a rate constant for the rearrangement of 222 in water of the order of 10^6–10^7 s^{-1}. Surprisingly, this value happens to be the same as that found by Park and Simmons[28] for the analogous macrobicyclic oxygen-free diamine; one would have expected the rate constant for the rearrangement of 222 to be, because of the interactions between water and the oxygen atoms, different from that of the hydrophobic diamine. More studies have been performed on the conformational behavior of 111 and 211, but it is evident that these smaller and more rigid structures cannot be compared with 222, a clear evidence of that being given by the fact that the IR spectrum of 111 in $CDCl_3$ does not show the C–D stretch satellite observed with 222 and due to hydrogen bonding of the *out* nitrogen sites.[24]

After this survey of the thermodynamics of the first protonation of 222, let us now look at the introduction of a second proton on the diamine (process 2). The data of Table II show that the behavior of 222 is very different from that of simple diamines such as dimethylpiperazine and triethylenediamine. The second nitrogen site of 222 is much more basic than that of the two simple diamines considered here. The entropy and volume of second protonation of 222 are larger than those of first protonation whereas it is the opposite for simple tertiary diamines. The case of the volumes is particularly striking since, as shown in the preceding section, the volume of $222H_2^{2+}$ is almost equal to that of $222H^+$ whereas the volume of a diprotonated simple diamine is much more negative than that of its monoprotonated analogue. This global behavior can be interpreted in terms of an internal protonation of the ligand, the second proton being located inside the intramolecular cavity of 222. When the proton goes inside the cavity, it has to break its strong structural interactions with bulk water and a large increase of entropy results, accompanied by an increase of enthalpy and a decrease of heat capacity. It is this highly favorable entropy of protonation that is responsible for the fact that the second nitrogen site of 222 is more basic than that of simple diamines.

The thermodynamic functions thus suggest that the proton of the monoprotonated 222 is located outside the cavity of the ligand and that the second proton of the diprotonated species is located inside the intramolecular cavity of 222. It is interesting to note that for the analogous diazabicycloalkaneammonium ions, Simmons and Park's NMR study[28] shows only the presence of *in*$^+$–*in*$^+$ and *out*$^+$–*out*$^+$ isomers in 50% trifluoroacetic acid, the undetectable *in*$^+$–*out*$^+$ isomer being, according to these authors, of higher free energy than that of the other isomers because of torsional and nonbonded repulsion effects. Is there any reason, however, for the hydrophilic 222 to behave in pure water like this hydrophobic species in 50% trifluoroacetic acid?

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Study of the Concentration Dependence of the Conductance of Aqueous Electrolytes

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Equivalent conductances (Λ) of $[Ca,Mg](NO_3)_2$–H_2O, $[Mg,Ni]Cl_2$–H_2O, $Na_2S_2O_3$–H_2O, and $NaNO_3$–H_2O systems were measured as functions of temperature (~20–70 °C) and concentration (from dilute to saturation point at ~20 °C). The dependence of Λ on temperature has been described by using the Vogel–Tammann–Fulcher (VTF) equation, whereas its dependence on concentration is found to be explainable by an isothermal expression of the form, $\Lambda = a_\Lambda \exp(b_\Lambda m + c_\Lambda m^2)$. In this expression a_Λ, b_Λ, and c_Λ are constant parameters and m is the concentration in molality. A comparison of the computed value of a_Λ of each system with its Λ_0 (equivalent conductance at infinite dilution) value has been made. The concentration dependences of specific conductance, of activation energies for conductance and viscous flows, and of Walden product have also been discussed. In each system a structural change appears to take place over a certain concentration range which has been considered to be a transition from a primitive to quasi-crystalline structure.

