

VISCOSITY OF LITHIUM CHLORIDE SOLUTIONS IN WATER-METHANOL MIXTURES

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The viscosities of LiCl in aqueous methanol solution (10 - 50%) were measured at various concentrations (1.0×10^2 to 8.0×10^{-2} mol.dm⁻³) and temperatures (30 - 46°C) respectively. The viscosity was interpreted in terms of Jones-Dole and Root density equations. Jones-Dole coefficients A and B and Root equation constants were evaluated by linear extrapolation using the least square method. The positive and increasing value of Jones-Dole B-coefficients lead to the conclusion that lithium chloride in aqueous methanol behaves as structure enhancer. Different activation parameters such as energy of activation (ΔE), free energy change ($G\Delta^*$) and entropy change of activation (ΔS^*) at different solvent composition and salt concentrations were also evaluated.

Key words: Viscosity, Jones-Dole coefficients, Root equation.

Introduction

The viscosity of aqueous solutions of various electrolytes has been measured carefully by many workers [1 - 12]. Jones and Dole's equation [13] for the viscosity of dilute solutions may be expressed as:

$$\frac{\eta}{\eta_0} = 1 + A \sqrt{C} + BC \dots \dots \dots (1)$$

where η is the viscosity of the solution and η_0 that of the pure solvent at a given temperature, C is the molar concentration, A and B represent interionic attraction and ion-solvent interaction respectively.

Fahim Uddin *et al.* [14-17], Lallan Singh [18] and Quraishi *et al.* [19] studied the viscosity of salt solutions at different temperatures in order to find out the dependence of activation energy (ΔE) on salt concentration. The present study reports the measurements of viscosity of lithium chloride solutions in water-methanol mixtures and evaluation of activation parameters and Root's equation constants A and B.

Experimental

LiCl (E. Merck) was used without further purification. Methanol of analar grade extra pure (BDH) was used as a solvent. Double distilled water was used throughout the course of experiment for preparing different % (v/v) solvents.

All the glassware used were of Pyrex and A grade quality. Viscosities were measured by means of jacketted Ostwald viscometer (type Techniconominal constant 0.05 Cs/S, capillary ASTMAD 445 USA), having constant circulation of water. A thermostatic bath (type, Haak-13 manufactured by Haak, Korlsuhe, Germany) was used to maintain the temperature constant using fluctuations being $\pm 0.1^\circ\text{C}$ during the

experimental work. Its pump was used for the circulation of water in the glass jacket of viscometer.

Densities were determined by using specific gravity bottle having capacity of 10 ml by volume. A stop watch (advance 85-Quartz) having least count of 0.5 sec. was used for the determination of time of flow of solutions. The percentage composition of solvent and temperature were varied in order to determine the viscosity while the concentration of salt solutions were kept constant. The viscosity coefficients of water used [20] for circulation were 7.975, 7.340, 6.783, 6.291 and 5.856 millipoise at 30, 34, 38, 42 and 46°C respectively. The reproductivity of results were checked for each measurement by noting the time of flow of liquid for a number of times in the viscometer. The standard deviations in the viscosity are ± 0.03 millipoise.

Results and Discussion

The viscosity of LiCl in aqueous-methanol solutions were determined over a wide range of concentration and percentage of solvent. The viscosity values obtained are reported in Table 1. Our results show that there is an increase in viscosity with the increase in concentration of salt as well as percentage composition of solvent.

The specimen graph of η_{sp}/\sqrt{C} vs. \sqrt{C} for LiCl in 30% aqueous methanol at 30°C is shown in Fig. 1. The values of viscosities corresponding to concentration of salt solutions at different temperatures are tabulated in Table 2. The values of 'A' and 'B' of Jones-Dole equation (1) are calculated from the intercepts and slopes of linear plots of η_{sp}/\sqrt{C} against \sqrt{C} . The values of 'A' and 'B' coefficients of Jones-Dole equation at different % compositions of solvent and temperatures are tabulated in Table 3. Results show that the values of

