EFFECT OF LITHIUM CHLORIDE AND SODIUM CHLORIDE ON IONIC INTERACTION OF DILUTE SOLUTION IN AQUEOUS BUTANOL

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The viscosities of LiCl and NaCl solutions for different concentrations in aqueous butanol (0-7%) mixtures at various temperatures were measured. The viscosity data was interpreted in terms of ion-solvent interactions. A regular increment in the viscosities with the increasing concentrations of salt as well as increasing in percent composition of aqueous-butanol mixtures is observed. The values of A & B coefficients of Jones-Dole equation have been determined graphically. It was found that A & B coefficients vary with concentration of LiCl and NaCl as with the composition of butanol mixtures and temperatures. The positive values of B- coefficient decreased with rise in temperature led to the conclusion that NaCl and LiCl in aqueous butanol mixtures behave as structure maker whereas, in aqueous medium NaCl and LiCl showing negative values of B-coefficient behave as structure breakers.

An attempt has also been made to determine the activation energy (E_η) as a function of concentration of LiCl and NaCl in aqueous-butanol mixtures. It shows that activation energy is influenced by the concentration of salts and percent composition of solvents.

Key words: Viscosity, Ionic interaction, Lithium chloride, Sodium chloride, Activation energy.

Introduction

The study of solute-solvent interactions by means of viscosity measurement have received a great interest among many researchers (Jones and Talley 1933; Moulik 1972; Afzal *et al* 1989; Das and Hazra 1997; Gangopadhyay and Lahiri 1998; Fahim Uddin and Saeed 2000; Kamal and Halder 2000) due to its simplicity and reliability in the results not only for compounds of high molecular weight but also for the electrolytes. Literature survey shows an exclusive area for the research of nature of compounds in different solvent as a function of certain parameters, intermolecular interactions, forces, orientation, solvation and behavior of electrolytes. Viscosity method offers an excellent source of primary data in the measurement of ionic interactions with the highest precision in experimental data. Although the nature of measurements readily reveal poor experimental technique but the validity of results made it excellent.

The nature of salt in mixed solvent system such as aqueous butanol mixtures can be interpreted in terms of Jones-Dole coefficients (Jones and Dole 1929) by using the relation.

$$\eta_{sp} = A \, (C)^{1/2} + B \cdot C \quad \ldots\ldots\ldots\ldots(1)$$

Where η_{sp} is the specific viscosity, C is the concentration and A and B are Jones-Dole coefficients representing ion-ion and ion-solvent interactions, characterizing the behavior of electrolytes.

The B-coefficient of Jones-Dole empirical expression of the relative viscosities of electrolyte solutions as a function of their concentration provides information concerning the solvation of the ions and their effects on the structure of solvent in the near environment of the solute particles. Because of the nature of the B-coefficient and their ion-additive properties, potentially important correlations exist between Jones-Dole coefficients and other ion-additive properties such as enthalpies, Gibbs free energy and entropies of hydration solvation and transfer between solvents. This seems that B-coefficients may also be used to provide the thermochemical data (Donald *et al* 1995). Present investigation reveals the study of nature of electrolytes such lithium chloride and sodium chloride a bulkier solvent type aqueous-butanol and their ion-ion and ion-solvent interactions.

Experimental

Materials. Extra pure lithium chloride and sodium chloride of E.Merck, butanol (BDH,Analar), double distilled water were used.

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Procedure. Different percent compositions of aqueous butanol solvent (v/v) 0%, 1%, 3%, 5% and 7% and solutions of lithium chloride and sodium chloride within the concentration range 1.0×10^{-2} to 8×10^{-2} mol.dm^{-3} were prepared.

Viscosities of the solutions were prepared in according to respective tables and were measured by Ostwald Viscometer type Techniconominal constant 0.1 Cs/S capillary ASTMAD 445. Densities of the solutions were measured by relative density bottles having a capacity of 10 ml. Time flow of solvent and solutions was observed by stop watch (Advance-85 Quartz) having a least count of 0.2 seconds. The temperature was maintained constant with the help of thermostatic water bath Haake-13 Karlsruhe, Germany having constant ± 0.01.