Introduction

In our earlier papers[1,2] we have successfully used an isothermal equation of the form

$$\eta = a_\eta \exp(b_\eta m + c_\eta m^2) \quad (1)$$

to describe the concentration dependence of viscosity (η) of electrolytic solutions in the concentration range from dilute to saturation point. In eq 1 a_η, b_η, and c_η are the empirical constants and m is the molality of the solution. It has been shown[1,2] that eq 1 is obtainable from the VTF equation by inserting the concentration dependences of its three parameters. Furthermore, the Adam–Gibbs configurational entropy model[3] appeared to provide a plausible theoretical basis[1] to eq 1. Describing the concentration dependence of conductance is also equally important. Since the VTF equation explains the temperature dependence of conductance also, in this paper an attempt has been made to employ eq 1 to analyze the concentration dependence of equivalent conductance of elecrolytic solutions by measuring the conductances of six aqueous solutions, viz., $Ca(NO_3)_2$–H_2O, $Mg(NO_3)_2$–H_2O, $MgCl_2$–H_2O, $NiCl_2$–H_2O, $Na_2S_2O_3$–H_2O, and $NaNO_3$–H_2O.

Experimental Section

The method of preparing the aqueous solutions is described elsewhere.[1,2] Conductivity measurements (accuracy 0.1%) of all the solutions were made as functions of temperature (~20–70 °C range) and concentration (from dilute to saturation point at ~20 °C) by using a Philips PR 9500 conductivity bridge and a dip-type cell of cell constant 1.081 cm^{-1}). Density values required for calculating equivalent conductances of the electrolytic solutions

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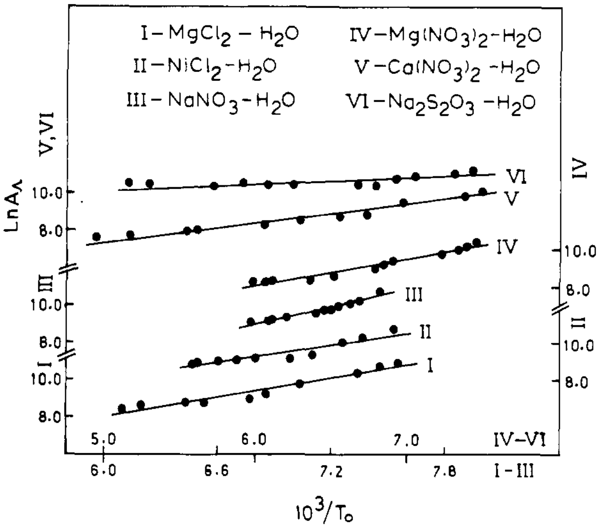

Figure 2. Plots of ln A_Λ vs. $1/T_0$ for aqueous electrolytes.

under interest were taken from the literature.[1,2,4]

Results and Discussion

The equivalent conductance (Λ) values of all the systems under study are listed in Table I. (See paragraph at end of text regarding supplementary material). These values are compared with the reported data[5-7] by plotting Λ vs. normality, N (Figure 1, supplementary material) and it was found that they (present and reported data) are comparable within about ±2%.

The non-Arrhenius type of temperature dependence of Λ, which is found to be less pronounced in the present study due to the relatively higher temperature range of measurement, has been analyzed by least-squares fitting the Λ data to the VTF equation

$$\Lambda = A_\Lambda T^{-1/2} \exp[-B_\Lambda/(T - T_0)] \qquad (2)$$

where A_Λ, B_Λ, and T_0 are constant parameters. The computed values of these parameters for the different systems are given in Table II (supplementary material). The present values of T_0 for the six solutions under interest are comparable with those obtained earlier[1,2,4] on the basis of viscosity study. Such an agreement between $T_0(\Lambda)$ and $T_0(\eta)$ of a particular system was observed in several anhydrous and hydrate melts[8-16] as well as in aqueous solutions,[17] which has led us to consider T_0 to behave apparently like a thermodynamic parameter. However, at low fluidities $T_0(\Lambda)$ and $T_0(\eta)$ values have been found to differ from each other.[18,19]

