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Phenomenological Theory of Ion Solvation by Viscosity Studies

G. MADHURAMBAL
Department of Chemistry, A.D.M. College for Women
Nagapattinam-611 001 (Tamilnadu), India

The relative viscosities of the uni-univalent, uni-bivalent, bi-univalent and bi-bivalent electrolytes KCl, Na_2SO_4, $MgCl_2$, $ZnSO_4$ in different solvent mixtures (20, 40 and 60% benzene-water) with varying concentrations of the salts at temperatures 30° and 35°C have been determined. The data has been analysed using Jones-Dole equation and Bresleu-Miller equation. The β coefficient values are found to be positive and so the salts can be considered as structure-makers in the solvent mixture. The particle interaction constant and the effective flow volume for all the electrolyies are calculated by the application of Bresleu-Miller equation.

Key words: Phenomenological, Theory, Ion solvation, Viscosity.

INTRODUCTION

The obstruction in the flow of liquid due to the presence of solute particles is believed to play a significant role in the viscosity of electrolytic solutions containing ionic species which promote the solvent structure in their vicinity. Although much work has been done in this direction in single solvent systems, yet the literature survey reveals inadequacy in mixed solvents especially when both the components have affinity for each other such as acetone-water, dioxane-water, carbon tetrachloride-water, and benzene-water systems. Electrical conductivities and viscosities of electrolyte solutions give some important information on the ion-ion and ion-solvent interaction. The nature of the ion-solvent interaction and the interpretation of thermodynamic and transport processes in terms of appropriate parameters such as effective radii of solvated ions can be well studied by the application of Jones-Dole equation and Bresleu-Miller equation.

The concentration dependence of the viscosity of dilute electrolyte solution is described by Jones-Dole semi-empirical equation

$$\eta/\eta_0 = 1 + AC^{1/2} + BC$$

where η and η_0 are the viscosities of the solution and solvent respectively, C is the molar concentration of the electrolyte and A and B are constants specific for the given solute-solvent system. Co-efficient A is determined by ion-ion electrostatic interaction and B is determined by ion-solvent interaction and solvent-solvent interaction[1].

The Jones-Dole equation is limited in its applicability to concentrations up to 0.1–0.2 M and no comparable treatment has been attempted for concentrated solution of electrolytes. However, Nightingale, Miller and Dosan have utilized the Eyring treatment of viscosity based on the theory of rate processes to investigate the viscosities of electrolyte solutions upto concentrations of the order of 10 M. Recently Bresleu-Miller noted the similarity in concentration between concentrated electrolyte solution and high volume fraction dispersions and utilized the equation obtained by Thomas for volume fractions < 0.25.

$$\eta/\eta_0 = 1 + 2.5\phi + 10.05\phi^2$$

where η and η_0 are the viscosities of the dispersion and dispersion medium respectively and ϕ is the measured volume fraction. By Thomas and Vand simplification treatment, we get

$$\ln\frac{\eta}{\eta_0} = \frac{2.5\phi}{1 - K\phi}$$

where K is termed as particle interaction constant. Substitution as in the Bresleu-Miller model of $\phi = CV_e$ yields the equation

$$\ln\frac{\eta}{\eta_0} = \frac{2.5CV_e}{1 - KCV_e}$$

Rearranging and taking logs to base 10 gives

$$\frac{C}{\log \eta/\eta_0} = \frac{2.303}{2.5V_e} - \frac{2.303KC}{2.5}$$

Thus a plot of $\frac{C}{\log \eta/\eta_0}$ against C should be linear with a slope of 2.303 K/2.5 and an intercept of $2.303/2.5V_e$ when $C = 0$. The effective flow volume as $C \rightarrow 0$ can be termed the limiting value V_e of the effective flow volume as distinct from the values of V_e obtained by Bresleu-Miller treatment[2].

EXPERIMENTAL

The AR samples of potassium chloride, sodium sulphate, magnesium chloride and zinc sulphate from Sarabhai (M) Chemicals were tested for purity and used. The salts were dried in an oven at 110°C for 4 h prior to use.

Benzene was dried by leaving in anhydrous calcium chloride for two days and the fraction distilling at 80°C was collected. The density was compared well with literature values.

Conductivity water was used for making solutions. Densities of the solution were measured using a bicapillary pycnometer having a capillary diameter of 0.75 mm and a volume of 26 mL. The values were precise to 5×10^{-5} g/mL.

Viscosity measurement at the specified temperatures were obtained using a series of British standard suspended level viscometers with flow times for water ranging from approximately 100 s to in excess of 1200 s.