Results and Discussion

Tables 1 and 2 summarizes the data of viscosities for different compositions of aqueous butanol mixtures in the presence of lithium chloride and sodium chloride. These results

Table 1

Viscosities of lithium chloride in aqueous-butanol

[Salt] x 10² (mol.dm⁻³)	η (m.p.) at different temperatures			
	30 °C	35 °C	40 °C	45°C
	0 % aqueous-butanol			
1.0	7.866	7.202	6.615	6.035
2.0	8.109	7.223	6.672	6.071
4.0	8.224	7.252	6.787	6.128
6.0	8.325	7.309	6.846	6.181
8.0	8.412	7.357	6.862	6.227
	1 % aqueous-butanol			
1.0	8.011	7.272	6.678	6.230
2.0	8.039	7.329	6.698	6.267
4.0	8.089	7.470	6.799	6.295
6.0	8.165	7.554	6.879	6.350
8.0	8.357	7.611	6.987	6.483
	3 % aqueous-butanol			
1.0	8.039	7.625	7.078	6.136
2.0	8.107	7.681	7.107	6.182
4.0	8.208	7.774	7.157	6.262
6.0	8.322	7.890	7.210	6.331
8.0	8.444	7.988	7.292	6.417
	5 % aqueous-butanol			
1.0	8.768	8.173	7.402	6.589
2.0	8.825	8.203	7.436	6.628
4.0	8.923	8.261	7.495	6.687
6.0	9.001	8.347	7.551	6.746
8.0	9.112	8.432	7.633	6.811
	7 % aqueous-butanol			
1.0	9.251	8.730	7.729	6.993
2.0	9.451	8.817	7.787	7.178
4.0	9.636	8.877	7.844	7.198
6.0	9.747	8.936	7.901	7.258
8.0	9.833	9.022	7.956	7.313

Table 2

Viscosities of sodium chloride in aqueous-butanol

[Salt] x 10² (mol.dm⁻³)	η (m.p.) at different temperatures			
	30 °C	35 °C	40 °C	45 °C
	0 % aqueous-butanol			
1.0	7.708	7.526	6.827	6.119
2.0	7.772	7.583	6.858	6.147
4.0	7.907	7.726	6.902	6.229
6.0	8.033	7.840	6.022	6.323
8.0	8.167	7.937	6.169	6.355
	1 % aqueous-butanol			
1.0	7.998	7.272	6.918	6.324
2.0	8.054	7.328	6.950	6.353
4.0	8.128	7.396	7.015	6.397
6.0	8.204	7.430	7.063	6.427
8.0	8.279	7.499	7.112	6.457
	3 % aqueous-butanol			
1.0	8.464	7.835	7.017	6.435
2.0	8.531	7.890	7.097	6.481
4.0	8.688	7.996	7.186	6.519
6.0	8.769	7.080	7.243	6.550
8.0	8.902	7.109	7.300	6.601
	5 % aqueous-butanol			
1.0	8.992	8.128	7.382	6.702
2.0	9.062	8.174	7.432	6.746
4.0	9.173	8.257	7.499	6.803
6.0	9.308	8.361	7.555	6.849
8.0	9.482	8.407	7.608	6.889
	7 % aqueous-butanol			
1.0	9.697	8.491	7.809	5.660
2.0	9.745	8.507	7.825	5.667
4.0	9.849	8.586	7.879	5.703
6.0	9.940	8.644	7.964	5.742
8.0	10.058	8.716	7.995	5.775

Table 3

The values of the parameters a and b of Jones-Dole equation at different composition of LiCl aqueous-butanol solvent at various temperatures.

Temperature °C	A and B- coefficients of Jones-Dole equation in different aqueous-butanol solvents				
	0%	1%	3%	5%	7%
	A-coefficient (lit.mol⁻¹)¹ᐟ²				
30	-0.040	-0.096	0.005	0.025	-0.126
35	-0.028	-0.158	0.002	0.024	0.054
40	0.090	-0.040	0.009	0.027	0.062
45	0.103	-0.012	0.103	0.085	0.256
	B-coefficient (lit.mol⁻¹)				
30	0.540	0.720	0.701	0.495	1.095
35	0.371	0.760	0.645	0.371	0.304
40	0.460	0.759	0.391	0.347	0.254
45	0.221	0.500	0.387	0.247	0.017

indicate a regular increment in the viscosities with the increasing concentration of salts. Furthermore, the results also

Table 4

The values of the parameters a and b of Jones-Dole equation at different composition of NaCl in aqueous-butanol solvent at various temperatures.

