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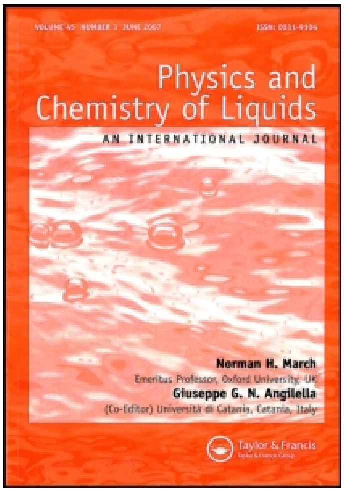

Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:
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To cite this Article Murthy, T. Srinivasa and Lakshminarayana, K.(1989) 'Conductance Studies of Alkali Metal Acetates in Acetic Acid-Acetonitrile Mixtures', Physics and Chemistry of Liquids, 20: 2, 167 — 176
To link to this Article: DOI: 10.1080/00319108908036403
URL: http://dx.doi.org/10.1080/00319108908036403

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Phys. Chem. Liq., 1989, Vol. 20, pp. 167–176
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CONDUCTANCE STUDIES OF ALKALI METAL ACETATES IN ACETIC ACID-ACETONITRILE MIXTURES

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(Received 11 January 1989)

Conductance behaviour of lithium, sodium and potassium acetates in 20% and 80% acetic acid-acetonitrile mixtures at 35° have been measured. The association constants were evaluated by Fuoss-Hsia equation of 20% acetic acid-acetonitrile mixtures by making use of TDC-12 Computer. Shedlovsky, Fuoss-Kraus extrapolation techniques were also employed to evaluate the association constants for these salts in both the solvent mixtures. The association constants obtained by these three methods were compared. The results were discussed in terms of various theories of ion pair formation i.e., Bjerrum, Fuoss, Denison-Ramsay, and Ebeling, Kraft, Yokoyama and Yamatera. Hydrodynamic radius was also calculated to understand the solvation of ions, in 20% and 80% acetic acid-acetonitrile mixtures.

KEY WORDS: Association constant, ion size, ion pairs.

INTRODUCTION

Conductance studies of electrolytes as well as ion pair formation in non-aqueous mixed solvents have appeared in several papers[1–5]. In order to explain the conductance behaviour of electrolytes when the dielectric constant of the medium is changed, a number of workers have undertaken the conductance measurements in mixed solvents. The conductance behaviour of Lithium bromide in acetone + bromo succinic acid was studied by Jones and Cunningham[2]. The solvent mixtures used are acetonitrile and methanol[4], acetone and propanol[3], acetonitrile + ethylene glycol[5] etc.

The present investigation is intended to study the conductance behaviour of electrolytes, when a solvent of high dielectric constant is mixed with a solvent of low dielectric constant (Acetic acid).

This paper deals with the conductance study of lithium, sodium and potassium acetates in acetic acid-acetonitrile mixtures. The conductance data is analysed for association parameters on the basis of Fuoss-Hsia equation, Fuoss-Kraus and Shedlovsky extrapolation techniques for the solvent mixture 20% acetic acid +80% acetonitrile. In case of other solvent i.e., 80% acetic acid +20% acetonitrile only Fuoss-Kraus and Shedlovsky extrapolation techniques are used. Different theories of ion-pair formation such as Bjerrum, Fuoss, Denison-Ramsey (DR), and Ebeling,

