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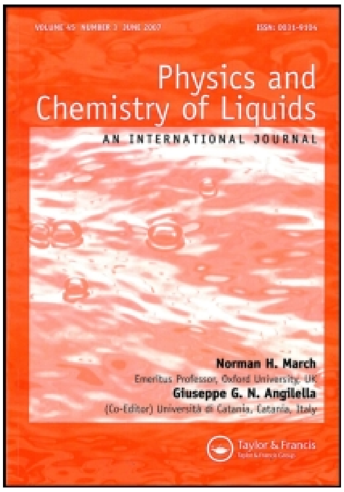

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Ion-Pair Formation in Solutions of Lithium Acetate in Acetonitrile—Water Mixtures at 25°C: A Conductometric Study

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ION-PAIR FORMATION IN SOLUTIONS OF LITHIUM ACETATE IN ACETONITRILE–WATER MIXTURES AT 25°C: A CONDUCTOMETRIC STUDY

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Conductance of lithium acetate in 0–90% acetonitrile–water mixtures at 25°C were measured. The association constants were calculated using the Fuoss–Hsia equation with Fernandez-Prini coefficients. The log K_A vs. $1/D$ plot was a straight line in accordance with the modified Denison–Ramsey theory of ion-pair formation. Walden products were also calculated. The results are interpreted in terms of solvent separated ion-pairs and contact ion-pairs.

KEY WORDS: Conductance, lithium acetate, acetonitrile-water, association constants, ion-pairs.

INTRODUCTION

Ion-pair formation in solutions of alkali metal halides and halides of small metal ions have been extensively investigated[1] both in aqueous and aquo-organic solvent mixtures. Recently D'Aparno *et al.*[2] reported lithium halides association in dioxane–water mixtures using Fuoss 80 conductance equation[3]. Such studies on acetates of small metal ions are sporadic[4]. The extended Fuoss–Hsia equation[5] with Fernandez-Prini coefficients[6], which is based on the hard sphere model can be used for the analysis of conductance data. Fuoss[7] and Lee and Wheaton[8] have put forward new conductance equations by considering different models for ion-pair formation. Per Beronius[9] commented that those equations which were based on solvent separated ion-pairs (SSIP) as well as contact ion-pairs (CIP) yielded same association constant values. Therefore, in the present investigation, the conductances of lithium acetate in 30, 40, 50, 70 and 90% (w/w) acetonitrile (AN)–water mixtures at 25°C were measured and analysed using Fuoss–Hsia equation with Fernandez-Prini coefficients. The results were used to test the applicability of various theories of ion-pair formation such as Bjerrum[10], Fuoss[11], Denison–Ramsey[12] and Ebeling–Kraeft–Yokoyama–Yamatera (EKYY)[13,14].

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EXPERIMENTAL

Lithium acetate (BDH 99% minimum purity) was used after repeated crystalizations (this had a purity >99.9%). Acetonitrile (BDH) was purified as described by Vogel[15] and had a specific conductance $<1.0 \times 10^{-7}$ S-cm^{-1}. Water with a specific conductance $<1.0 \times 10^{-6}$ S-cm^{-1} was used. The experimental arrangement was the same as reported earlier[16]. The overall accuracy of the measured molar conductances was better than ±0.05%.

RESULTS AND DISCUSSION

The observed molar conductances of lithium acetate at 25°C in AN–water mixtures are presented in Table 1. The dielectric constants and viscosity coefficients of the solvent mixtures were taken from literature[17]. The conductance data was analysed using Fuoss–Hsia equation[5] with Fernandez-Prini coefficients[6].

$$\Lambda = \Lambda_0 - s(\alpha c)^{1/2} + E\alpha c \ln(\alpha c) + J_1\alpha c - J_2(\alpha c)^{3/2} - K_A\Lambda y_\pm^2 \alpha c \qquad (1)$$

where the various symbols have their own significance. All the calculations were carried out as reported earlier[18] and the results are summarised in Table 2 along with the Walden product ($\Lambda_0\eta$), association constant (K_A) and standard deviation (σ).

The functional dependence of log K_A on $1/D$ was used to test the applicability of various theories of ion-pair formation. Bjerrum and EKYY theories predict curves which are concave downwards. A linear plot passing through origin is expected

Table 1 Concentrations and corresponding molar conductances of lithium acetate in acetonitrile–water mixtures at 25°C.