The viscometers were calibrated with high purity conductivity water using the equation $\eta/\rho = ct - B/t$ where η is the absolute viscosity, ρ is the density and t, the flow time in seconds. The values of viscosity and density of water at the specified temperatures were taken from Hardy *et al.*[3] and Swindeles *et al.*[4] for flow times less than 1000 s, the reproducibility is ±0.25 s and for flow times in excess of 100 s, the reproducibility is better than ±1 s, the time measurements being carried out using stop-watches which had negligible errors in absolute-time measurement over the times involved and which were of ±0.01 s accuracy. All the viscosity and density measurements were carried out in a constant temperature bath controlled to within ±0.02° of the specified temperature.

The solutions of various electrolytes ranging from 0.1 m to 1 m concentrations were prepared in 20%, 40% and 60% solvent mixtures (benzene, water) and the viscosities and densities were measured. The measured values were applied in Jones-Dole equation and Bresleu-Miller equations.

RESULTS AND DISCUSSION

The viscosity data are analysed by means of Jones-dole equation $(\eta/\eta_0 - 1) = A\sqrt{C} + BC$ where η is the viscosity of the solution and η_0 that of the pure solvent, C the concentration of the solution and A and B are constants. The β coefficients of the electrolytes are determined by applying the least square method to the linear portion of the relation between $(\eta/\eta_0 - 1)/\sqrt{C}$ and $\sqrt{C}$. The values are given in Table-1.

By applying Bresleu and Miller equation and taking the simplified form of the equation

$$\frac{C}{\log \eta/\eta_0} = \frac{2.303}{2.5V_e} - \frac{2.302KC}{2.5}$$

the plot of $\frac{C}{\log \eta/\eta_0}$ against C is linear with a slope of 2.303K/2.5 and as intercept of $2.303/2.5V_e$ when C tends to 0, the effective flow-volume or the limiting value V_e can be calculated. The β-coefficient values are given in Table-1.

Treatment of Jones-Dole equation

From the data given in Table-1, we can interpret the behaviour of the electrolytes in solvent benzene.

According to Stockes and Mills, $\eta_0 BC = \eta^E + \eta^A + \eta^D$. At a particular temperature and concentration therefore B could be expected to be governed by the specialized viscosity effects such as the Einstein effect η^E, dipole orientation effect η^A and the structure-breaking effect η^D. For the uni-univalent electrolyte KCl, up to 40% the ion-ion attraction decreases slightly and the ion-solvent interaction, solvent-solvent interaction increases but the negative effect is seen in the 60% benzene-water solvent mixture. This may be due to this that solvent-solvent interaction is greater in magnitude when compared with ion-solvent interaction. Due to this effect a decrease in B values is observed. But at the same time when the temperature is increased, we observe a decrease in both the A and B values and this shows that temperature has an important role in deciding the ion-ion interaction, ion-solvent interaction and solvent-solvent interaction. For the uni-univalent electrolyte and also with the cations and anions having the same ionic radii, the ion-ion interaction and the ion-solvent interaction take the predominant role when compared with solvent-solvent interaction.

When comparing the relative viscosity, the relative viscosity decreases as the composition of the solvent increases for KCl which shows that solvent-solvent interaction increases but the net effect is a positive effect.

TABLE-1

Temp. (°C)	Solvent (%)	Name of electrolyte	C (M)	$\frac{C}{\log \eta/\eta_0}$	$\frac{\eta/(\eta-1)}{\sqrt{c}}$	β
30	20	KCl	1.0	8.6014	0.3069	0.3069
			0.6	4.9230	0.4183	0.5400
			0.3	2.5599	0.5655	1.0324
			0.2	1.8308	0.6395	0.4300
		$MgCl_2$	0.8	4.8348	0.5184	0.5796
			0.4	2.5844	0.6769	1.0454
			0.2	1.4976	0.7080	1.3000
		Na_2SO_4	0.8	2.3228	1.3528	0.5725
			0.4	1.9478	0.9558	1.5113
			0.2	1.2142	1.0318	2.3061
		$ZnSO_4$	0.8	3.9665	0.6608	0.788
			0.4	1.9328	0.9655	1.5266
			0.2	0.9991	1.3092	2.9274
	40	KCl	0.6	6.1359	0.3242	0.4185
			0.3	2.6867	0.5352	0.9772
			0.2	2.4412	0.4642	1.0380
		$MgCl_2$	0.6	3.8521	0.5569	0.7189
			0.3	1.9800	0.7622	1.3915
			0.15	1.3749	0.7374	1.9039
		Na_2SO_4	0.6	1.8335	1.4516	1.8740
			0.3	1.4772	1.08885	1.9872
			0.15	0.8720	1.2438	3.2397
		$ZnSO_4$	0.6	1.6428	1.7022	2.1975
			0.3	0.9022	2.1000	3.8341
			0.15	0.8080	1.3770	3.5555
	60	KCl	1.0	5.1380	0.5654	0.5654
			0.6	3.2962	0.6721	0.8677
			0.3	2.2011	0.6731	1.2289
			0.2	1.4403	0.8425	1.8839
		$MgCl_2$	0.4	2.5988	0.6725	1.0633
			0.25	1.6725	0.8217	1.6433
			0.1	0.9022	0.9194	2.9072
		Na_2SO_4	0.4	1.1303	1.9901	3.1467
			0.2	0.7918	1.7639	3.9443
			0.1	0.6230	1.4138	4.4709
		$ZnSO_4$	0.4	—	0.8334	1.3241
			0.2	0.7152	2.0270	4.5192
			0.1	0.4262	2.2650	7.1626