B-coefficient are positive and increase with the increase in % composition of solvent and temperature respectively except at 46°C in 50% aqueous methanol. The variation of 'B' with change in solvent composition represents the electrostatic ion-solvent interaction in aqueous methanol. The smaller change in the density of an ion causes strong electrostatic interaction. Smaller the ion, stronger the electrostatic intervention and greater the size of solvated ion. 'B' coefficients may be looked at in terms of four separated contributions. According to

TABLE 1. VISCOSITIES OF LiCl IN AQUEOUS METHANOL SOLUTION AT 30°C IN DIFFERENT PERCENT COMPOSITION (v/v %) OF SOLVENT.

[Salt] × 10 ² (mol. dm ⁻³)	Viscosities (millipoise) at composition of solvent (v/v %)				
	10%	20%	30%	40%	50%
1.0	9.217	11.09	12.29	13.27	13.37
2.0	9.321	11.18	12.42	13.33	13.50
3.0	9.392	11.23	12.50	13.36	13.56
4.0	9.478	11.29	12.59	13.40	13.64
5.0	9.535	11.32	12.68	13.45	13.72
6.0	9.564	11.36	12.77	13.49	13.78
7.0	9.650	11.39	12.81	13.54	13.84
8.0	9.708	11.45	12.89	13.63	13.63

TABLE 2. VISCOSITIES OF LiCl IN 30% AQUEOUS-METHANOL AT DIFFERENT TEMPERATURES.

[Salt] × 10 ² (mol. dm ⁻³)	Viscosities (m.p.)				
	30°C	34°C	38°C	42°C	46°C
1.0	12.29	11.18	10.27	9.062	8.723
2.0	12.42	11.25	10.15	9.149	8.811
3.0	12.50	11.28	10.23	9.180	8.868
4.0	12.59	11.36	10.42	9.232	8.951
5.0	12.68	11.44	10.50	9.314	9.007
6.0	12.77	11.53	10.43	9.368	9.085
7.0	12.81	11.67	10.56	9.401	9.166
8.0	12.89	11.73	10.64	9.456	9.220

TABLE 3. VALUES OF A AND B OF THE JONE-DOLE EQUATION EVALUATED FOR LiCl SOLUTION AT DIFFERENT TEMPERATURES AND % COMPOSITION OF SOLVENT.

Temperature (°C)	The values of the Parameters A and B of the Jone-Dole Equation (Lit.mol.)									
	10%		20%		30%		40%		50%	
	A	B	A	B	A	B	A	B	A	B
30	0.2369	0.1431	0.1242	0.1187	0.1983	0.1935	0.0395	0.2466	0.2018	0.0521
34	0.0185	0.7339	0.2437	0.4922	0.1150	0.3912	0.1353	0.4576	0.2145	0.5692
38	0.0215	0.7646	0.1000	0.8893	0.0085	0.5367	0.0950	0.5866	0.0220	1.0848
42	-0.0122	0.8316	0.0679	0.9544	-0.0005	0.5891	0.0182	0.6623	-0.0347	1.4582
46	-0.0116	0.9250	0.0702	1.6387	-0.0154	0.8669	0.0612	0.8675	-0.0714	0.9376

Stokes and Mills [21]:

$$\eta^{\circ} BC = \eta^A + \eta^E + \eta^D \dots \dots \dots (2)$$

where η^E is the increase in viscosity due to the size and shape of the ion, η^A is the increase in viscosity due to the orientation of solvent molecules around the ions and η^D is the decrease in viscosity because of deformation of the solvent structure. At given concentration, therefore, the change in 'B' coefficients may be due to completion between these viscosity factors. Positive values of 'B' coefficients reveal that LiCl - water mixtures behave as structure enhancer.

Feakins *et al.* [22] studied the viscosity of LiCl, NaCl, KCl, RbCl and CsCl in aqueous methanol. They found that LiCl and NaCl behaved as structure maker and KCl, RbCl and CsCl as structure breaker. Viscosity of alkali metal chlorides such as LiCl, NaCl, RbCl and CsCl in 2-methoxyethanol was studied by Nandi *et al.* [23]. It was found that positive values of 'B' coefficients for LiCl indicate the structure breaking effect while the negative values for NaCl and NaBr in methoxyethanol provide evidence for structure enhancing role.

