

## Measurement of Viscosity and Ion-solvent Interactions (B-Coefficient) from 20 To 50°C for Aqueous Electrolytes of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>++</sup>, Ca<sup>++</sup> and Sr<sup>++</sup>

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**Summary:** Viscosities of aqueous solutions of nitrates of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>++</sup>, Ca<sup>++</sup> and Sr<sup>++</sup> were determined by using a thermostated Ubbelohde flow, viscometer in the range of concentrations and temperatures from 20 to 50°C. From the experimental results; Ion-Solvent interaction terms ( $\beta$ -Coefficients) were calculated in the concentration range 0.1 to 4M, by using an empirical equation of the form:  $\eta = a_0 \exp(b_0 M + C_0 M^2)$ . It was concluded that the viscosities of these ions in aqueous solutions could be understood in terms of hydration number, charge on the ion and the ionic radius. Ratio of the viscosities of the nitrates and chlorides with common cations were also calculated and interpreted in terms of hydration of cations, anions and ion pair formation.

### Introduction

The viscometric behavior of electrolytes in water has been an interesting topic of study. The purpose of such studies was to determine the  $\beta$ -coefficient of the Jones-Dole equation [1]. This equation is of the form as:

$$\eta/\eta_0 = 1 + Ac^{1/2} + Bc \quad (1)$$

where  $\eta/\eta_0$  is the viscosity of the electrolyte solution relative to the solvent, water, while A, B are the ion-ion and ion-solvent interaction coefficients respectively. The values of A, B depends upon the particular electrolyte, temperature and solvent under study, c is the molar concentration of the solution. The Jones-Dole equation is applicable at lower concentration, but like so many other equations in the literature [2-4] it fails at higher concentrations. Other equations [5,6] as well as Vand equation [7] is applicable at higher concentrations, but unfortunately, the theoretical concept on which Vand equation was developed is not applicable at higher concentrations. Mahiuddin and Ismail [8] has developed an empirical equation form the Vogel-Tamman-Fulcher (VTF) equation [9] in the form as:

$$\eta = a_0 \exp(b_0 M + C_0 M^2) \quad (2)$$

Where  $\eta$  is the absolute viscosity of the electrolyte solution,  $a_0$ ,  $b_0$ , and  $c_0$  are constants and M is the molar concentration. A least square fitting of

the viscosity data to this isothermal equation has been made and an excellent fit was obtained for all the systems under study, to confirm further the suitability of the above equation,  $\ln\eta$  was plotted against  $(b_0 M + C_0 M^2)$  for all the systems. Straight lines were obtained in all the cases, showing the success of the equation at higher concentrations.

### Results and Discussion

Times of flow were determined for various aqueous electrolytes under study at wide range of concentration and temperatures from 20 to 50°C. The densities of various systems were measured. The viscosities were determined from the formula  $\eta_1/\eta_2 = t_1 d_1 / t_2 d_2$ , where  $\eta_1, t_1, d_1$  are the absolute viscosity, time of flow and density of the solution, while  $\eta_2, t_2$  and  $d_2$  are the same quantities for the solvent water. To study the effect of concentration on viscosity, the later was plotted against concentration for all the systems under study as shown in Figs. (1-5). Out of the five systems all of them, except K<sup>+</sup> gave ascending curves. It means that viscosity generally increases with the increase in concentration of the solution. But this increase in viscosity is more at lower temperatures than at higher temperatures. Further, the ions, which have high charge and smaller size e.g. Mg<sup>++</sup>, Ca<sup>++</sup> increase the viscosity to higher degree than those of smaller charge and larger size e.g. K<sup>+</sup> [10]. The relative viscosity of dilute electrolyte solutions has been an effective method for

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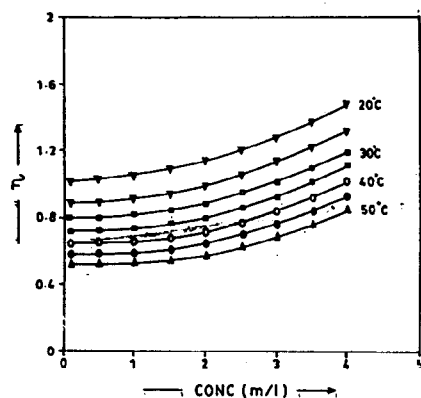


Fig. 1 Viscosity (cP) curves for aqueous sodium nitrate.