Temp. (°C)	Solvent (%)	Name of electrolyte	C (M)	$\frac{C}{\log \eta/\eta_0}$	$\frac{\eta/(\eta-1)}{\sqrt{c}}$	β
35	20	KCl	0.6	3.6658	0.5909	0.6728
			0.3	2.5540	0.7000	1.0352
			0.2	1.5733	0.7603	1.7002
		$MgCl_2$	0.8	4.3682	0.5865	0.6557
			0.4	2.6277	0.6638	1.0494
			0.2	1.3466	0.9118	2.0387
		Na_2SO_4	0.8	0.8084	1.0368	1.1586
			0.4	1.9127	0.9779	1.5464
			0.2	1.1798	1.0677	2.3873
		$ZnSO_4$	0.8	—	0.6488	1.7230
			0.4	1.9127	0.9780	1.5463
			0.2	1.0352	1.2527	2.8012
	40	KCl	1.0	8.0941	0.3290	0.3290
			0.6	5.2469	0.3888	0.5020
			0.3	3.5040	0.3978	0.7263
			0.2	2.3616	0.4814	1.0765
		$MgCl_2$	0.6	3.6246	0.5989	0.7932
			0.3	1.9929	0.6549	1.3808
			0.15	1.3797	0.7344	1.8963
		Na_2SO_4	0.6	2.5406	0.9327	1.2042
			0.3	1.4641	1.1006	2.0094
			0.15	0.8762	1.2464	3.2209
		$ZnSO_4$	0.6	1.6612	1.0000	2.1618
			0.3	1.2425	1.3576	2.4787
			0.15	0.8020	0.3896	3.5880
	60	KCl	0.6	12.5686	0.1500	0.2661
			0.3	14.6141	0.0883	0.1613
			0.2	17.6273	0.0591	0.1323
		$MgCl_2$	0.4	4.0033	0.4090	0.6467
			0.25	1.7099	0.8004	1.6009
			0.1	0.8540	0.9786	3.0946
		Na_2SO_4	0.4	2.0870	0.8771	1.3868
			0.2	1.0662	1.2078	2.7008
			0.1	0.5877	1.5355	4.8558
		$ZnSO_4$	0.4	1.4265	1.4345	2.2681
			0.2	1.1360	1.1176	2.4991
			0.1	0.5918	1.5040	4.7562

For the bi-univalent electrolyte magnesium chloride at 30°C, both the slope and intercept increase as the solvent composition increases. This shows the ion-ion interaction, the ion-solvent interaction and the solvent-solvent interaction. But at the same time at higher temperatures in 40% benzene-water, the combined effect of ion-ion interaction, ion-solvent interaction and solvent-solvent interaction is reduced considerably and again in 60% benzene-water it increases to a large extent. Thus this shows that magnesium ion shows strong positive solvation at 60% benzene and the Cl^- shows positive but weak solvation.

For the uni-bivalent electrolyte sodium sulphate at 30°C a similar effect like bi-univalent electrolyte is observed but an enormous increase in the B ion value is observed at 60% benzene-water system. This explains that solvent interaction plays an important role in the solvent mixture. But at higher temperatures, for the uni-bivalent electrolyte at 20% benzene-water, only ion-ion interaction is higher and the solvent interaction is negligible. But as the solvent composition increases, the solvent interaction (B) increases very rapidly which shows the phenomenon of structure-breaking effect. The ion-ion interaction also increases as the solvent mixture composition increases.

