Study of the Comparative Solvation Behaviour of Na^+ and Cu^+ Cations in Acetonitrile + N,N-Dimethylformamide Mixtures at 298.15 K

Dip Singh Gill, Hardeep Anand, Avnesh Kumari, and J. K. Puri

Department of Chemistry, Panjab University, Chandigarh – 160 014, India

Reprint requests to Prof. D. S. G.; E-mail: dipgill@yahoo.com; Fax + 91-172-2545074.

Z. Naturforsch. **59a,** 615 – 620 (2004); received April 26, 2004

Viscosity and molar conductance of Bu_4NBPh_4, Bu_4NClO_4, $[Cu(CH_3CN)_4]ClO_4$, $NaClO_4$ and $NaBPh_4$ have been measured in the concentration ranges 0.02 – 0.5 mol dm^{-3} and 0.0005 – 0.0065 mol dm^{-3} at 298.15 K in AN + DMF mixtures containing 0, 10, 20, 40, 60, 75, 80, 90, and 100 mol % DMF. The viscosity data have been analyzed by the extended form of the Jones-Dole equation in the form: $(\eta/\eta_0) = 1 + AC^{1/2} + BC + DC^2$ to evaluate B and D parameters and the conductance data by the Shedlovsky equation to evaluate Λ_o and K_A values of the salts. Ionic viscosity B–coefficients ($B_\pm$) and ionic molar conductances ($\lambda^\circ{}_i$) have been calculated by using Bu_4NBPh_4 as a reference electrolyte. Solvated radii (r_i) for Na^+, Cu^+ and $ClO_4{}^-$ have been estimated by using Gill's modification of Stokes' law. The variation of $B_\pm$ and r_i as a function of mol % DMF shows that both Na^+ and Cu^+ are highly solvated in AN + DMF mixtures over the entire composition region. The solvation passes through a maximum between 40 to 80 mol % DMF. Both Na^+ and Cu^+ are more strongly solvated between 40 to 80 mol % DMF. Cu^+ is relatively more strongly solvated than Na^+ in AN + DMF mixtures. $ClO_4{}^-$ shows poor solvation in AN + DMF mixtures.

Key words: Viscosity B-coefficients; Solvation; Solvated radii; Na^+; Cu^+; Acetonitrile and N,N-Dimethylformamide.

Introduction

The highly ionic copper (I) salts are unstable as solids and in water and many organic solvents [1, 2]. This unstability has hindered physico-chemical studies of Cu^+ salts in pure and mixed solvents. All previous investigations of the solvation of Cu^+ are limited to acetonitrile (AN), benzonitrile (BN), some other nitriles and their binary mixtures with other organic solvents [3 – 5]. In most of these studies Cu^+ is found to be preferentially solvated by AN, pyridine (PY) and triethylphosphite (TEP) [6]. Since stabilized copper (I) salt solutions are applied in the hydrometallurgy of copper, search for new solvent systems is necessary. AN and N,N – Dimethylformamide (DMF) have nearly the same dielectric constant (AN: 36, DMF: 37.6). These solvents have different Gutmann numbers (AN: 14.1, DMF: 26.6) [7], which makes them considerably different regarding their solvating capacities. DMF solvates the cations to a large extent, while AN strongly solvates both the cations and anions. Mixtures of AN with DMF are therefore expected to be good solvents for a comparative study of the solvation behaviour of Cu^+ and Na^+, which have almost the same ionic radii (Cu^+: 0.090 nm, Na^+: 0.095 nm) and different mechanisms of their solvation [8, 9]. Therefore in the present work the solvation behaviour of Cu^+ and Na^+ cations in AN + DMF mixtures over the entire composition range was studied.

Experimental

Bu_4NBPh_4, Bu_4NClO_4, $[Cu(CH_3CN)_4]ClO_4$ and $NaClO_4$ were prepared by the method reported in [3, 4]. $NaBPh_4$ (Analytical Grade $>$ 99%, Merck) was used without further purification. AN and DMF were purified as before, and their water content was estimated by the Karl Fischer titration method. Mixtures of DMF with AN, used for the present study, were prepared by weight, and their physical properties were determined. An Ubbelohde suspended bulb viscometer with a flow time of 250 seconds for distilled water at 298.15 K was used for the viscosity measurements of the pure solvents, solvent mixtures and electrolytic solutions. The viscometer was calibrated using triply distilled water ($\eta^\circ = 0.00890$ P) [10] and purified AN ($\eta^\circ = 0.00341$ P) [11]. A series of concentrations for each salt were prepared by adding stock solutions of appropriate concentrations to a known quantity of solvent or solvent mixture taken in the viscometer. The

0932–0784 / 04 / 0900–0615 $ 06.00

measurements in all cases were repeated with two different stock solutions to get reproducible results. The overall accuracy of the viscosity measurements was estimated to be better than ±0.1%.