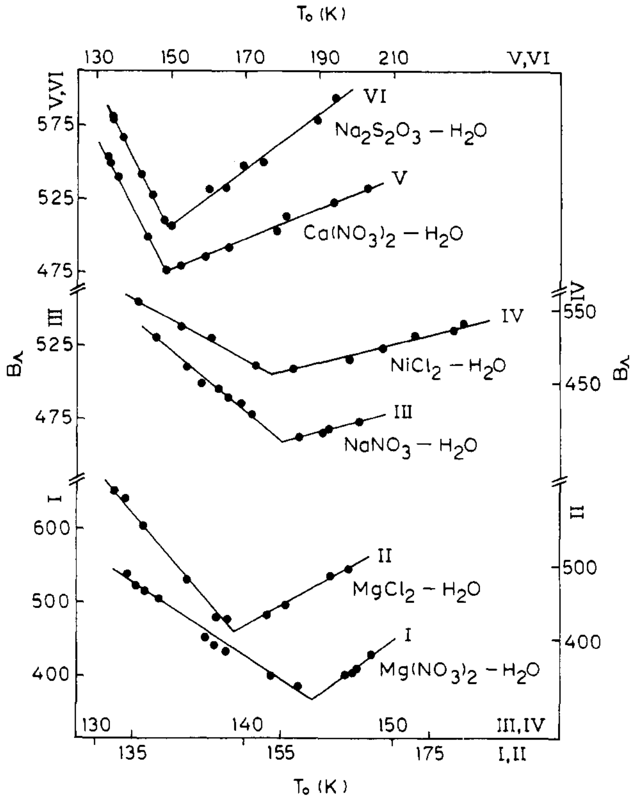

Figure 3. Plots of B_Λ vs. T_0 for aqueous electrolytes.

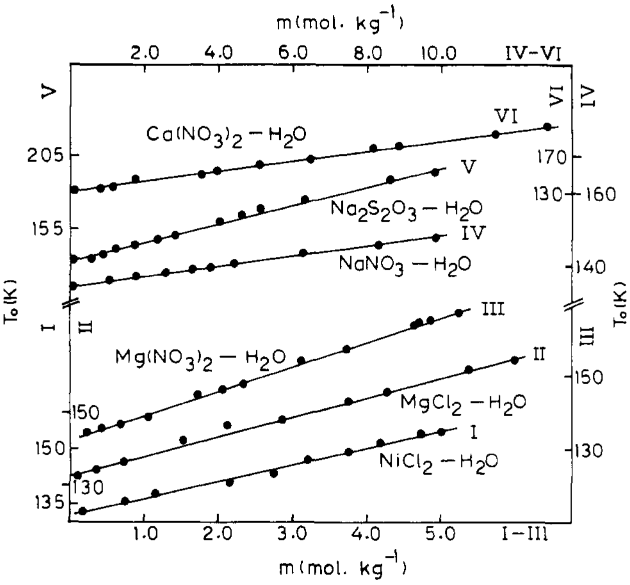

Figure 4. Plots of T_0 vs. m for aqueous electrolytes.

The concentration dependence of the A_Λ, B_Λ, and $T_0(\Lambda)$ parameters are illustrated in Figures 2–4 and are found to be representable by the same empirical expressions used in the case of the viscosity study.[1] Such empirical expressions were earlier[1] shown to be derivable from the Adam–Gibbs model.[3] The values of the critical concentration (concentration at which B_Λ or B_η has the minimum value) obtained for each electrolytic solution from its conductance and viscosity[1,2,4] studies are seen to be closely comparable with each other.

By insertion of the concentration dependences of A_Λ, B_Λ, and T_0 into eq 2, an isothermal expession similar to eq 1 may also written for Λ as

$$\Lambda = a_\Lambda \exp(b_\Lambda m + c_\Lambda m^2) \qquad (3)$$

a_Λ, b_Λ, and c_Λ are another set of constant parameters which depend

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TABLE III: Least-Squares-Fitted Values of the Parameters of Eq 3 for the Equivalent Conductance of Aqueous Electrolytes[a]