The values of 'A' show irregular variation with % composition of solvent and temperature. This is due to the fact that electrostatic ion-solvent interaction varies with the aqueous alcoholic medium. Results show that values of 'A' decrease with the rise of temperature, but in some cases it increases. This may be due to the interpenetration effect (cation - cation) [24] and (cation - anion) [25].

The effect of temperature on viscosity is given by [26]

$$\eta = A.e^{\Delta E/RT} \dots \dots \dots (3)$$

$$\log \eta = \log A + \frac{\Delta E}{2.303 RT} \dots \dots \dots (4)$$

where ΔE is the change in energy of activation, R is gas constant and T is absolute temperature. Change in energy of activation (ΔE) at different solvent composition and salt concentrations were also determined by plotting $\log \eta$ against $1/T$. A specimen graph for LiCl in 30% aqueous methanol is

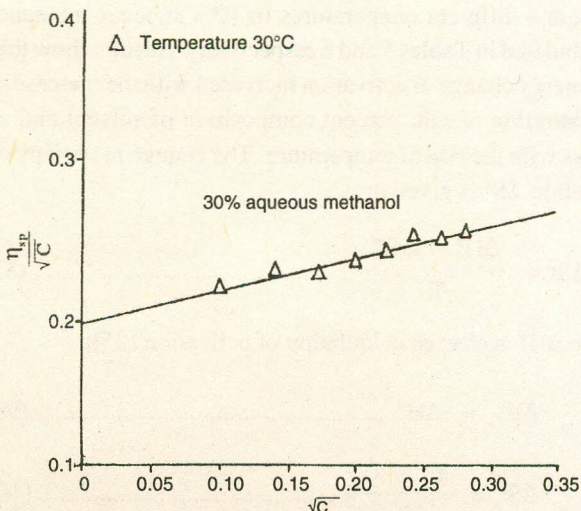


Fig. 1. Plot of $\frac{\eta_{sp}}{\sqrt{C}}$ vs \sqrt{C} for LiCl in 30% aqueous methanol at 30°C.

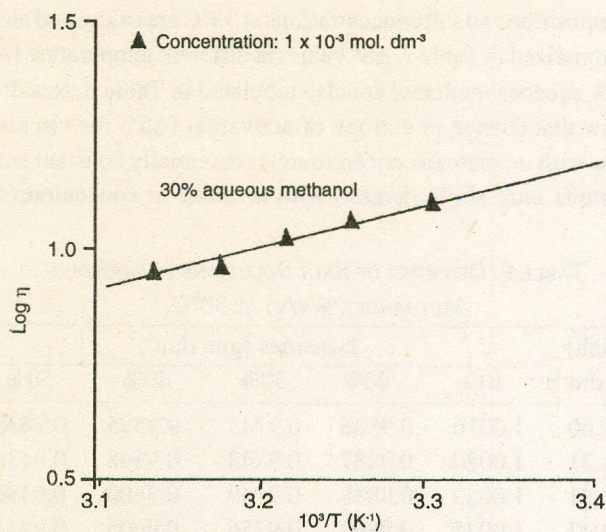


Fig. 2. Plot of $\log \eta$ vs $\frac{10^3}{T}$ for 1×10^{-2} mol. dm^{-3} LiCl in 30% aqueous methanol.

