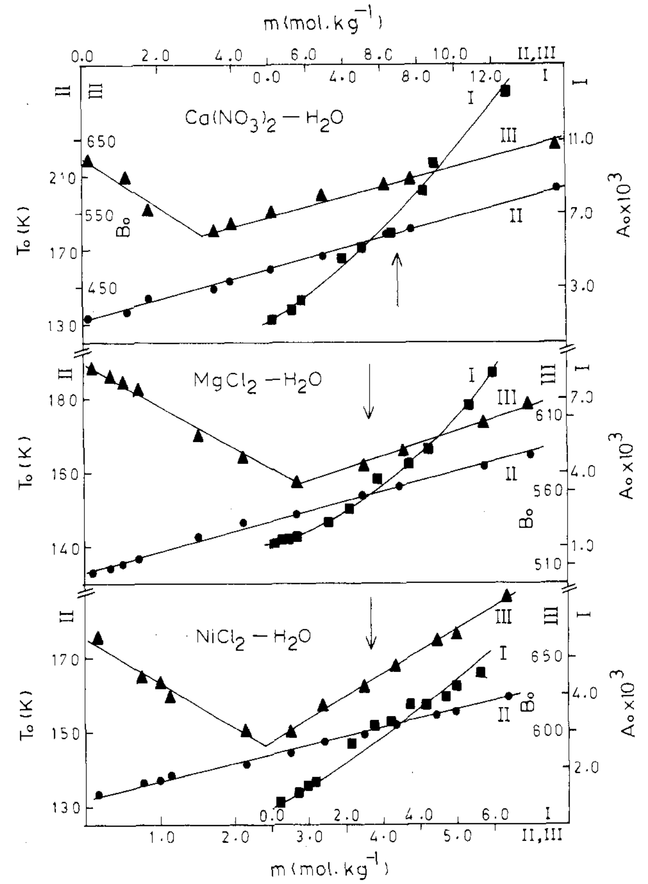

Figure 7. Plots of the A_0, B_0, and T_0 parameters of the $Ca(NO_3)_2$-H_2O, $MgCl_2$-H_2O, and $NiCl_2$-H_2O systems vs. the molality of the respective solutes.

present case which is obviously due to relatively higher temperatures of the viscosity measurement. The computed values for the A_0, B_0, and T_0 parameters are listed in Table IV (supplementary material). The values of these parameters for the $Ca(NO_3)_2$-H_2O system are comparable with those of Angell and Bressel[16] except at low concentrations. At low concentrations Angell and Bressel observed that T_0 for the solution becomes almost invarient with the concentration instead of showing a linear dependence as noticed by us. This discrepancy in our T_0 values may also be attributed to the fact that in the present study the temperature range of the viscosity measurement does not extend far below the ambient temperature. Moreover, as pointed out by Moynihan et al.[22] during the least-squares fitting different sets of A_0,B_0,T_0 values appear to fit the data without much difference in the standard deviations. For the $MgCl_2$-H_2O and $NiCl_2$-H_2O systems the computed T_0 values are comparable within ~10–15 K with their reported[23] T_g values.

The empirical nature of the concentration dependences of the A_0, B_0, and T_0 parameters (Table IV) for the three systems under study is illustrated in Figure 7. From this figure it may be noted that in the $Ca(NO_3)_2$-H_2O system the nature of the concentration dependences of the A_0 and B_0 parameters (as well as that of T_0 at higher concentrations as mentioned above) is similar to that observed by others[16] on the basis of the viscosity measurement made over a wider range of temperature. The concentration (critical concentration) at which the trend in the concentration dependence of B_0 changes is found to have a value characteristic of the electrolytic solution, viz., 3.2, 2.85, and 2.4 m for the $Ca(NO_3)_2$-H_2O, $MgCl_2$-H_2O, and $NiCl_2$-H_2O systems, respectively.

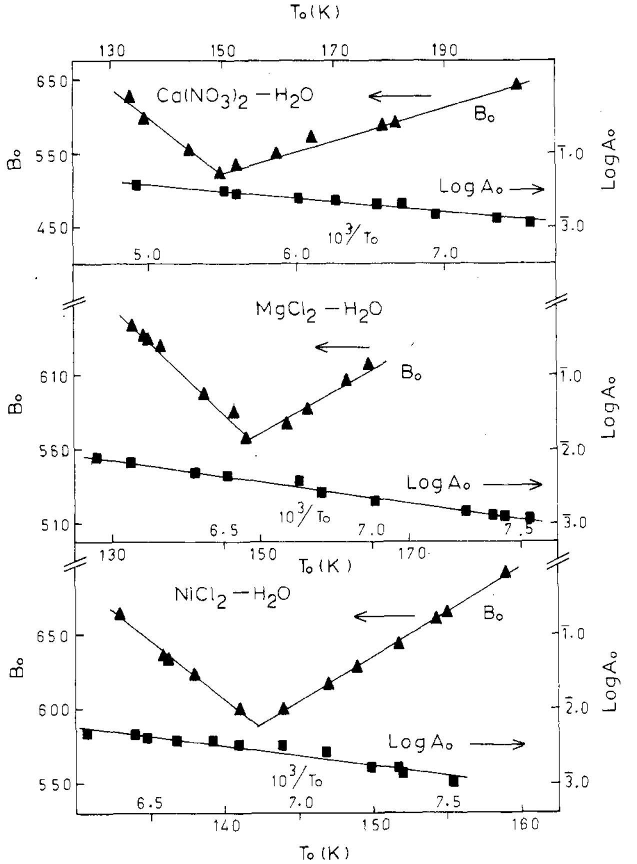

Figure 8. Plots of log A_0 and B_0 vs. $1/T_0$ and T_0, respectively, for the $Ca(NO_3)_2$-H_2O, $MgCl_2$-H_2O, and $NiCl_2$-H_2O systems.