T, K	concn range, mol·kg^{-1}	a_Λ	b_Λ	10^2c_Λ	SD in ln Λ
			$Ca(NO_3)_2$-H_2O		
298.0	0.1305-12.79	71.64 (0.8611)	−0.4289 (0.2813)	0.3485 (1.1556)	0.085 (0.037)
308.0	0.1305-12.79	86.24 (0.7001)	−0.4330 (0.2898)	0.5638 (0.8213)	0.078 (0.036)
323.0	0.1305-12.79	109.22	−0.4376	0.8152	0.071
			$Mg(NO_3)_2$-H_2O		
298.0	0.2297-4.8578	72.08 (0.8820)	−0.4687 (0.3166)	1.3265 (1.1667)	0.035 (0.001)
308.0	0.2297-5.2393	85.13 (0.7225)	−0.4651 (0.2967)	1.2520 (1.4372)	0.036 (0.012)
323.0	0.2297-5.2393	106.70 (0.5476)	−0.4894 (0.3218)	1.8173 (0.6555)	0.028 (0.027)
			$MgCl_2$-H_2O		
288.0	0.1145-5.3787	70.95	−0.4105	−0.2256	0.051
308.0	0.1145-5.9872	106.12 (0.7609)	−0.4532 (0.3126)	0.7654 (2.0284)	0.041 (0.017)
323.0	0.1145-5.9872	135.73 (0.5831)	−0.4664 (0.3163)	1.0073 (1.6353)	0.043 (0.018)
			$NiCl_2$-H_2O		
293.0	0.1736-4.9901	88.84	−0.5115	1.1854	0.035
308.0	0.1736-4.9901	116.02 (0.7408)	−0.5255 (0.3581)	1.7627 (1.0879)	0.035 (0.020)
323.0	0.1736-4.9901	146.07 (0.5596)	−0.5562 (0.3751)	2.7205 (0.3878)	0.046 (0.018)
			$Na_2S_2O_3$-H_2O		
288.0	0.0823-9.8184	128.64 (1.0887)	−0.3642 (0.4672)	0.1059 (−0.3331)	0.070 (0.047)
308.0	0.0823-9.8184	192.96 (0.7288)	−0.3459 (0.4067)	0.6212 (−0.4531)	0.065 (0.043)
323.0	0.0823-9.8184	245.30 (0.5664)	−0.3308 (0.3799)	0.8272 (−0.5406)	0.066 (0.016)
			$NaNO_3$-H_2O		
288.0	0.1113-9.8626	79.37	−0.2437	0.9926	0.041
308.0	0.1113-9.8626	122.14 (0.7191)	−0.2721 (0.1097)	1.2545 (−0.0596)	0.071 (0.014)
323.0	0.1113-9.8626	155.73 (0.5561)	−0.2858 (0.1061)	1.3729 (−0.0262)	0.086 (0.011)

[a] Values of the corresponding parameters of eq 1 are given within the parentheses and are taken from ref 1, 2, and 4.

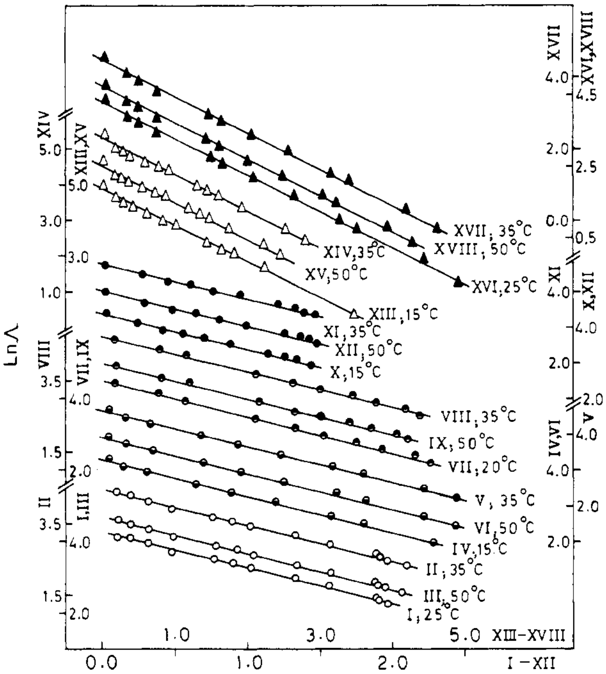

Figure 5. Plots of ln Λ vs. $b_\Lambda m + c_\Lambda m^2$ for aqueous electrolytes: (○) $Mg(NO_3)_2$, (◒) $MgCl_2$, (◓) $NiCl_2$, (●) $NaNO_3$, (△) $Na_2S_2O_3$, and (▲) $Ca(NO_3)_2$ solutions.

on the temperature of the solution. The values of these parameters obtained by least-squares fitting the Λ data to eq 3 are listed in Table III. It is evident from Table III and also from the linearity of the plot of ln Λ vs. $b_\Lambda m + c_\Lambda m^2$ (Figure 5) that eq 3 describes satisfactorily the concentration dependence of Λ in the entire experimental range of concentration. We have shown earlier[1,2] that an equation of type 1 or 3 is reducible to the forms of other expressions being used for describing the concentration dependence of transport properties, demonstrating thereby the superiority of eq 1 or 3.