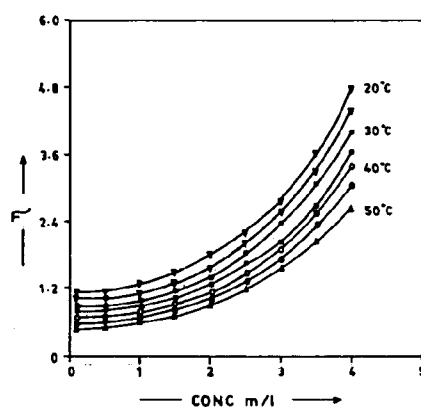


Fig. 4 Viscosity (cP) curves for aqueous calcium nitrate.

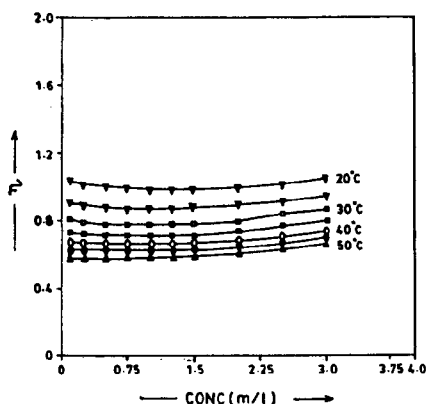


Fig. 2 Viscosity (cP) curves for aqueous potassium nitrate.

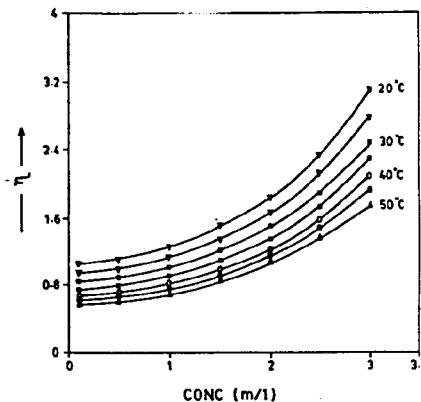


Fig. 5 Viscosity (cP) curves for aqueous strontium nitrate.

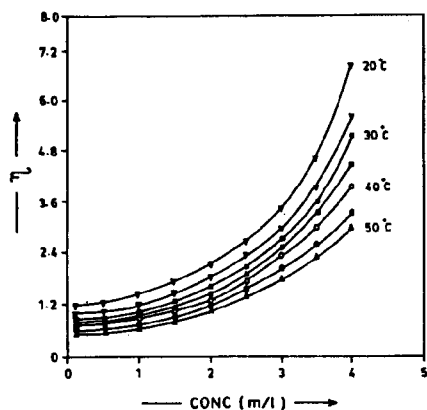


Fig. 3 Viscosity (cP) curves for aqueous magnesium nitrate.

studying ion-solvent interaction through the use of the Jones-Dole equation. For this purpose, Jones-Dole equation was rearranged to give

$$(\eta/\eta_0-1)/c^{1/2} = A + Bc^{1/2} \quad (3)$$

$(\eta/\eta_0-1)/c^{1/2}$  was plotted against  $C^{1/2}$  to get  $\beta$ -coefficient from the slope of the plot.

Our systems deviated from the Jones-Dole equation at higher concentrations and thus it could not be applied to get  $\beta$ -coefficients.  $\beta$ -Coefficient is a measure of the ion-solvent interaction. It measures the order or disorder produced by the dissolved ion in the solvent structure [11,12]. Those ions, which are smaller in size with high charge, such as  $Mg^{++}$ ,  $Ca^{++}$ ,

are strongly hydrated giving positive,  $\beta$ -coefficient. It means that the order of the solvent is increased by these ions. The ions having larger size and smaller charge are least hydrated. Such ions contribute little to the structure of the solvent. Still, there are some ions like K, which give negative  $\beta$ -coefficient. The -ive  $\beta$ -coefficient is related to the -ive hydration, a term extensively used by the Russian chemist [13] to discuss the structure breaking property of some ions in water. At higher concentrations,  $\text{Na}^+$  ions also give -ive  $\beta$ -coefficients.