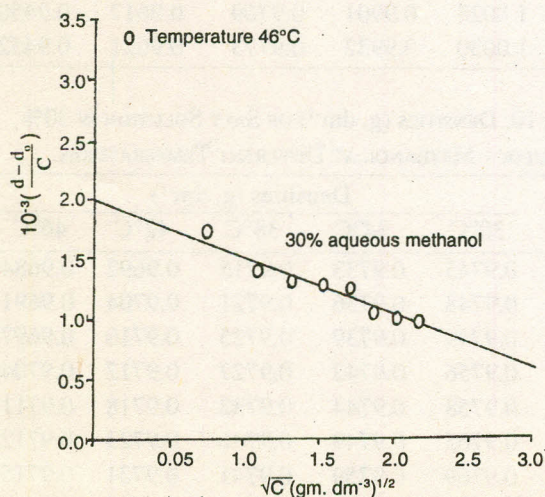


Fig. 3. Plot of $\frac{d-d_0}{C}$ vs \sqrt{C} for LiCl in 30% aqueous methanol at 46°C.

shown in Fig. 2. The values of ΔE are summarized in Table 4. Results show that ΔE increases as the percentage composition of aqueous methanol increases at a fixed concentration of salt solution and decreases as the salt concentration increases at a fixed percent composition of solvent. This is due to configuration changes by means of shearing, interatomic and intermolecular forces. This is in agreement with Ward theory [27].

TABLE 4. ENERGY OF ACTIVATION (ΔE) AT DIFFERENT SOLVENT COMPOSITIONS AND SALT CONCENTRATIONS.

[Salt] $\times 10^2$ (mol. dm^{-3})	Energy of activation (ΔE) (k j. mol. $^{-1}$)				
	10%	20%	30%	40%	50%
1.0	15.62	17.58	17.70	17.29	19.06
2.0	15.59	16.10	17.69	16.86	19.05
3.0	15.57	15.98	17.68	16.74	19.03
4.0	15.54	15.47	17.63	16.61	18.99
5.0	15.46	15.28	17.62	16.20	18.91
6.0	15.41	15.78	17.60	15.86	18.63
7.0	15.30	14.30	17.56	15.76	18.45
8.0	15.21	14.06	17.53	15.72	17.93

TABLE 5. FREE ENERGY CHANGE OF ACTIVATION (ΔG^*) AT DIFFERENT SOLVENT COMPOSITIONS AND SALT CONCENTRATIONS AT 30°C.

[Salt] $\times 10^2$ (mol. dm^{-3})	(ΔG^*) (k J. mol. $^{-1}$)				
	10%	20%	30%	40%	50%
1.0	67.60	68.27	68.73	69.11	69.33
2.0	67.62	68.29	68.75	69.12	69.35
3.0	67.64	68.30	68.77	69.13	69.36
4.0	67.67	68.31	69.79	69.14	69.38
5.0	67.68	68.32	68.81	69.15	69.39
6.0	67.69	68.33	68.83	69.16	69.40
7.0	67.71	68.34	68.84	69.17	69.41
8.0	67.73	68.35	68.85	69.18	69.43

TABLE 6. FREE ENERGY CHANGE OF ACTIVATION (ΔG^*) AT DIFFERENT TEMPERATURE AND 10% AQUEOUS-METHANOL.

[Salt] $\times 10^2$ (mol. dm^{-3})	(ΔG^*) (k . J. mol. $^{-1}$)				
	30°C	34°C	38°C	42°C	46°C
1.0	67.60	68.34	68.99	69.61	70.39
2.0	67.62	68.36	69.02	69.63	70.41
3.0	67.64	68.38	69.04	69.65	70.43
4.0	67.67	68.40	69.06	69.67	70.46
5.0	67.68	68.42	69.08	69.69	70.48
6.0	67.69	68.43	69.10	69.71	70.51
7.0	67.71	68.46	69.12	69.73	70.53
8.0	67.73	68.48	69.15	69.76	70.55

The free energy change of activation (ΔG^\ddagger) for viscous flow is given by [26]:

$$\Delta G^\ddagger = RT \ln \frac{\eta V}{\eta N} \quad \dots\dots\dots (5)$$

where h is Planck's constant and N is Avogadro number. V may be regarded as the volume of one mole of solution particles and is given by:

$$V = \frac{1000}{n_1 + \nu n_2} \text{ cm}^3 \quad \dots\dots\dots (6)$$

where ν is the number of species into which a solute molecule dissociates and n_2 is the number of moles of solute per litre of solution. The number of moles of solvent ' n_1 ' per litre of solution is given by:

$$n_1 = \frac{1000 l - n_2 M_2}{M_1} \quad \dots\dots\dots (7)$$

where M_1 and M_2 are the molecular weights of the solvent and solute respectively. Free energy change of activation (ΔG^\ddagger) at different percent solvent composition, salt concentration at