Temperature °C	A and B- coefficients of Jones-Dole Equation in different aqueous-butanol solvents				
	0%	1%	3%	5%	7%
	A-coefficient ($dm^3.mol^{-1}$)$^{1/2}$				
30	-0.020	0.015	0.098	0.107	-0.012
35	0.106	0.005	0.073	0.096	-0.022
40	0.648	0.035	0.065	0.095	-0.032
45	0.718	0.022	0.031	0.087	-0.033
	B-coefficient ($dm^3.mol^{-1}$)				
30	0.560	0.838	0.501	0.484	0.573
35	0.200	0.827	0.447	0.239	0.450
40	-1.422	0.700	0.438	0.205	0.441
45	-1.621	0.650	0.276	0.193	0.399

Table 5

Energy of activation data for lithium chloride and sodium chloride in 0-7% aqueous-butanol

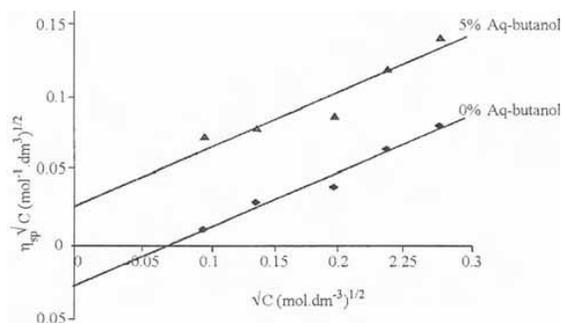| [Salt] 10^2 (mol.dm^{-3})	Activation energy E_η (k. J. mol^{-1})				
	Aqueous-butanol solvent				
	0 %	1 %	3 %	5 %	7 %
	LiCl				
1.0	13.79	13.13	13.73	14.90	15.52
2.0	14.89	13.16	13.83	14.93	15.54
4.0	14.92	13.26	13.90	15.02	15.64
6.0	15.07	13.27	14.14	15.06	15.76
8.0	15.30	13.31	14.21	15.18	15.87
	NaCl				
1.0	11.86	13.16	14.46	15.22	26.38
2.0	11.99	13.38	14.60	15.34	26.64
4.0	12.10	13.83	15.18	15.59	26.81
6.0	12.29	14.38	15.43	15.93	26.92
8.0	12.54	14.93	15.73	16.65	27.22

Fig 1. Plot of $\eta_{sp}/\sqrt{C}$ versus$\sqrt{C}$ for LiCl in 0% and 5% aqueous butanol at 35°C.
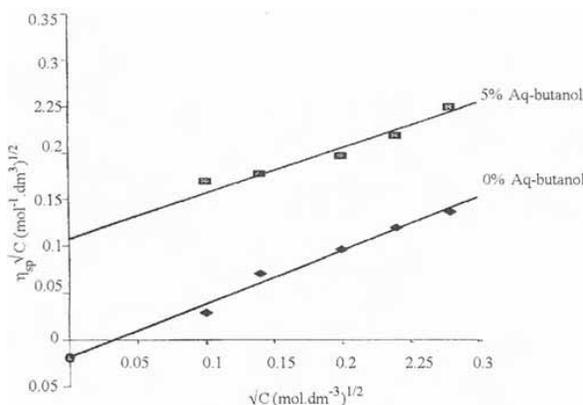

Fig 2. Plot of $\eta_{sp}/\sqrt{C}$ versus$\sqrt{C}$ for NaCl in 0% and 5% aqueous butanol at 35°C.

show that viscosities of salt solutions increase with increase in percent compositions of aqueous butanol mixtures at fixed temperature and decrease with the rise of temperature.

The values of A and B-coefficients of Jones-Dole equation (Jones and Dole 1929) have been determined graphically from the intercept and slopes of linear plots of $\eta_{sp}/\sqrt{C}$ versus$\sqrt{C}$ respectively. The representative plots for lithium chloride and sodium chloride in 0% and 5% aqueous butanol solvents at 35°C and 30°C are shown in Figs 1 and 2 respectively. These results indicate an irregular variation in values of A for various compositions of aqueous butanol solvents and solute temperatures. Besides negative and positive values of A, results show an incomplete dissociation and ion-association of electrolyte in aqueous butanol solvent. As in the unperturbed solution, each ion is associated with a spherically symmetric ionic cloud of oppositely charged sheering forces. These forces generated under an applied linear velocity gradient, cause the ionic clouds to deform from a spherical to an ellipsoidal form. If the influence of incomplete dissociation and ion association regarded by Jones-Dole equation (Jones and Dole 1929) in terms of A and B-coefficients. To understand this irregular variation in the values of A-coefficient, the structure of solvent must be taken into consideration. In the present case, oxygen of butanol ($CH_3.CH_2.CH_2.CH_2.OH$) has a tendency of holding water molecules. This may lead to intermolecular hydrogen bonded salts instead of formation of three dimensional clusters (Saeed 1993) with the variation in percent composition of aqueous butanol content; the viscosities of salt vary because of complex formation. Variation in A values is attributed actually to the size of the ions which differ in their degree of hydration.

The low value of A at low butanol content may be due to the fact that the degree of hydration is greater than ion-ion interactions. Similar observations have been obtained for the system sodium citrate solutions in acidic aqueous methanol (FahimUddin *et al* 1989). It shows that both ion-ion interaction and ion-solvent interaction vary with the composition of the solvents.