The conductances were measured with a calibrated Digital Conductivity Meter, Model NDC-732 from Naina Electronics, Chandigarh, at a frequency of 1000 Hz. The conductance cell was similar to that reported by Shedlovsky [12], with platinized platinum electrodes. The cell constant was determined using aqueous potassium chloride solutions in the concentration range $(3-70)\cdot 10^{-4}$ mol dm^{-3}. All measurements were carried out in a water thermostat bath maintained at (298.15 ± 0.01) K. A range of concentrations of the salts in each case was produced by adding stock solutions of appropriate concentrations to a known quantity of the solvent mixtures taken in the cell. The accuracy of the present conductance measurements was ±0.2%.

Results and Discussion

The viscosity and molar conductance of Bu_4NBPh_4, Bu_4NClO_4, $[Cu(CH_3CN)_4]ClO_4$, $NaClO_4$ and $NaBPh_4$ were measured in the concentration ranges 0.02 – 0.5 mol dm^{-3} and 0.0005 – 0.0065 mol dm^{-3} at 298.15 K in AN + DMF mixtures, containing 0, 10, 20, 40, 60, 75, 80, 90, and 100 mol % DMF. Since the viscosity measurements were made at high concentrations, the viscosity data have been analyzed by the extended Jones-Dole equation in the form [13]

$$\eta/\eta_o = 1 + AC^{1/2} + BC + DC^2. \tag{1}$$

This equation was rearranged in the form

$$\frac{\left(\dfrac{\eta-\eta_o}{\eta_o C^{1/2}} - A\right)}{C^{1/2}} = B + DC; \qquad \psi^* = \frac{\psi - A}{C^{1/2}} = B + DC \tag{2}$$

to evaluate B and D. The A values for the calculation were taken as A_η (reported in Table 2) and evaluated by the Falkenhagen-Vernon equation [14]

$$A_\eta = \frac{0.2577\Lambda_o}{\eta_o(\varepsilon_o T)^{1/2}\lambda_1^o\lambda_2^o}\left[1 - 0.6863\left(\frac{\lambda_1^o - \lambda_2^o}{\Lambda_o}\right)^2\right], \tag{3}$$

where $\Lambda_o = \lambda_1^o + \lambda_2^o$, λ_1^o and λ_2^o are the limiting ionic conductances for the cation and anion, η_o and ε_o are the viscosity and dielectric constant of the solvent or solvent mixture without salt, and T is absolute temperature. For the evaluation of A_η using (3), η_o and ε_o values for various AN + DMF solvent mixtures were taken from Table 1. The λ_1^o and λ_2^o values for various ions (listed in Table 3) were evaluated from some conductance measurements made in the present work, and some obtained from conductance results already available at a few of the compositions of the mixtures employed in this work [15]. In the present work the conductance data were analyzed by the Shedlovsky equation to obtain Λ_o and K_A values and hence λ_1^o and λ_2^o values. The B and D values obtained by the least squares method from the linear plots of ψ^* versus C in all cases are reported in Table 4.

Table 1. Density (ρ_o), viscosity (η_o), dielectric constant (ε_o), ultrasonic velocity (u_o) and isentropic compressibility ($K_s{}^\circ$) for some AN + DMF mixtures at 298.15 K.