In another attempt  $\beta$ -coefficients were calculated from the parameters  $a_0$ ,  $b_0$  of the empirical isothermal equation No. 2 by least square fitting. Least square fitting can be applied when plots of  $\ln \eta$  Vs  $(b_0M + c_0M^2)$  yielded straight lines. These plots are given in Figures (6-10). The calculated values of  $a_0$ ,  $b_0$  are given in the Tables (1-5). It is known from the literature that the values of  $c_0$  are smaller than  $b_0$  [14], hence at very low concentration the  $c_0 M$  term may be neglected. Thus equation (1) becomes similar to the Einstein equation [15] or the Jones-Dole equation, without the ion-ion interaction terms ( $c_0$  values)  $(\exp(b_0M / (1+b_0M)))$  where  $c = M$  at lower concentrations. Thus the product of  $a_0$  and  $b_0$  is equivalent to the viscosity  $\beta$ -coefficient [16]. Further, neglecting the  $c_0$  term, equation (2) can be reduced to the Vand equation, thereby providing a description of the success of the Vand equation at higher concentrations. Also, at lower concentration the reduced form of equation (2) is similar to the Arrhenius isothermal equation. The  $a_0$  values decrease and that of  $b_0$  increase from 20 to 50°C. But the product of  $a_0$  and  $b_0$  which is equivalent to the  $\beta$ -coefficient (measure of the ion-solvent interaction) decreases with the rise in temperature. The  $\beta$ -coefficient, having large temperature coefficient, varies much more from electrolyte to electrolyte [17]. Since the electrolyte ions are hydrated, forming co-spheres in the solution. By raising the temperature, these co-spheres are more or less broken down due to the increase in the thermal agitation of water dipoles. This process decreases the ion-solvent interaction and hence the  $\beta$ -coefficient. Since  $\text{K}^+$  is least hydrated, so the effect is not much pronounced here.

An attempt has been made to compare the viscosities of nitrates and chlorides with common cations. For this purpose ratio was calculated between the viscosities of the nitrates under study

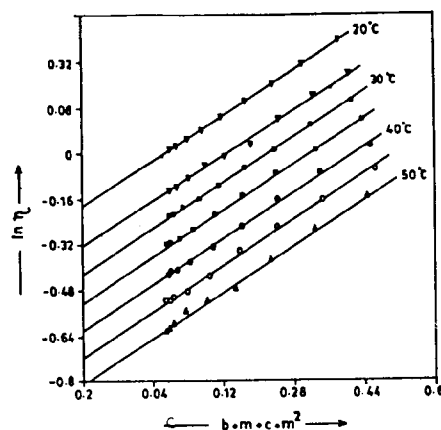


Fig. 6 Plots of  $\ln \eta$  vs  $(b_0M + c_0M^2)$  for the NaCl-H<sub>2</sub>O system.

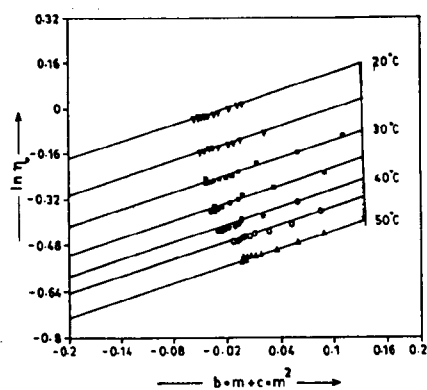


Fig. 7 Plots of  $\ln \eta$  vs  $(b_0M + c_0M^2)$  for the KCl-H<sub>2</sub>O system.