30°C, and different temperatures in 10% aqueous methanol are tabulated in Tables 5 and 6 respectively. Results show that free energy change of activation increased with the increase in concentration of salt, percent composition of solvent and as well as with the rise of temperature. The change in entropy of activation ΔS^\ddagger is given by :

$$\Delta S^\ddagger = \frac{\Delta H^\ddagger - \Delta G^\ddagger}{T} \quad \dots\dots\dots (8)$$

where ΔH^\ddagger is change in enthalpy of activation [25]:

$$\text{thus, } \Delta E^\ddagger = \Delta H^\ddagger \quad \dots\dots\dots (9)$$

$$\text{and } \Delta S^\ddagger = \frac{E^\ddagger - G^\ddagger}{T} \quad \dots\dots\dots (10)$$

change in entropy of activation ΔS^\ddagger values at different solvent composition and salt concentrations at 30°C are calculated and summarized in Table 7. ΔS^\ddagger values at different temperature for 10% aqueous methanol are also tabulated in Table 8. Results show that change in entropy of activation (ΔS^\ddagger) for viscous flow with increase in concentration is essentially constant and exhibits only slight decrease with increase in concentration

TABLE 7. ENTROPY CHANGE OF ACTIVATION (ΔS^\ddagger) (k J. deg.⁻¹ mol.⁻¹) AT DIFFERENT PERCENT SOLVENT COMPOSITION AND SALT CONCENTRATIONS AT 30°C.

[Salt] × 10 ² (mol. dm ⁻³)	ΔS^\ddagger (k J. deg. ⁻¹ mol. ⁻¹)				
	10%	20%	30%	40%	50%
1.0	-0.1715	-0.1673	-0.1684	-0.171	-0.1659
2.0	-0.1717	-0.1722	-0.1685	-0.1725	-0.1660
3.0	-0.1718	-0.1726	-0.1686	-0.1729	-0.1661
4.0	-0.1720	-0.1744	-0.1688	-0.1733	-0.1662
5.0	-0.1723	-0.1750	-0.1689	-0.1747	-0.1666
6.0	-0.1726	-0.1767	-0.1690	-0.1758	-0.1675
7.0	-0.1730	-0.1783	-0.1692	-0.1762	-0.1682
8.0	-0.1733	-0.1791	-0.1693	-0.1764	-0.1699

TABLE 8. ENTROPY CHANGE OF ACTIVATION (ΔS^\ddagger) AT DIFFERENT TEMPERATURES AND 10% AQUEOUS-METHANOL.

[Salt] × 10 ² (mol. dm ⁻³)	ΔS^\ddagger (k J. deg. ⁻¹ mol. ⁻¹)				
	30°C	34°C	38°C	42°C	46°C
1.0	-0.1715	-0.1717	-0.1716	-0.1716	-0.1717
2.0	-0.1717	-0.1718	-0.1718	-0.1716	-0.1718
3.0	-0.1718	-0.1720	-0.1719	-0.1717	-0.1720
4.0	-0.1720	-0.1721	-0.1721	-0.1719	-0.1722
5.0	-0.1723	-0.1724	-0.1724	-0.1721	-0.1725
6.0	-0.1725	-0.1727	-0.1726	-0.1724	-0.1727
7.0	-0.1729	-0.1731	-0.1730	-0.1728	-0.1731
8.0	-0.1733	-0.1735	-0.1734	-0.1732	-0.1735

TABLE 9. DENSITIES OF SALT SOLUTIONS IN AQUEOUS-METHANOL (% v/v) AT 30°C.