Although a_Λ may be interpreted as the equivalent conductance at infinite dilution, its comparison with the reported[20] Λ_0 values for the different electrolytic solutions under study has revealed that the values of a_Λ are ~50–60% lower than the corresponding Λ_0 values. Such a vast difference between a_Λ and Λ_0 values is, however, not surprising and may be attributed to two factors. Firstly, eq 3 takes into account only the ion–solvent interactions as discussed in the earlier papers.[1,2] Secondly, unlike Λ_0 values the values of a_Λ are obtained on the basis of the high-concentration conductance data. In fact, higher values for a_Λ were obtained when only limited conductance data lying in the low-concentration region (below the critical concentration, m_c) are least-squares fitted to eq 3. It is important to recognize here that eq 3 as such cannot be employed to represent the conductance data of an electrolytic solution at very low concentrations, which is also apparent from the fact that at such low concentrations T_0 becomes almost in-

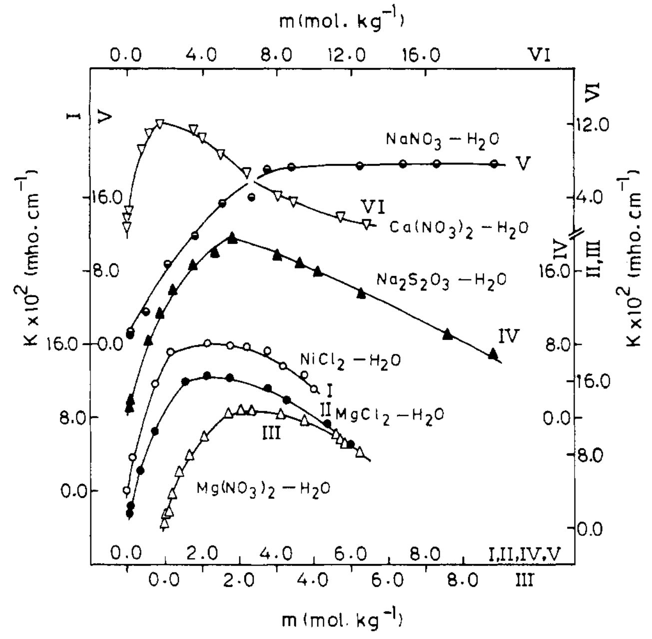

Figure 6. Plots of conductivity vs. m for aqueous electrolytes.

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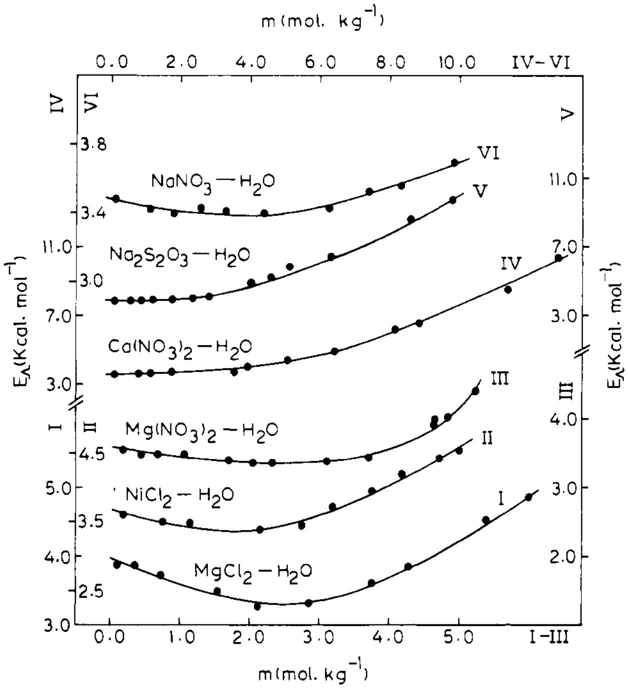

Figure 7. Plots of E_Λ vs. m for aqeuous electrolytes.