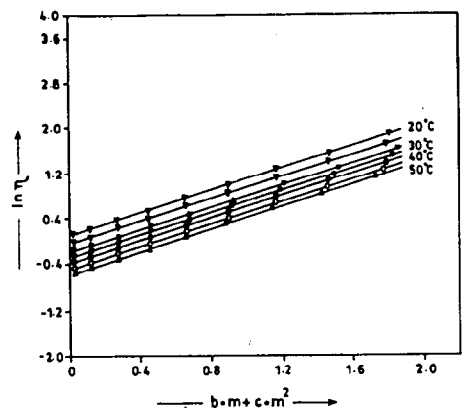


Fig. 8 Plots of  $\ln \eta$  vs  $(b_0M + c_0M^2)$  for the MgCl<sub>2</sub>-H<sub>2</sub>O system.

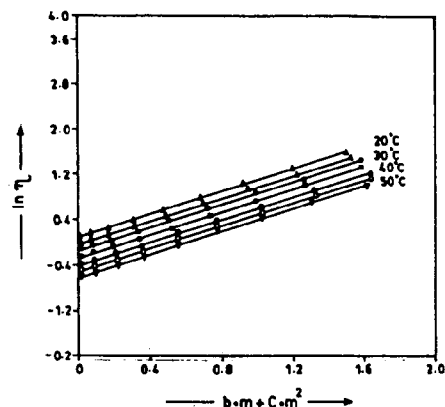


Fig. 9 Plots of  $\ln \eta$  vs  $(boM + CoM^2)$  for the  $CaCl_2-H_2O$  system.

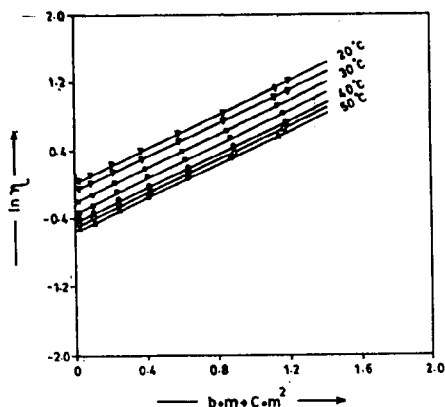


Fig. 10 Plots of  $\ln \eta$  vs  $(boM + CoM^2)$  for the  $SrCl_2-H_2O$  system.

Table 1: Interaction coefficients for  $NaNO_3$

Temp. (°C)	ao	bo	$\beta$
20	1.00059	0.0227	0.0228
25	0.8790	0.2710	0.0165
30	0.7951	0.0116	0.0092
35	0.7239	-0.0040	-0.0029
40	0.6543	-0.0128	-0.0084
45	0.5959	-0.0239	-0.0142
50	0.5429	-0.0263	-0.0143

Table 2: Interaction coefficients for  $KNO_3$

Temp. (°C)	ao	bo	$\beta$
20	1.0195	0.0717	0.0731
25	0.8983	0.0708	0.0636
30	0.8037	0.0697	0.0560
35	0.7290	0.06895	0.0503
40	0.6750	0.0491	0.0331
45	0.3657	0.0140	0.0089
50	0.5844	0.0058	0.0034

Table 3: Interaction coefficients for  $Mg(NO_3)_2$

Temp. (°C)	ao	bo	$\beta$
20	1.1008	0.2118	0.2232
25	0.9439	0.2179	0.2057
30	0.8177	0.2213	0.1810
35	0.7646	0.2227	0.1703
40	0.6992	0.2235	0.1563
45	0.6042	0.2247	0.1369
50	0.5610	0.2260	0.1268

Table 4: Interaction coefficients for  $Ca(NO_3)_2$

Temp. (°C)	ao	bo	$\beta$
20	1.0897	0.1076	0.1173
25	0.9662	0.11150	0.1077
30	0.8474	0.1213	0.1028
35	0.7493	0.1356	0.1016
40	0.6537	0.1432	0.0936
45	0.6141	0.1474	0.0905
50	0.5351	0.1584	0.0848