Mol% DMF	ρ_o (g cm^{-3})	η_o (poise)	ε_o	u_o (m s^{-1})	$10^6 \cdot K_o$ (bar^{-1})
0	0.77685	0.00341	36.0	1280.8	78.5
10	0.79947	0.00381	36.3	1294.9	74.6
20	0.81165	0.00422	36.4	1328.6	69.8
40	0.86332	0.00503	36.8	1360.3	62.6
60	0.89606	0.00611	37.0	1399.2	57.0
75	0.91686	0.00685	37.2	1413.4	54.6
80	0.92156	0.00701	37.3	1417.6	54.0
90	0.93441	0.00748	37.5	1427.8	52.5
100	0.94559	0.00796	37.6	1448.6	50.4

The viscosity B-coefficients for all the electrolytes in Table 4 are large and positive. The B values for Bu_4NBPh_4 and $NaBPh_4$ are the largest, and for $NaClO_4$ the smallest (Table 4). This is a common feature in most of the non-aqueous solvents like methanol [16], sulpholane [17], DMSO [18], HMPTA [19], N-methylpropionamide [20], formamide [21] and ethylene carbonate [22]. In DMF + AC mixtures in which both DMF and AC are dipolar aprotic solvents, Gill and Sharma [23] found that the viscosity B-coefficients for all the electrolytes studied were positive and increased as the DMF composition increased in the mixtures. In AN + DMF mixtures also, which consist of two dipolar aprotic solvents and have been used in the present study, the viscosity B-coefficients for various electrolytes studied are also positive and fairly large. Das and coworkers [24, 25] found that the B-coefficients for KCl in the binary mixtures of two dipolar protic solvents, such as water + methanol, however, were negative.

In AN + DMF mixtures no viscosity study was already available at higher concentrations with which

Table 2. A_η ($dm^{3/2}\ mol^{-1/2}$) values calculated using the Falkenhagen-Vernon equation for some salts in AN + DMF mixtures at 298.15 K.

	$10^2 \cdot A_\eta$								
	Mol % DMF								
Salt	0	10	20	40	60	75	80	90	100
Bu_4NBPh_4	2.43	2.45	2.50	2.44	2.55	2.57	2.63	2.41	2.41
Bu_4NClO_4	1.80	1.78	1.74	1.75	1.67	1.66	1.65	1.63	1.64
$CuClO_4$	1.76	1.79	1.79	1.75	1.70	1.67	1.69	1.55	1.52
$NaClO_4$	1.62	1.79	1.65	1.75	1.51	1.51	1.50	1.56	1.54
$NaBPh_4$	2.17	2.46	2.37	2.43	2.28	2.31	2.36	2.29	2.25

Table 3. $\lambda^\circ{}_i$ ($S\ cm^2\ mol^{-1}$) and r_i (nm) values for some ions in AN + DMF mixtures at 298.15 K.

	Mol % DMF													
	0		10		20		40		60		80		100	
Ion	$\lambda^\circ{}_i$	r_i	$\lambda^\circ{}_i$	r_i	$\lambda^\circ{}_i$	r_i	$\lambda^\circ{}_i$	r_i	$\lambda^\circ{}_i$	r_i	$\lambda^\circ{}_i$	r_i	$\lambda^\circ{}_i$	r_i
Bu_4N^+	62.6	0.51	55.6	0.51	48.5	0.52	41.9	0.51	34.1	0.52	28.6	0.53	26.5	0.51
Cu^+	65.1	0.49	55.2	0.50	48.8	0.52	39.1	0.54	31.3	0.55	28.3	0.54	31.0	0.45
Na^+	78.0	0.43	60.2	0.48	50.1	0.51	41.8	0.53	34.5	0.54	34.1	0.53	30.4	0.46
Ph_4B^-	57.4	0.54	50.8	0.55	44.8	0.56	38.4	0.55	30.4	0.56	26.4	0.56	24.2	0.55
$ClO_4{}^-$	103.3	0.35	94.1	0.35	90.3	0.34	75.8	0.34	66.0	0.33	57.8	0.32	50.8	0.32

Table 4. *B* ($dm^3\ mol^{-1}$) and *D* values calculated by the use of extended equation for some salts in AN + DMF mixtures at 298.15 K.