30% AN *D = 65.85* *η = 0.00955 poise*		*40 % AN* *D = 61.05* *η = 0.00849 poise*	
10^4C/mol dm^{-3}	Λ/S cm^2 mol^{-1}	10^4C/mol dm^{-3}	Λ/S cm^2 mol^{-1}
294.71	59.905	298.31	57.883
252.61	60.661	255.69	58.934
196.48	61.954	198.87	60.286
160.75	62.754	162.71	61.408
136.02	63.512	137.68	62.424
117.89	64.035	119.32	62.904
91.014	64.949	105.29	63.488
80.901	65.347	92.124	63.934
66.192	65.940	81.888	64.360
56.009	66.460	73.700	64.849
48.541	66.804	61.416	65.472
37.477	67.336	46.062	66.404
27.256	68.103	37.080	67.384
19.987	68.615	23.031	68.125
16.119	68.996	17.273	68.703

(Continued)

Table 1 (*Continued*)

50% AN *$D = 55.85$* *$\eta = 0.00765$ poise*		*70% AN* *$D = 46.50$* *$\eta = 0.00560$ poise*	
10^4C/mol dm^{-3}	*Λ/S cm^2 mol^{-1}*	10^4C/*mol dm^{-3}*	*Λ/S cm^2 mol^{-1}*
283.28	57.167	279.32	44.914
220.23	57.185	244.31	46.484
180.27	58.710	217.17	47.904
152.53	59.804	177.68	50.322
132.20	60.725	150.35	52.351
116.64	61.374	130.30	54.045
90.723	62.592	114.97	55.523
74.228	63.608	89.422	58.203
62.808	64.321	73.164	60.060
54.434	64.882	61.908	61.934
42.026	65.854	53.653	63.297
30.564	66.951	41.424	65.418
22.414	67.260	30.126	67.826
16.010	68.781	22.093	69.786
		16.245	71.497

90% AN *$D = 39.12$* *$\eta = 0.00387$ poise*	
10^4C/mol dm^{-3}	*Λ/S cm^2 mol^{-1}*
84.577	36.347
65.782	39.718
53.822	42.275
45.542	44.418
39.469	46.260
35.290	47.704
30.473	49.602
27.087	51.121
24.378	52.468
22.162	53.674
19.660	55.168
18.193	56.123

Table 2 Association parameters of lithium acetate at 25°C.

Solvent	*q/Å*	*Λ_0/S cm^2 mol^{-1}*	*K_A/dm^3 mol^{-1}*	*σ*	*$\Lambda_0\eta$*
30% AN	4.255	72.409	1.669	0.083	0.6915
40% AN	4.589	72.973	3.111	0.136	0.6195
50% AN	5.017	73.553	6.190	0.188	0.5627
70% AN	6.025	81.578	41.74	0.252	0.4568
90% AN	7.162	82.288	290.6	0.171	0.3185

according to DR theory whereas Fuoss theory predicts a straight line with a finite intercept. The K_A value for lithium acetate in water[19] at 25°C is 15.01 dm^3mol^{-1}. It is observed that there is no association in 10 and 20% acetonitrile–water mixtures. When small amounts of acetonitrile were added to aqueous solutions of lithium acetate, Li^+ ions get heavily solvated by acetonitrile molecules and prevents the acetate ions from reaching the Li^+ ions and no association can be detected in 10 and 20% acetonitrile in water. At higher percentages of acetonitrile, however, the decrease in dielectric constant dominates the solvation and hence, the association is observed from 30% acetonitrile onwards. Similar behavior was observed in the case of silver acetate in acetonitrile–water mixtures, where association was observed from 40% acetonitrile onwards[16]. This was attributed to the more preferential solvation of Ag^+ ions by acetonitrile than to the Li^+ ions. Leaving the K_A value for water, the rest of the values exhibit a good linear trend when log K_A was plotted against $1/D$ (Figure 1) with a correlation coefficient of 0.996 with 206.51 and -2.843 as slope and intercept respectively. Equating the experimental slope to $|Z_+Z_-|e^2/(2.303\ akT)$, the average ion-size parameter (a) for lithium acetate in these solvents was found to be 1.18 Å. If the intercept value i.e., -2.843 is equated to 3 log a + log(4π N/3000), the

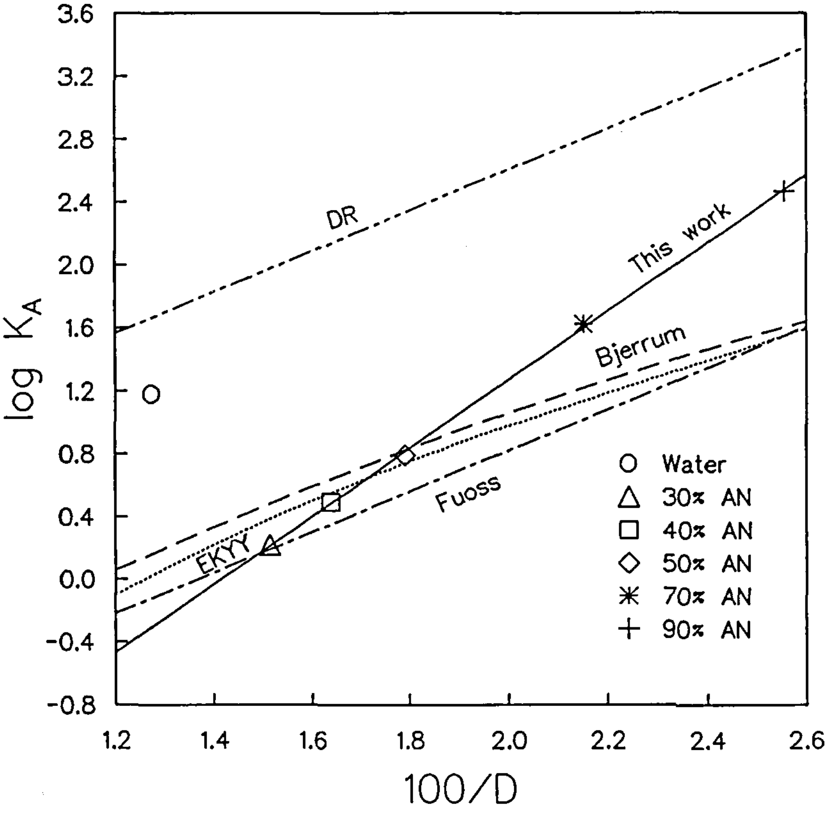

Figure 1 Log K_A versus 100/D for lithium acetate at 25°C.