The B-coefficient of Jones-Dole equation describes the ion-solvent interaction. Temperature and composition of solvent may affect the values of B-coefficient. In both LiCl-aqueous butanol and NaCl- aqueous butanol systems the values of B-coefficient are positive and decreased with the rise in temperature. But there is an irregular increase or decrease in the values of 'B' with percent composition of solvent at all temperatures. Butanol is bulkier (C_4H_9-OH) than water (H-OH) (Saeed 1993; FahimUddin *et al* 2001). It does not show strong hydrogen bonding. The results depicted in Tables 3 and 4 indicate that NaCl in aqueous medium having negative B-coefficient behaves as structure breaker whereas, in aqueous-butanol mixtures LiCl and NaCl having positive values of 'B' decreased with the rise in temperature and behave as structure maker. The variation of B-values with change in percent composition of solvent represents the electrostatic ion-solvent interaction in aqueous butanol.

Activation energy (E_η) at various concentrations of LiCl and NaCl in aqueous butanol was determined from the following Arrhenius relation (Fahim Uddin and Saeed 2000).

$$\eta = A \exp (E_\eta / RT) \quad\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (2)$$

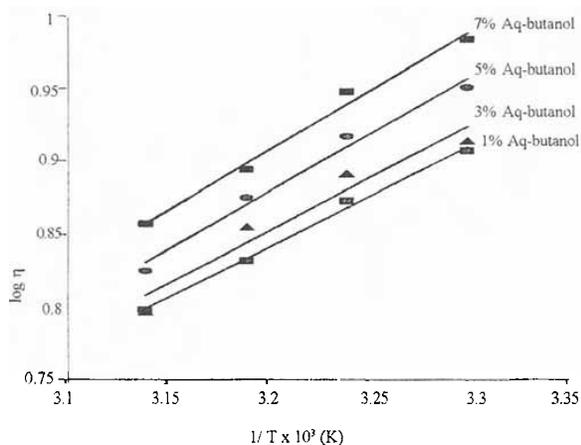where A is constant which depends upon the solvent used and T is absolute temperature. The values of energy of acti-

Fig 3. Plot of lon η versus 1/T for 4.0x10⁻² (mol.dm⁻³) LiCl 1%, 3% 5% and 7% aqueous butanol.
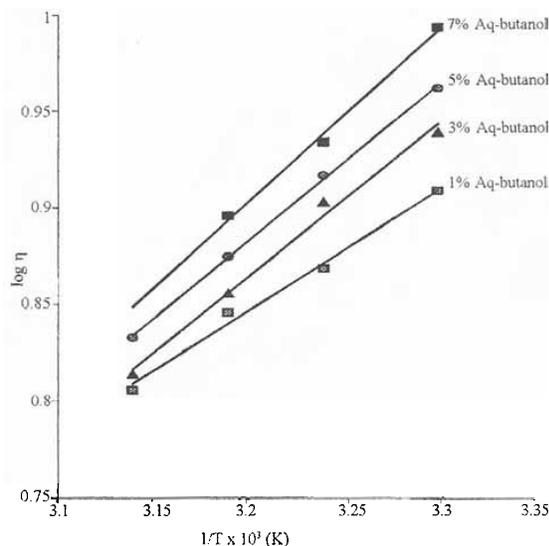
Fig 4. Plot of log η versus 1/T for 4.0x10⁻² (mol.dm⁻³) NaCl in 1%,3%,5% and 7% aqueous butanol.

vation have been determined graphically from the plot of log η versus reciprocal of temperature. The representative plots for 4.0x10⁻² mol.dm⁻³ LiCl and NaCl in 1%, 3%, 5% and 7% aqueous butanol are shown in Figs 3 and 4 respectively. The values of energy of activation as a function of salt concentrations and solvent compositions have been summarized in Table 5. The results show that activation energy is influenced by concentration of salts and percent composition of solvent. The activation energy increased regularly with the increase in concentration range 1.0 x 10⁻² to 8.0 x 10⁻² mol.dm⁻³ of salts and also indicate that increase in percent composition of aqueous butanol mixtures. In aqueous medium for both salts LiCl and NaCl, the activation energy increases with increase in concentration of salts and it is due to the availability of greater number of ions at higher concentration of salt. This produces hindrance in the mobility of ions and makes it difficult to produce vacant sites in the solvent matrix resulting in the high energy of activation. These results of activation energy are in agreement with the values of activation energy of sodium oxalate and sodium tartarate (FahimUddin and Farooqui 1984; FahimUddin *et al* 1990).

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