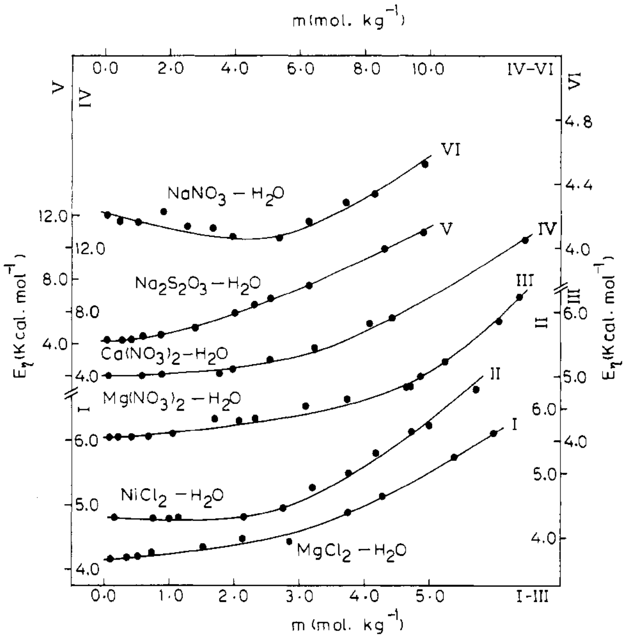

Figure 8. Plots of E_η vs. m for aqueous electrolytes.

variant with concentration.[17] An attempt to incorporate the ion–ion interaction term in eq 3 has been made in a subsequent paper.[21]

It is also interesting to study the trend in the variation of specific conductance with concentration. We have, therefore, plotted specific conductance vs. m isotherms at 35 °C (Figure 6) for all the electrolytic solutions under investigation. From Figure 6 it is apparent that specific conductance maxima occur at 2.0, 2.2, 2.25, 2.25, and 2.85 mol·kg^{-1} for $Ca(NO_3)_2$–H_2O, $NiCl_2$–H_2O, $MgCl_2$–H_2O, $Mg(NO_3)_2$–H_2O, and $Na_2S_2O_3$–H_2O systems, respectively, whereas in the case of the $NaNO_3$–H_2O system specific conductance becomes rather constant beyond 4 m instead of showing a decrease. The concentration of maximum specific conductance of a particular electrolyte has been found to be almost independent of temperature as observed in the case of several other systems also.[22] The value 2.0 m (at 35 °C) obtained by us for the $Ca(NO_3)_2$–H_2O system is in good agreement with the value 2.01 m (at 0 °C) reported by Angell and Bressel.[17] The specific conductance maximum is seen to be a general feature of electrolytic solutions[23-28] and is explainable in terms of charge concentration and ionic mobility factors.[22] The observed difference in the m_{max} (concentration corresponding to conductivity maximum) values of the different electrolytes studied here may be qualitatively described by speculating a correlation between m_{max} and the radii of hydrated ions.[22] The specific conductance maximum may also be predicted from eq 3 after modifying it to express the specific conductance, κ. The values of m_{max} so obtained by using the least-squares-fitted values of a_Λ, b_Λ, and c_Λ are 2.23, 2.11, 2.30, 2.10, 3.20, and 4.10 mol·kg^{-1} for $Ca(NO_3)_2$–H_2O, $NiCl_2$–H_2O, $MgCl_2$–H_2O, $Mg(NO_3)_2$–H_2O, $Na_2S_2O_3$–H_2O, and $NaNO_3$–H_2O systems, respectively. The reasonably good agreement found between the experimental (Figure 6) and computed values of m_{max} is worth noting.