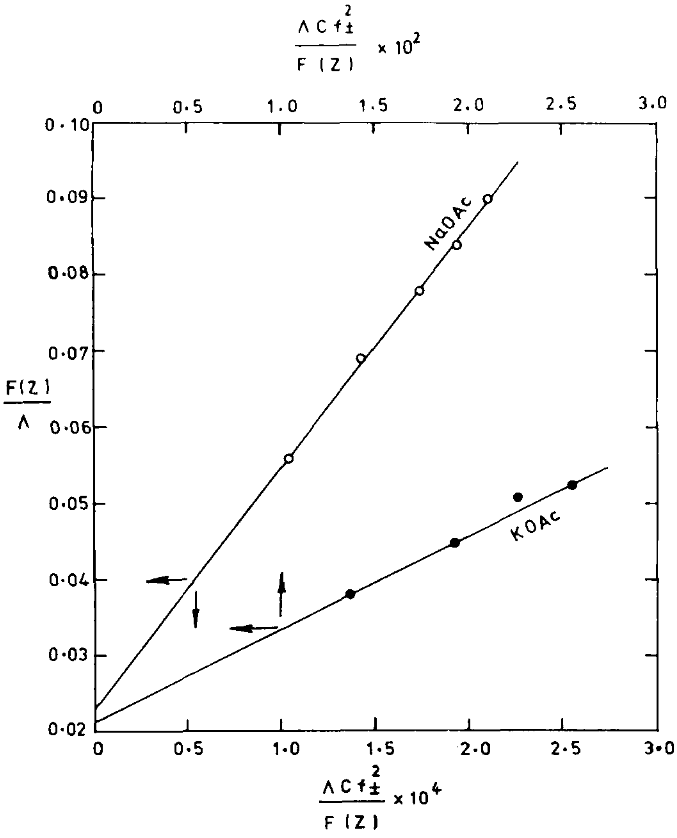

Figure 1 Fuoss-Kraus extrapolation (80% acetic acid + 20% acetoitrile).

Kraft, Yokoyama and Yamatera (EKYY) have been utilized to explain the behaviour of salts in these two solvent mixtures.

The Fuoss-Hsia equation[6] is one of the most complete conductance equations available today and contains $C^{3/2}$ term also. The Fuoss-Hsia equation with Fernandez-Prini coefficients[7] is used here which can be written as

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

Where S is the limiting law slope, and other symbols have their usual significance. The distance parameter 'a' in Fuoss-Hsia equation is replaced by Bjerrum critical distance (q) and the values of Λ_0 and K_A corresponding to

$$a = q = \frac{e^2}{2DkT}$$

are taken as the association parameters.

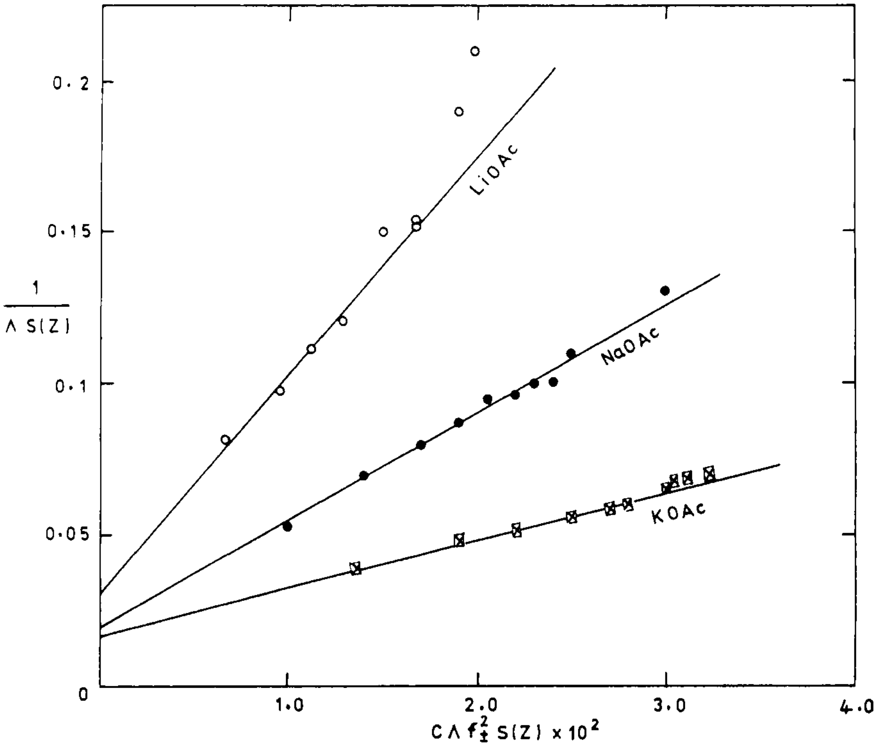

Figure 2 Shedlovsky extrapolation (80% acetic acid + 20% acetonitrile).

The other two methods to analyze the conductance data are Fuoss-Kraus and Schedlovsky extrapolation techniques.