	Mol % DMF																	
Salt	0		10		20		40		60		75		80		90		100	
	B	*D*	*B*	*D*	*B*	*D*	*B*	*D*	*B*	*D*	*B*	*D*	*B*	*D*	*B*	*D*	*B*	*D*
Bu_4NBPh_4	1.28	1.28	1.32	0.83	1.50	0.44	1.72	0.13	2.06	0.38	1.97	0.72	1.94	0.65	1.79	0.60	1.93	0.39
	(1.32)[a]		(1.32)[a]				(1.69)[a]								(1.80)[a]		(1.92)[a]	
Bu_4NClO_4	0.83	0.11	0.83	0.07	0.91	0.06	1.01	0.15	1.31	0.16	1.24	0.29	1.17	0.49	1.04	0.29	1.13	0.33
	(0.81)[a]		(0.81)[a]				(1.00)[a]								(1.06)[a]		(1.12)[a]	
$CuClO_4$	0.80	0.10	0.80	0.04	0.82	0.24	0.98	0.05	1.16	0.04	1.12	0.16	1.05	0.16	0.96	0.07	0.91	0.07
	(0.77)[a]		(0.80)[a]				(0.98)[a]								(0.98)[a]		(0.94)[a]	
$NaBPh_4$	1.25	0.37	1.32	0.43	1.52	0.57	1.56	0.39	1.84	0.18	1.75	0.35	1.73	0.33	1.64	0.56	1.68	
	(1.26)[a]		(1.31)[a]				(1.58)[a]								(1.64)[a]		(1.70)[a]	31.8
$NaClO_4$	0.79	0.04	0.83	0.09	0.89	0.01	0.93	0.03	1.08	0.10	1.03	0.06	0.97	0.06	0.88	0.03	0.87	
	(0.74)[a]		(0.80)[a]												(0.89)[a]		(0.89)[a]	0.07
	(0.79)[b]		(0.83)[b]		(0.89)[b]		(0.93)[b]		(1.08)[b]		(1.03)[b]		(0.97)[b]		(0.88)[b]		(0.87)[a]	

[a] Ref [15]; [b] values obtained by adding ionic values for Na^+ and $ClO_4{}^-$ from Table 5.

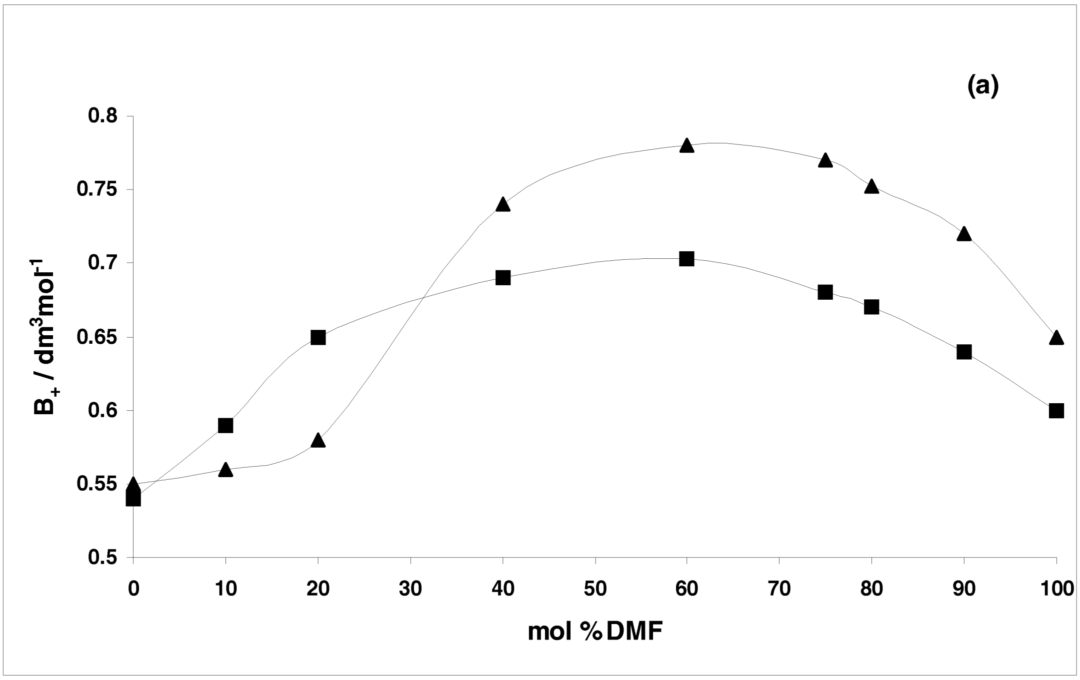
the present *B*-coefficients of the electrolytes can be directly compared. Viscosity *B*-coefficients of some of these salts at low concentrations in AN + DMF mixtures at some of the present compositions, however, were reported by Gill and Cheema [15]. These values are reported in Table 4, in parentheses for comparison with the present values. From Table 4 it is evident that the *B* values obtained using higher concentrations remain within ±0.05 units in agreement with the values obtained using low concentrations, which indicates only a small ion-association of these salts in these solvent systems.