'a' value was calculated to be 0.83 Å. Thus Fuoss theory predicts different 'a' values of 1.18 and 0.83 Å from the slope and intercept of the same plot for the same ion-pair studied. On the other hand the finite value of the intercept could be accommodated by the modified DR expression as

$$K_A = K_A^{\circ} \exp(|Z_+ Z_-| e^2/aDkT)$$

The experimental results then fit in to this expression as

$$\log K_A = -2.843 + 206.51/D$$

or

$$K_A = 0.00144 \exp(475.6/D) \quad \text{and} \quad a = 1.18\ \text{Å}$$

This is approximately 37% less than the crystallografic value of 1.87 Å (sum of the ionic radii of Li^+ and CH_3COO^- ions, 0.60 and 1.27 Å respectively[19]). Such a low value for other electrolytes are also reported in the literature[18,20]. Bodenseh and Ramsey[20] reported the 'a' value for tetrapropylammonium bromide obtained from the slope of the straight line of the plot of log K_A vs. $1/D$ was approximately 17% less than the corresponding minimum distance in the crystals. Similarly, for silver acetate in acetonitrile–water mixtures is 12% less than the crystallografic value. These deviations could be due to the fact that each ion-pair is an isolated entity in solution and the ion in that is bound or coordinated with only one ion of opposite charge whereas in the crystaline state it is coordinated with more than one oppositely charged ions. Figure 1 also shows the theoretical log K_A vs. $1/D$ plots corresponding to Bjerrum, Fuoss, DR and EKYY theories using 'a' = 1.87 Å.

References

1. L. G. Sillen and A. E. Martell, *Stability Constants of Metal-Ion Complexes, Supplement No. 1*, Chemical Society, London, Special Publication No. 25, 1971.
2. A. D'Aprano, F. Accascina and R. M. Fuoss, *J. Soln. Chem.*, **19**, 65 (1990).
3. R. M. Fuoss, *Proc. Natl. Acad. Sci. U.S.A.*, **77**, 34 (1980).
4. F. H. MacDougall and L. E. Topol, *J. Phys. Chem.*, **56**, 1090 (1952).
5. R. M. Fuoss and K. L. Hsia, *Proc. Natl. Acad. Sci. U.S.A.*, **57**, 1550 (1966); **58**, 1818 (1967).
6. R. Fernandez-Prini, *Trans. Faraday Soc.*, **65**, 3311 (1969).
7. R. M. Fuoss, *J. Phys. Chem.*, **78**, 1383 (1974); **79**, 525 (1975); **80**, 2091 (1976); **82**, 2427 (1978); *J. Soln. Chem.*, **7**, 771 (1978).
8. W. H. Lee and R. J. Wheaton, *J. Chem. Soc. Faraday Trans. II*, **74**, 743, 1456 (1978); **75**, 1128 (1979); *Acta Chem. Scand.*, **A34**, 307 (1980).
9. P. Beronius, *Acta Chem. Scand.*, **A34**, 309 (1980).
10. N. Bjerrum, *Kgl. Danske Vidensk, Selsk.*, **7**, 9 (1926).
11. R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).
12. J. T. Denison and J. B. Ramsey, *J. Am. Chem. Soc.*, **77**, 2615 (1955).
13. H. Falkenhagen, W. Ebeling and W. D. Kraeft, *Ionic Interactions*, S. Petrucci, Ed.; Academic Press, New York, Vol. 1, 1971, p. 104.
14. H. Yokoyama and H. Yamatera, *Bull. Chem. Soc. Jpn.*, **48**, 1770 (1975).
15. A. I. Vogel, *A Text Book of Practical Organic Chemistry*, Longman, London, 1955, p. 407.
16. J. Anathaswamy, B. Sethuram and T. Navaneeth Rao, *Indian J. Chem.*, **15A**, 9 (1977).
17. A. D'Aparno and R. M. Fuoss, *J. Phys. Chem*, **73**, 400 (1969).
18. U. G. K. Raju, B. Sethuram and T. Navaneeth Rao, *Bull. Chem. Soc. Jpn.*, **55**, 283 (1982).
19. J. Anathaswamy, B. Sethuram and T. Navaneeth Rao, *Electrochemica Acta*, **29**, 925 (1981).
20. H. K. Bodenseh and J. B. Ramsey, *J. Phys. Chem.*, **69**, 543 (1965).