[Salt] (g. dm ⁻³)	Densities (gm. dm ⁻¹)				
	10%	20%	30%	40%	50%
0.60	1.0016	0.9886	0.9745	0.9595	0.9435
1.21	1.0020	0.9887	0.9748	0.9598	0.9438
1.81	1.0023	0.9888	0.9749	0.9600	0.9439
2.42	1.0025	0.9890	0.9756	0.9605	0.9441
3.02	1.0026	0.9891	0.9758	0.9610	0.9443
3.62	1.0027	0.9897	0.9765	0.9614	0.9445
4.23	1.0028	0.9901	0.9769	0.9617	0.9450
4.83	1.0030	0.9932	0.9773	0.9621	0.9452

TABLE 10. DENSITIES (g. dm⁻¹) OF SALT SOLUTION IN 30% AQUEOUS-METHANOL AT DIFFERENT TEMPERATURES.

[Salt] (g. dm ⁻³)	Densities (g. dm ⁻¹)				
	30°C	34°C	38°C	42°C	46°C
0.60	0.9745	0.9733	0.9715	0.9692	0.9684
1.21	0.9748	0.9736	0.9721	0.9704	0.9691
1.81	0.9749	0.9739	0.9725	0.9710	0.9697
2.42	0.9756	0.9742	0.9727	0.9712	0.9704
3.02	0.9758	0.9744	0.9732	0.9718	0.9711
3.62	0.9765	0.9749	0.9736	0.9723	0.9712
4.23	0.9769	0.9759	0.9741	0.9731	0.9715
4.83	0.9773	0.9763	0.9744	0.9736	0.9719

TABLE 11. THE VALUES OF A AND B CONSTANTS OF ROOT'S EQUATION FOR SALT SOLUTIONS AT DIFFERENT PERCENT COMPOSITIONS OF SOLVENT.

Temperature °C	10%		20%		30%		40%		50%	
	A	B	A	B	A	B	A	B	A	B
30	0.0002	0.00006	-0.072	2.958	0.065	2.699	1.128	-2.340	0.698	-1.502
34	0.0012	-0.00032	1.535	-4.137	8.762	-36.81	1.431	-2.954	0.868	-1.892
38	0.0009	-0.00025	0.906	-0.536	1.050	-1.652	1.336	-1.839	0.233	-1.891
42	0.0019	-0.00026	0.205	1.547	0.784	1.200	5.368	-20.830	2.798	-8.399
46	0.0013	-0.00029	0.014	1.659	2.068	-5.227	1.381	-1.838	3.997	-14.900

(1.0×10^{-2} to 8×10^{-2} mol. dm⁻³). The ΔS^\ddagger values are negative and same behaviour is observed with increase in percent compositions of solvent except at 30 and 50% aqueous methanol. ΔS^\ddagger values also show the same behaviour (i.e. slight decrease in ΔS^\ddagger) with increase in temperature.

Densities of the salt solutions in aqueous methanol at different compositions of solvent were also determined. On the basis of Hückel theory that the partial molal volume of an electrolyte in dilute aqueous solution is proportional to the square root of the normality and mathematically shown by Root's equation [28].

$$d = d_0 + AC - BC^{3/2} \dots\dots\dots (11)$$

where A and B are constants specific to salt, d and d₀ are densities of salt solution and pure solvent respectively. On transforming equation (11); we get equation (12) i.e.

$$\frac{d - d_0}{C} = A - B\sqrt{C} \dots\dots\dots (12)$$

Thus a plot of $\frac{d - d_0}{C}$ against \sqrt{C} should be linear with intercept A and slope B of the plot. Densities of salt solutions in aqueous methanol (% v/v) at 30°C and different temperature in 30% aqueous methanol are tabulated in Tables 9 and 10 respectively. Results indicate that the densities increase with the increase in percent composition of solvent as well as with the increase in temperature. This is according to Root's equation. Linear plots were obtained by plotting $\frac{d - d_0}{C}$ against \sqrt{C} . The specimen graph for density data of lithium chloride in 30% aqueous methanol at 46°C is shown in Fig. 3. The values of A and B constants of Root's equation at different temperatures and percent composition (% v/v) of solvent are tabulated in Table 11. Although results show a linear relationship but deviation is observed in the values of the parameters A and B with the increase in percent composition of solvent as well as with increase in temperature. It is also according to Redick and Rosenfeld [29] that Root's equation was found to hold within the limits of experimental error for solutions of alkali halides. This equation was also found fit only for lower concentrations.