Table 5: Interaction coefficients for  $Sr(NO_3)_2$

Temp. (°C)	ao	bo	$\beta$
20	1.0036	0.1299	0.1304
25	0.9066	0.1335	0.1210
30	0.8011	0.1458	0.1168
35	0.7081	0.1646	0.1166
40	0.6361	0.1727	0.1099
45	0.6041	0.1731	0.1046
50	0.5673	0.1735	0.0984

and chlorides from the literature [14, 18]. The plots of the ratio of the viscosities of the nitrates and chlorides of the five metal cations at different temperatures were calculated and have shown similar behavior at different temperatures. Therefore, the data at 40°C as a representative for other temperatures are shown in Fig 11. It is observed that at lower concentrations, the viscosities of the nitrates are comparable to those of the corresponding chlorides. When the concentrations of the two types of electrolytes are increased in the solutions, the viscosities of the chlorides increase over that of the nitrates. It is because that owing to their smaller size, both the cation and anion are hydrated in the chloride solution. In case of the nitrate solution, it is the cation, which is hydrated while due to its larger size the anion is slightly unhydrated. When the concentration of the solution is further increased, the viscosities of the nitrates begin to increase, till a maximum is reached at higher concentration. This behavior can be explained on the basis of ion-pair formation in the nitrate solution [19]. Since the nitrate ion is slightly unhydrated, it can attract the oppositely charged ion in the solution effectively. Hence large species are formed in the nitrate solution, increasing the viscosity over those of the chlorides.

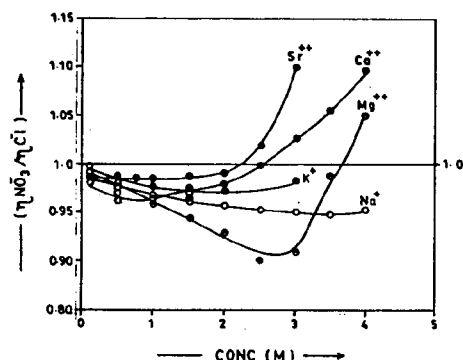


Fig. 11 Plots of ratio of the viscosities of nitrates and chlorides vs concentration.

Ion-pair formation is further confirmed by the cryoscopic data [20], plotted in Fig.12. The plot shows that all the nitrates under study exhibit ion-pair formation, to a greater extent than the corresponding chlorides, especially at higher concentrations. Thus the due depression in the freezing point is suppressed more in case of nitrates as compared to the corresponding chlorides. This behavior results in the increase of viscosity of the nitrates over those of the chlorides, at higher concentrations.

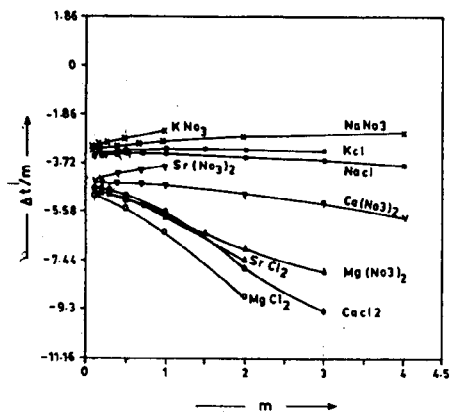


Fig. 12 Plots of  $\Delta t/m$  vs  $m$  for various nitrates and chlorides in water.

### Experimental

An Ubbelohde flow viscometer was used for the determination of time of flow of various systems under study. The thermostat was provided with an electric stirrer, a heating coil, a thermoregulator and a thermometer measuring upto 1/10th of a degree. The time of flow of distilled water was measured three times each on three different days giving an average of  $13 \pm 0.25$  seconds at  $20^\circ\text{C}$ . The times of flow of

aqueous solutions of  $\text{NaNO}_3$ ,  $\text{KNO}_3$ ,  $\text{Mg}(\text{NO}_3)_2$  and  $\text{Sr}(\text{NO}_3)_2$ , obtained from Merck analytical grade electrolytes, were measured three times for each solution and agreed to within  $\pm 0.2$  seconds. The range of study of various aqueous electrolytic solutions was from 0.1M to 4M wherever possible. The densities of the solutions were measured by means of calibrated Pycnometer of about  $25\text{cm}^3$  volume. The accuracy of the Pycnometer was upto 0.01%. Details of experimental procedure is published elsewhere [14, 18, 21].

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