For the bi-bivalent electrolyte zinc sulphate at 30%, both the A and B values increase rapidly, which shows an increase in the ion-ion interaction, the ion-solvent interaction and solvent-solvent interaction. So the solvation and as well as the structure-breaking effect is predominant in the symmetric electrolytes, during the increase in the composition of solvent benzene. At higher temperatures, *i.e.*, at 35°C, we observe a decrease in the A and B values at 40% benzene-water mixture. A and B values are higher for 20%. and as well as 60% benzene-water mixture.

Treatment of Bresleu and Miller

From the data given in Table-1, we can understand the behaviour of the electrolyte. The effective molar volume for zinc sulphate is negligible at all the different solvent compositions. For KCl at 20% solvent mixture at temperature 30°C and for 40% benzene mixture at 35°C it is comparatively negligible and for the other electrolytes magnesium chloride and sodium sulphate at 35°C and 60% benzene-water mixture it is negligible. As V_e increases with increase in temperature for KCl, this shows that the disruption of the normal water structure equilibrium by increased temperature provides more free water molecules for subsequent interaction. With increase in solvent composition for sodium sulphate the effective molar volume constantly increases with increase in concentration which suggests the ion-dipole interaction between the sodium ion and water molecules and gives rise to electrostrictive hydration of sodium ion. Increasing the salt concentration causes further disruption of the water equilibrium releasing more free water which results in continuous increase in V_e. But in all the other electrolytes except zinc sulphate the effective flow volume with increase in solvent composition has no comparable effects.

Potassium chloride and magnesium chloride: As the temperature increases, the reduced viscosity increases with increase in concentration in 20% benzene-water mixture. This shows the predominance of ionic solvation and the action of the field of the ion in producing the long range order of solvent molecules and "the structure-breaking effect". With less influence. But for sodium sulphate, the viscosity decreases as the temperature increases at higher concentration in the same solvent mixture, and for zinc sulphate, this phenomenon is observed at lower concentration. This may be due to the predominance of structure-breaking effect and the steric effect over the ionic solvation and the production of long range order of solvent molecules. As the solvent composition increases, the η_r of the solution decreases with increases in temperature which shows the predominance of the solvent effect in the electrolytes potassium chloride and magnesium chloride. But in sodium sulphate and zinc sulphate a random behaviour is observed with increase in concentration as well as increase in solvent composition with increase in temperature. This may be attributed to the combination of solvation effect, structure-breaking effect and steric effect.

Discussion of Jones-Dole β-coefficient with temperature

As the temperature increases, β-coefficient decreases for all the electrolytes in the various 20%, 40% and 60% solvent mixtures. But only for uni-bivalent, bi-univalent electrolytes in 60% benzene-water there is increase in β-coefficient. This shows that all the salts are stronger promotors of water structure in benzene-water mixture. But the uni-bivalent and bi-univalent salts like magnesium chloride and sodium sulphate at 60% benzene-water mixture show slight structure-breaking effect. This suggests that due to solvation the structure-breaking effect is reduced.

The determination of viscosities and applications of various theories propose that the solvation of the ions is the most important factor determining the behaviour of electrolytes. As the β-ion value alone is very much influenced by the various solvents, it is studied. The reduced viscosities of various electrolytes with different concentrations, in varying proportions of benzene-water mixture at different temperatures, are determined. From the results, the following conclusions regarding the interaction are achieved.

(1) For cations the influence of hydration on B ion is dominant, apart from a certain effect due to the structure disruption. The hydration effect increases as the crystal ionic radius decreases and as the charge goes up; it acts by increasing the viscosity (increase of the effective particle size).

(2) At very high intensities of the field of the ions, a long range ordering effect of the ion on the solvent molecules becomes noticeable (sometimes described as the formation of a second hydration shell or moleculear cluster). This applies perhaps to the ions Mg^{2+}. This effect again causes a viscosity increase.

(3) The anions are thought to cause chiefly structure-breaking of the solvent, an effect which gains importance as the crystal ionic radius goes up and tends to lower the viscosity. In addition there may be a weak hydration effect.

(4) Steric influences for sulphate ions only.

(5) As the temperature increases, the ice structure of water breaks down and

consequently the contribution with certain solute ions for Cl′ makes this disruption of structure to decrease. For the predominantly structure-breaking ion like Cl^-, a rise in temperature is accompanied by a less rapid decrease of the solution viscosity (η) than of the solvent viscosity (η_0).

(6) The temperature coefficient becomes negative for the strongly hydrated ions which causes long-range ordering of solvent molecules. This long-range order further enhances the viscosity increase due to hydration.

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