References

1. G. D. Singh and A. Sherma, J. Chem. Soc. Farad. Trans. I, **78**, 475 (1982).
2. E. de Valera, D. Feakins and W. E. Waghorne, J. Chem. Soc. Farad. Trans. I, **85**, 4227 (1983).
3. M. Afzal, M. Saleem and M. T. Mahmood, J. Chem. Engg. Data, **34**, 339 (1989).
4. M. Afzal, H. Ahmed and Z. Ali, J. Chem. Soc. Pak., **13**, 4 (1991).
5. D. Nandi and D. K. Hazara, J. Chem. Soc. Farad. Trans. I, **85**, 4227 (1989).
6. B. N. Gosh, J. Indian Chem. Soc., **LXII**, 189 (1985).
7. W. J. Willard, K. Y. Kim, S. J. Ray and D. Jean, J. Chem. Engg. Data, **29**, 52 (1984).
8. D. Feakins, W. E. Waghorne and K. G. Lawrence, J. Chem. Soc. Farad. Trans. I, **82**, 563 (1986).
9. A.C. Upadhyay and P. B. Das, J. Indian Chem. Soc., **LXIII**, 965 (1986).
10. S. Mahiuddin and K. Ismail, J. Phys. Chem., **87**, 5241 (1983).
11. S. Mahiuddin and K. Ismail, Can. J. Chem., **60**, 2883 (1982).
12. K. Ganapathy and M. Ramanujan, J. Indian Chem. Soc., **57**, 613 (1980).
13. G. Jones and M. Dole., J. Amer. Chem. Soc., **51**, 2950 (1929).
14. F. Uddin and A. N. Farooqui, Pak. j. sci. ind. res., **27**, 273 (1984).
15. F. Uddin, I. M. Adhami and M. Zahid, Kim Ve Sanayi, **32**, 108 (1989).
16. M. Zahid and S. M. Husaini, J. Sci. Res., **19**, 1 (1990).
17. F. Uddin, I. Hussain and I. M. Adhami, J. Pure Appl. Sci., **11**, 33 (1992).
18. L. Singh, R. T. Singh and R. C. Jha, J. Indian Chem. Soc., **LVII**, 966 (1981).
19. M. M. Quraishi and A. K. M. Ahsanullah, Pak. j. sci. ind. res., **12**, 349 (1970).
20. J. F. Swindells, National Bureau of Standards, Unpublished data.

21. R. H. Stokes and R. Mills, *Viscosity of Electrolytes Related Properties* (Pergamon Press, N.Y., 1965), Vol. V, pp. 33.
22. D. Feakins, D.J. Freemantle and K.G. Lawrence, *J. Chem. Soc. Farad. Trans. I*, **70**, 795 (1974).
23. D. Nandi and D. K. Hazra, *J. Chem. Soc. Farad. Trans. I*, **83**, 4227 (1989).
24. R. Gopal and K. Singh, *Z. Physik. Chem. Trank. Ausg.* **69**, 81 (1970).
25. S. R. C. Hughes and D. H. Princes, *J. Chem. Soc. (A)*, 1093 (1967).
26. E.R. Nightangle and R.F. Benck, *J. Phys. Chem.*, **63**, 1777 (1959).
27. J. Ward, *Proc. Roy. Soc. A* **176**, 412 (1940).
28. W. C. Root, *J. Amer. Chem., Soc.*, **55**, 850 (1933).
29. Redrick and Rosenfeld, *Z. Physik. Chem., A* **155**, 65 (1931).