It is worthwhile to make a comparative study of conductance and viscous flows in terms of the corresponding activation energies, E_Λ and E_η. These activation energies are calculated[13] from the parameters of the VTF equation for viscosity[1,2,4] and conductance. The values of E_Λ (Figure 7) and E_η[1,2,4] (Figure 8) obtained thus at 298 K are plotted vs. m for all the electrolytic solutions under study. In every system studied here, both E_Λ and E_η appear to decrease slightly or to remain almost invariant with m up to a particular concentration, m_a, and beyond this concentration they increase with m. Similar behavior was also reported in several other aqueous systems.[22] The value of m_a for a particular solution has been found to be comparable with its critical concentration. Such a trend in the concentration dependence of E_Λ and E_η is explainable in the light of the concentration dependences of the VTF parameters from which these energies are calculated. In all the electrolytic solutions considered here the E_η/E_Λ ratio is found to have an almost constant value lying in the range ~1.1–1.3 at any temperature and concentration which is in accordance with the earlier observations.[9,11,13,22] The higher activation energy required for viscous flow compared to that for conductance flow actually is manifested in a higher value for B_η than B_Λ. Although a qualitative description[11] is available to account for the higher value of E_η than E_Λ, the exact reason for this observation is not known and warrants a thorough understanding of the mechanism of transport process taking place in solutions and liquids.

Furthermore, we have made an attempt to describe the dependence of Λ on viscosity by analyzing the concentration dependence of their product. A plot of $\Lambda\eta$ product against molality is made and such isotherms at 35 °C for all the electrolytes under investigation are illustrated in Figure 9. From these isotherms it is apparent that in the case of each electrolyte $\Lambda\eta$ passes through a minimum and the concentration, m_w, at which this minimum occurs is a characteristic of the electrolyte considered as was the case with m_c, m_{max}, and m_a also. However, the value of m_w seems to be independent of temperature as indicated by Seward.[29] The observed values of m_w at 35 °C are around 5.0, 3.0, 2.5, 3.0, 6.7, and 1.0 mol·kg^{-1} for $Ca(NO_3)_2$–H_2O, $Mg(NO_3)_2$–H_2O, $MgCl_2$–H_2O, $NiCl_2$–H_2O, $NaNO_3$–H_2O, and $Na_2S_2O_3$–H_2O systems, respectively. It may be noted that the Walden products of aqueous solutions generally show this kind of behavior.[29-31] Such a be-

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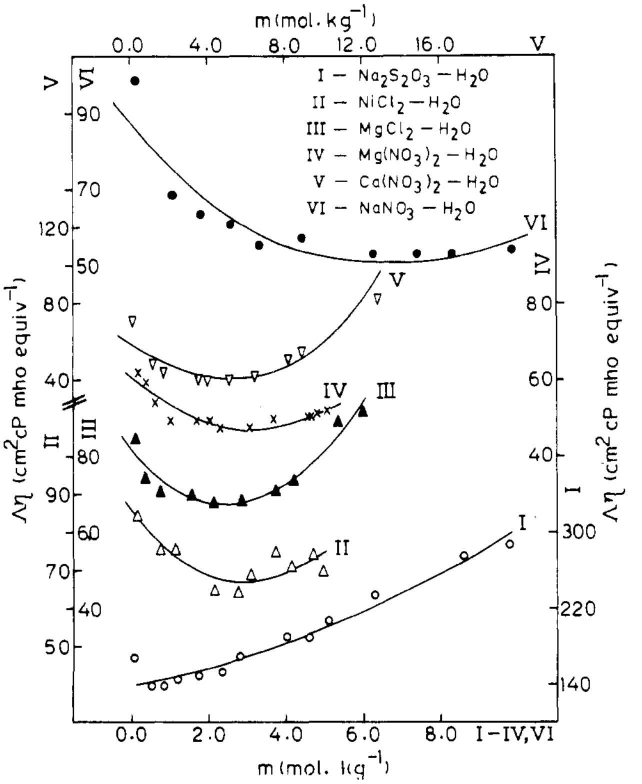

Figure 9. Plots of Walden product vs. m for aqueous electrolytes. Different notations denote the observed values and the solid curves represent the calculated values using eq 4.