Table 5. Ionic $B\pm$ ($dm^3\ mol^{-1}$) coefficients of some ions in AN + DMF mixtures at 298.15 K.

Mol % DMF	$B_\pm/dm^3\ mol^{-1}$				
	Ph_4B^-	Bu_4N^+	$ClO_4{}^-$	Na^+	Cu^+
0	0.71	0.58	0.25	0.54	0.55
10	0.73	0.59	0.24	0.59	0.56
20	0.82	0.67	0.24	0.65	0.58
40	0.94	0.77	0.24	0.69	0.74
60	1.14	0.93	0.38	0.70	0.78
75	1.09	0.89	0.35	0.68	0.77
80	1.07	0.87	0.30	0.67	0.75
90	0.98	0.80	0.24	0.64	0.72
100	1.07	0.87	0.26	0.61	0.65

Ionic B_+ and B_- Coefficients in AN + DMF Mixtures

The *B* values calculated from the extended Jones-Dole equation are further split into the contribution of individual ions to provide $B_\pm$-coefficients of various ions. The division of the observed *B*-coefficients of the salts have been an arbitrary process [26–28]. The viscosity *B*-coefficients of the electrolytes have been



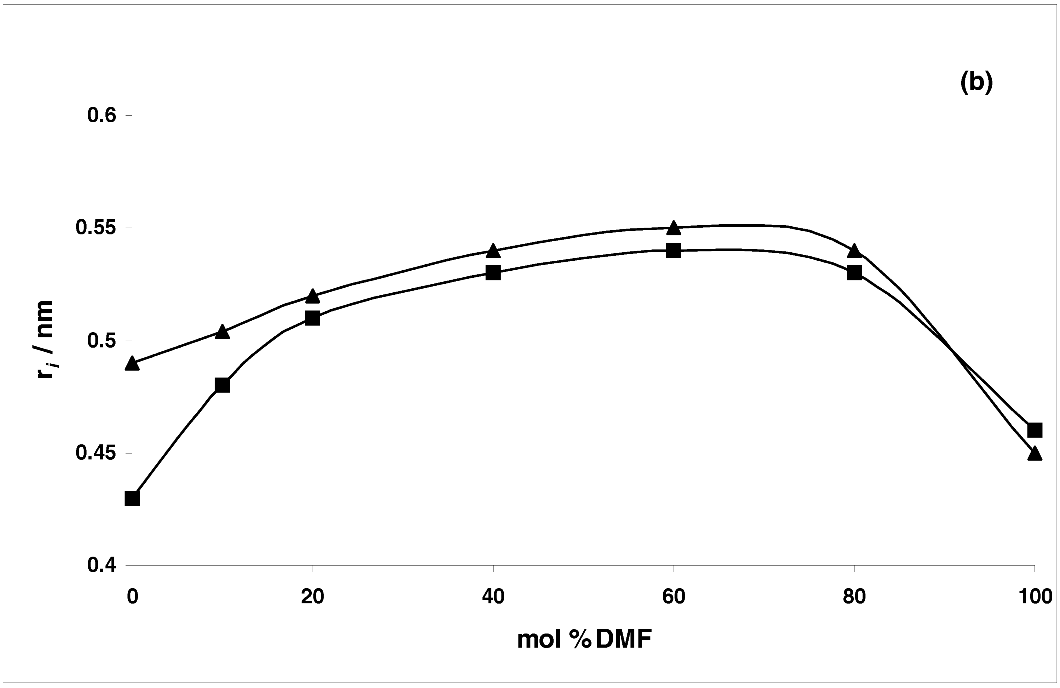


Fig. 1. Plot of ionic viscosity B_+ coefficients (Fig. 1a) and solvated ionic radii r_i (Fig. 1b) for Na^+ and Cu^+ cations as a function of mol % DMF in AN + DMF mixtures at 298.15 K. ■ – Na^+; ▲ – Cu^+.

found to be an additive property of the respective ionic components i.e., $B = B_+ + B_-$ for strong electrolytes in aqueous and non-aqueous solvents and their binary mixtures.