The empirically found linear increase of T_0 with m may be described in terms of the interactions taking place in the electrolytic system. Since the contribution to viscosity from ion–ion interaction is relatively significant only at very low concentrations (in the concentration range where the Jones–Dole[3] equation is valid), in the experimental range of the concentration the ion–solvent interaction may be considered to dominate. The ion–solvent interaction through solvation of the solute particles causes a decrease in the configurational entropy of the solution with increasing concentration which, in turn, results in an increase of T_0 with concentration. Thus T_0 may be related to the hydration phenomenon in terms of the probability, p, of finding a solvent particle in the hydration shells of the solute particles. The linearity of the plot of T_0 vs. m (Figure 7) therefore appears to show a direct correlation[24] between T_0 and p. It is noted that a close dependence of T_0 on the hydration number was also revealed earlier by the attempt made by Angell and Sare[23] to correlate T_0 with the viscosity B coefficient and the pK_a of the conjugate acid of the anion of the solute. The empirical concentration dependence of T_0 may be written as

$$T_0 = T_0(0) + Qm \qquad (3)$$

where $T_0(0)$ is the T_0 of pure water and Q is the slope. The value of $T_0(0)$ for all of the systems studied here is found to be 132 ± 1 K which is in agreement with the reported glass transition temperature (139 K) for amorphous

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[22] C. T. Moynihan, C. R. Smalley, C. A. Angell, and E. J. Sare, *J. Phys. Chem.*, **73**, 2287 (1969).

[23] C. A. Angell and E. J. Sare, *J. Chem. Phys.*, **52**, 1058 (1970).

[24] This is because the probability, p, is equal to $nm/55.51$, where n is the total hydration number of the solute particle.

water.[25] The values of Q for the $Ca(NO_3)_2$–H_2O, $MgCl_2$–H_2O, and $NiCl_2$–H_2O systems are 5.60, 5.41, and 4.66 mol^{-1} kg, respectively.

It is interesting to find from Figure 8 that the observed concentration dependences of the A_0 and B_0 parameters (Figure 7) are representable by empirical expressions of the form

$$A_0 = A^* \exp(-B^*/T_0) \qquad (4)$$

$$B_0 = B_1 - CT_0 \qquad (5)$$

where A^*, B^*, and B_1 are constants. C remains constant up to the critical concentration beyond which it appears to depend on T_0 according to an expression, $C = b_1/T_0 - a_1$, where a_1 and b_1 are also constants. The values of these empirical constants, viz., A^*, B^*, B_1, C, a_1, and b_1, for the different systems under study may be estimated from the intercepts and slopes of the linear plots in Figure 8. Equations 4 and 5 seem to be obtainable[26] from the Adam–Gibbs equation[27] after substituting into it the presumably linear dependence of the configurational heat capacity on temperature.

With the concentration dependences of the A_0, B_0, and T_0 parameters having been discussed, it may now be shown[28] that by utilizing the above empirical relations between these parameters and the molality (eq 3–5) the VTF equation approximates eq 2. Therefore, the Adam–Gibbs model[27] from which the VTF equation may be derived appears to provide a plausible theoretical interpretation to empirical eq 2.

From Table III it may be seen that c_0 is a very small value compared to b_0. Therefore, at very low concentrations the c_0m^2 term may be neglected and eq 2 becomes similar to the Einstein[2] equation or the Jones–Dole[3] equation without the ion–ion interaction term (at low concentrations, $\exp(b_0m) \approx 1 + b_0m$ and $m \approx c$). Accordingly, the product of the a_0 and b_0 terms must be equivalent to the viscosity B coefficient. The values for the B coefficients at 25 °C calculated in this manner using the least-squares fitted values of a_0 and b_0 for $Ca(NO_3)_2$, $MgCl_2$, and $NiCl_2$ aqueous solutions are 0.241, 0.298, and 0.325, respectively, which are comparable with the literature values.[10] Moreover, using the relationship between m and c and neglecting the c_0 term, we can reduce eq 2 to the Vand equation, thereby providing a description to the success of the Vand equation at higher concentrations. Another noteworthy point is that the reduced form of eq 2 at low concentrations, i.e., $a_0 \exp(b_0c)$, is similar to the Arrhenius isothermal equation[29-31] as well as to the equation suggested by Carbonell.[32] Furthermore, the reduced form of eq 2 [$\eta = a_0 \exp(b_0m)$] may be written in terms of T_0 as $\eta = a' \exp(b'T_0)$, where a' and b' are again constant terms. The fact that the plots of log η vs. T_0 are fairly linear (Figure 9 (supplementary material)) for all of the three systems under study implies that T_0 is the key parameter in controlling the concentration dependence of the viscosity. This appears to be the reason for the success shown by the AB equation in describing the concentration dependence of η even though during its derivation the variation in the value of A_0 with concentration was completely ignored.