havior of $\Lambda\eta$ is usually explained only in qualitative terms and no expression is avaiable in the literature which can predict such a $\Lambda\eta$ minimum. Yao and Bennion[32] made an attempt to employ the semiempirical Wishaw–Stokes equation[33] for this purpose, but this equation also failed to predict the falling and rising portions of the $\Lambda\eta$ product. Therefore, it is worth examining the feasibility of our isothermal equation in explaining the behavior of $\Lambda\eta$ vs. concentration isotherm. In the light of eq 3, $\Lambda\eta$ may be written as

$$\Lambda\eta = a_{\Lambda\eta} \exp(b_{\Lambda\eta}m + c_{\Lambda\eta}m^2) \qquad (4)$$

where $a_{\Lambda\eta} = a_\Lambda a_\eta$, $b_{\Lambda\eta} = b_\Lambda + b_\eta$, and $c_{\Lambda\eta} = c_\Lambda + c_\eta$. It may be noted that in all the systems studied here except for $Na_2S_2O_3$–H_2O solutoin b_Λ has a larger value than b_η with a negative sign (Table III). Accordingly, $b_{\Lambda\eta}$ becomes a negative quantity and eq 4 predicts a decrease in $\Lambda\eta$ with m at low concentrations. As the concentration increases, the value of the positive $c_{\Lambda\eta}m^2$ term keeps on increasing and at some concentration it dominates over the negative $b_{\Lambda\eta}m$ term. Beyond this particular concentration (m_w) therefore $\Lambda\eta$ will increase with concentration. Substituting the least-square-fitted values of a_Λ, a_η, b_Λ, b_η, c_Λ, and c_η (Table III) into eq 4, we calculated $\Lambda\eta$ for the different solutions and the values thus obtained are also plotted in Figure 9. It is interesting to note that there is a reasonably good agreement between the observed and calculated values of $\Lambda\eta$. In the dilute concentration region, however, the fitting is not as satisfactory as in the concentrated region. This is due to the fact that the ion–ion interaction has not been taken into account in our isothermal equations which becomes dominating in the dilute region. This may also be the reason for not obtaining a $\Lambda\eta$ minimum from eq 4 in the case of $Na_2S_2O_3$–H_2O solution. It is further interesting to note that the values of m_w obtained from eq 4 after equating $d(\Lambda\eta)/dm$ to zero (5.17, 3.13, 2.52, 2.94, and 6.8 mol·kg^{-1} for $Ca(NO_3)_2$–H_2O, $Mg(NO_3)_2$–H_2O, $MgCl_2$–H_2O, $NiCl_2$–H_2O, and $NaNO_3$–H_2O systems, respectively) are closely comparable with their observed values. Moreover, the $\Lambda\eta$ data may be least-squares fitted directly to the three-parameter eq 4 and the values of $a_{\Lambda\eta}$, $b_{\Lambda\eta}$, and $c_{\Lambda\eta}$ obtained thus are found to be comparable with their values calculated from the viscosity and conductance parameters given in Table III.

Finally, in the light of the above discussion of B_Λ parameter (critical concentration), specific conductance, activation energy, and $\Lambda\eta$ product it may be recognized that some sort of structural transition takes place in an electrolytic solution when the concenration is varied from dilute to very high value as proposed by other workers[17,22] also. This transition may be visualized as from a primitive structure to a quasi-crystalline structure. From the values of m_c, m_{max}, m_a, and m_w it is apparent that such a transition does not occur at a definite concentration, but takes place over a concentration range. This provides evidence that in the transition region both the primitive (water as continuous dielectric medium) and quasi-crystalline behaviors coexist, which is in accordance with the view of Angell and co-workers.[17,34] The presence of some amount of quasi-crystallinity within the dielectric medium in the concentration range where the transition occurs must cause a liquid-liquid phase separation when the temperature of the solution is sufficiently lowered. Experimental evidence for the occurrence of such a liquid–liquid phase separation has been provided by the low-temperature light scattering studies made by Hsich et al.[35]

Registry No. H_2O, 7732-18-5; $Ca(NO_3)_2$, 10124-37-5; $Mg(NO_3)_2$, 10377-60-3; $MgCl_2$, 7786-30-3; $NiCl_2$, 7718-54-9; $Na_2S_2O_3$, 7772-98-7; $NaNO_3$, 7631-99-4.

Supplementary Material Available: Table I, listing the equivalent conductance (Λ) values of all the systems as functions of concentration and temperature; Table II, listing least-squares-fitted values of the parameters of eq 2; and Figure 1, showing equivalent conductance vs. normality isotherms (18 pages). Ordering information is given on any current masthead page.

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