A number of attempts has been made to split *B* values into ionic contributions in non–aqueous elecrolyte solutions. Tuan and Fuoss [29] proposed the equality of $B_{Bu_4N^+} = B_{Ph_4B^-}$ for AN solutions on the basis of the result of Kunze and Fuoss [30] that these ions have similar mobilities in methanol. Krumgal'z [31] found that for the ions, which are not solvated in solution, i. e. for i-Am_3BuN^+, i-Am_4N^+, Ph_4As^+ and Ph_4B^-, the *B*-coefficients in various solvents could be resolved into the constituent ions using the relations

$$\frac{B_{R_4N^+}}{B_{R'_4N^+}} = \frac{r^3_{R_4N^+}}{r^3_{R'_4N^+}} \tag{4}$$

and

$$B_{R_4N^+} - B_{R'_4N^+} = B_{R_4NX} - B_{R'_4NX} \tag{5}$$

Gill and Sharma [23] had proposed a method for resolving *B*-coefficients of the electrolytes in DMF + AC mixtures into the contributions of individual ions. The justification for this model had also been given by Gill and coworkers [32, 33] from conductance measurements. This model is based on the following equations

$$\frac{B_{Ph_4B^-}}{B_{Bu_4N^+}} = \frac{r^3_{Ph_4B^-}}{r^3_{Bu_4N^+}} = \left(\frac{5.35}{5.00}\right)^3 \tag{6}$$

and

$$B_{Ph_4B^-} + B_{Bu_4N^+} = B(Bu_4NBPh_4) \tag{7}$$

where $B(Bu_4NBPh_4)$ is the observed *B*-coefficient for Bu_4NBPh_4 from the experimental data.

Using (6) and (7), the viscosity *B*-coefficients of Bu_4NBPh_4 in AN + DMF mixtures have been resolved into the contribution of Bu_4N^+ and Ph_4B^-. From these values and the *B*-coefficients for all other electrolytes studied (Table 4), B_+ and B_--coefficients for Cu^+, Na^+ and $ClO_4{}^-$ have been calculated and are reported as $B_\pm$ in Table 5.

A self-consistency of the viscosity data in the present investigation can be checked by comparing the B-coefficients of $NaClO_4$ from Table 4 with the corresponding *B* values obtained by adding B_{Na^+} and $B_{ClO4}{}^-$ from Table 5, and written in parenthesis in Table 4. In all cases except for pure AN the agreement between the two sets of values is within ±0.03 dm^3 mol^{-1}.

Comparative Solvation of Na^+ and Cu^+ Cations

The B_+ values for Na^+ and Cu^+ are larger than the B_- value for $ClO_4{}^-$. This shows that Cu^+ and Na^+ are more strongly solvated than the $ClO_4{}^-$. The B_+ values both for Na^+ and Cu^+ ions are comparable to that of Bu_4N^+ in the AN rich region and become smaller than that of Bu_4N^+ in the DMF rich region of the AN + DMF mixture. The B_+ values for both Na^+ and Cu^+ are plotted against mol % DMF in the mixture (Fig. 1a).These values pass through a maximum between 40 to 80 mol % DMF, showing that Cu^+ and Na^+ cations have maximum solvation between 40 to 80 mol % DMF. Such a behaviour is also depicted by the solvated radii of these cations in AN + DMF mixtures. The evaluated solvated radii from the limiting ionic conductances, using Gill's modification of Stoke's law [32, 33], reported in Table 3 are also plotted in Figure 1b. This plot also shows that both for Na^+ and Cu^+ cations, the solvated radii pass through a maximum, showing thereby that both these ions have maximum solvation between 40 to 80 mol % DMF. Cu^+ shows relatively stronger solvation than Na^+ in AN + DMF mixtures (Fig. 1). $ClO_4{}^-$ shows poor solvation in AN + DMF mixtures. The solvation of Na^+ and Cu^+ passing through a maximum is also confirmed by ultrasonic velocity measurements which we have already reported [34].

Conclusions

Both Na^+ and Cu^+ are highly solvated in AN + DMF mixtures over the entire composition range. This solvation passes through a maximum between 40 and 80 mol % DMF and again falls down. Cu^+ is relatively more strongly solvated than Na^+ in AN + DMF mixtures. $ClO_4{}^-$ shows poor solvation in AN + DMF mixtures.

Acknowledgement

A. K. thanks the CSIR, New Delhi, for the award of JRF.

[1] H. L. Yeager and B. Kratochvil, J. Phys. Chem. **73**, 1963 (1969).