Finally, it is also worthwhile to make an attempt to provide a structural interpretation to the observed minimum in the B_0 vs. m or T_0 plot. The sudden change in the nature of the concentration dependence of B_0 envisages some kind of structural transition at the critical concentration. For the $Ca(NO_3)_2$–H_2O system such a structural transition may therefore be expected to occur around 3.2 m, which is in accordance with the observation of Angell and Bressel.[16] They suggested that this transition is perhaps due to the incompatibility of the network water structure with an ionic liquid structure involving anions and hydrated cations leading to liquid–liquid phase separation at sufficiently low temperature. For the $NiCl_2$ solution Maisano et al.[21] suggested that a structural transition occurs around 2 m which is comparable with the critical concentration of the $NiCl_2$–H_2O system observed in the present study. Moreover, the critical concentrations of the three solutions under study appear to fall in the region where Gurney's cospheres for solutes of divalent cations may be visualized to start overlapping.[16,23,33] Furthermore, in the light of the attempts made by others[34,35] to correlate viscosity isotherms with the melting point curves of binary systems containing organic salts, it is interesting to find in the present study that the critical concentration values for the three aqueous systems are comparable with their respective first eutectic points. Therefore, although in the absence of an intensive structural study it may not be possible to know the exact nature of the structural transition occurring around the critical concentration, a transition to a quasicrystalline or latticelike[36] structure may, however, be anticipated in view of the above considerations.

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Registry No. $Ca(NO_3)_2$, 10124-37-5; $NiCl_2$, 7718-54-9; $MgCl_2$, 7786-30-3.

Supplementary Material Available: Least-squares fitted values of the parameters of the density equation, viscosities of the systems as a function of concentration and temperature, least-squares fitted values of the parameters of eq 1 for the viscosities of the systems (Tables I, II, and IV), and plots of these values (Figures 1, 2, 4–6, and 9) are available as supplementary material (14 pages). Ordering information is available on any current masthead page.

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(25) J. A. McMillan and S. C. Los, *Nature (London)*, **206**, 806 (1965).

(26) A low-temperature study on the heat capacities of electrolytic solutions [C. A. Angell and J. C. Tucker, *J. Phys. Chem.*, **84**, 268 (1980)] has revealed an almost linear dependence of the heat capacity on temperature before and after the glass transition. If we assume such a linear variation in the heat capacity even at high temperatures, the configurational entropy, S_c, of the electrolytic solution may be written as $S_c = C_1 \ln(T/T_0) + C_2(T - T_0)$, where C_1 and C_2 are constants whose values depend upon the heat capacities of the glass and liquid. Substitution of this value of S_c in the Adam–Gibbs equation (ref 27) gives an expression for η which on approximation takes the form, $\eta = A_1 \exp(-B_1/T_0)T^{1/2} \exp[(B_1 - CT_0)/(T - T_0)]$, where $A_1 = A \exp(B_1C_2/C_1)$, $B_1 = B/C_1$, and $C = B_1C_2/C_1$. A and B are constants. The approximations made are $\ln(T/T_0) \approx (T - T_0)/T_0$ and $1/(1 + C_2T_0/C_1) \approx 1 - C_2T_0/C_1$ since C_2T_0 is usually very much less than C_1. This equation for η on comparison with eq 1 provides expressions for A_0 and B_0 (eq 4 and 5).

(27) G. Adam and J. H. Gibbs, *J. Chem. Phys.*, **43**, 139 (1965).

(28) The approximations made in obtaining eq 2 are $1/(T - T_0(0) - Qm) \approx [1 + Qm/(T - T_0(0))]/(T - T_0(0))$ and $1/(T_0(0) + Qm) \approx [1 - Qm/T_0(0)]/T_0(0)$.

(29) S. Arrhenius, *Z. Phys. Chem.*, 1, 285 (1887).

(30) J. N. Sugden, *J. Chem. Soc.*, **129**, 174 (1926).

(31) I. K. Taimni, *J. Phys. Chem.*, **33**, 52 (1929).

(32) J. Carbonell, *Afinidad*, **25**, 451 (1968).

(33) R. W. Gurney, "Ionic Processes in Solutions", Dover Publications, New York, 1953.

(34) N. S. Kurnakov, D. Krotkov, M. Oksmann, I. Beketov, S. Perelmutter, F. Kanov, and I. Finkal, *Z. Anorg. Allgem. Chem.*, **135**, 81 (1924).

(35) R. H. Ewell, *J. Chem. Phys.*, **5**, 967 (1937).

(36) H. P. Bennetto and J. J. Spitzer, *J. Chem. Soc., Faraday Trans. 1*, **74**, 2385 (1978).