[2] I. D. MacLeod, D. M. Muir, A. J. Parker, and P. Singh, Aust. J. Chem. **30**, 1423 (1977).

[3] D. S. Gill, J. Singh, R. Singh, T. Zamir, and T. I. Quickenden, Indian. J. Chem. **38A**, 913 (1999).

[4] D. S. Gill, L. Rodehueser, P. Rubini, and J. J. Delpuech, J. Chem. Soc. Faraday Trans. **91**, 2307 (1995).

[5] D. S. Gill, V. Pathania, B. K. Vermani, L. Byrne, and T. I. Quickenden, J. Mol. Liq. **111**, 85 (2004).

[6] D. S. Gill, R. Singh, H. Anand, and J. K. Puri, J. Mol. Liq. **98 – 99**, 15 (2002).

[7] B. Kratochvil and H. L. Yeager, Topics in Current Chemistry **27**, 1 (1972).

[8] D. A. Owensby, A. J. Parker, and J. W. Diggle, J. Amer. Chem. Soc. **96**, 2682 (1974).

[9] S. Arland and B. Tagesson, Acta. Chimica Scand. **A31**, 615 (1977).

[10] J. F. Swindells, J. R. Coe, and T. B. Godfrey, J. Res. Natl. Bur. Stand. **48**, 1 (1952).

[11] D. S. Gill, J. Soln. Chem. **8**, 691 (1979).

[12] R. M. Fuoss and T. Shedlovsky, J. Amer. Chem. Soc. **71**, 1496 (1983).

[13] M. Kaminsky, Z. Phys. Chem. **12**, 206 (1957).

[14] J. Falkenhagen and E. L. Vernon, Phys. Z. **33**, 140 (1932).

[15] D. S. Gill and J. S. Cheema, Z. Phys. Chem. N.F.**134**, 205(1983).

[16] R. L. Kay, T. Vituccico, C. Zawoyaski, and D. F. Evans, J. Phys. Chem. **70**, 2336 (1966).

[17] A. Sacco, G. Petrella, and M. Castagnolo, J. Phys. Chem. **80**, 749 (1976).

[18] R. T. M. Bicknell, K. G. Lawrence, M. A.Seelay, D. Feakins, and L. Werblan, J. Chem. Soc. Faraday Trans. 1, **72**, 307 (1976).

[19] A. Sacco, G. Petrella, M. D. Monica, and M. Castagnolo, J. Chem. Soc. Faraday Trans. 1, **73**, 1936 (1977).

[20] F. J. Millero, J. Phys. Chem. **72**, 3209 (1968).

[21] J. M. McDowell and C. A. Vincet, J. Chem. Soc. Faraday Trans. 1, **70**, 1862 (1974).

[22] G. Petrella and A. Sacco, J. Chem. Soc. Faraday Trans. 1, **74**, 2070 (1978).

[23] D. S. Gill and A. N. Sharma, J. Chem. Soc. Faraday Trans. 1, **78**, 475 (1982).

[24] N. C. Das and P. B. Das, Indian J. Chem. **15A**, 824 (1977).

[25] B. Das, K. Singh, and P. K. Das, J. Indian. Chem. Soc. **49**, 561 (1972).

[26] W. M. Cox and J. H. Wolfenden, Proc. Roy. Soc. London **145**, 475 (1934).

[27] M. Kaminsky, Discuss. Faraday Soc. **24**, 171 (1957).

[28] R. W. Gurney, Ionic Processes in Solutions, McGraw-Hill, New York 1953.

[29] D. F. T. Tuan and R. M. Fuoss, J. Phys. Chem. **67**, 1343 (1963).

[30] R. W. Kunze and R. M. Fuoss, J. Phys. Chem. **67**, 385 (1963).

[31] B. S. Krumgal'z, Russ. J. Phys. Chem. **47**, 956 (1973); **48**, 1163 (1974).

[32] D. S. Gill, J. Chem. Soc. Faraday Trans. 1, **77**, 751 (1981).

[33] D. S. Gill and M. B. Sekhri, J. Chem. Soc. Faraday Trans. 1, **78**, 119 (1982).

[34] D. S. Gill, Hardeep Anand, and J. K. Puri, J. Mol. Liq. **108**, 265 (2003).