Fuoss-Kraus extrapolation technique makes use of the equation

$$\frac{F(z)}{\Lambda} = \frac{1}{\Lambda_0} + K_a C \Lambda f_{\pm}^2/\Lambda_0^2 F(z) \tag{1}$$

where

$$F(Z) = 1 - Z[1 - Z(1 - \cdots)^{-1/2}]^{-1/2} \tag{2}$$

$$Z = S(\Lambda C)^{1/2}/\Lambda_0^{3/2} \tag{3}$$

where K_A = association constant.

$F(Z)$ is related to the degree of dissociation by the equation

$$\alpha = \frac{\Lambda}{\Lambda_0 F(Z)} \tag{4}$$

The procedure adopted to get K_A and Λ_0 is similar to that described by Narahari and Lakshminarayana[19].

The conductance data is also analysed using the Shedlovsky extrapolation technique which makes use of the equation

$$\frac{1}{\Lambda} s(z) = \frac{1}{\Lambda_0} + K_A C f_{\pm}^2 s(z)/\Lambda_0^2 \tag{5}$$

where

$$s(z) = 1 + Z + \frac{Z^2}{2} + \frac{Z^3}{8} + \cdots \tag{6}$$

and α is related to $s(z)$ by the equation

$$\alpha = \frac{\Lambda s(z)}{\Lambda_0} \tag{7}$$

The procedure adopted to evaluate Λ_0 and K_A is similar to the one adopted for Eq. (1).

To predict the ion size parameter different theories have been proposed such as Bjerrum[8], Fuoss[9], Denison-Ramsay[10] and EKYY[11,12]. Every theory of ion pair formation is based on a particular model and predicts an expression for the association constants in terms of the solvent properties such as dielectric constant and solute properties such as "ion size parameter (a). The ion size parameter required by each of the theories to predict the experimentally determined association constants are calculated. These are compared with the known interionic distances taken from crystallographic data. From the known values of the crystallographic data 'a' values are substituted in the association constant expressions for calculating theoretical K_A values, i.e., K_B, K_F, K_{DR} and K_{EKYY}. These values can also be compared with the experimental values of K_A.

To understand the solvation of ions hydrodynamic radius of particular electrolyte can be measured. This involves the equation

$$\left[\frac{1}{r_s^+} + \frac{1}{r_s^-}\right]^{-1} = \frac{0.820}{\Lambda_0 \eta}$$

The factor $[1/r_s^+ + 1/r_s^-]^{-1}$ can be calculated for an electrolyte from the experimentally obtained Λ_0 values in different solvents and known viscosities of concerned solvents.

EXPERIMENTAL

Preparation of Reagents

Acetic acid (BDH analar) is refluxed with acetic anhydride (BDH analar) for 12–15 hours and fractionally distilled and the middle fraction distilling between 115–116°C is collected.

Acetonitrile is refluxed with phosphorous pentoxide till there is no colour change and distilled. The distillate is refluxed with potassium carbonate for several hours and fractionally distilled. The middle fraction distilling between 79–80°C is collected for use. Sodium acetate anhydrous (BDH analar), potassium acetate (Riedel reagent grade), lithium acetate (Fluka) are used after drying at 110°C in an air oven.

Fresh solutions are prepared and measurements are carried out. Mixtures of acetic acid and acetonitrile are prepared by weight with freshly distilled solvents.

Conductivity Meter and Measurements

Conductivity bridge supplied by Toshniwal Instruments, India (Model CL 01/02A) was used. The resistance can be measured to an accuracy of 2% in the range from 0.1 ohm to 10 meg ohm. The conductivity cell is a special dip type which is intended for solutions of low conductance.

All measurements were made in the thermostat maintained at 35° ± 0.01°C. The cell constant was determined by making use of solutions of potassium chloride of known specific conductivity.

RESULTS AND DISCUSSION

The equivalent conductance of lithium acetate (LiOAc), sodium acetate (NaOAc) and potassium acetate (KOAc) in 80% acetic acid (AcOH) + 20% acetonitrile (ACN) and 20% AcOH + 80% ACN is presented in Table 1.

Table 1 Equivalent conductance of lithium, sodium and potassium acetates at 35°C.

C	*20% AcOH + 80% ACN*			*80% AcOH + 20% ACN*		
	LiOAc	*NaOAc*	*KOAc*	*LiOAc*	*NaOAc*	*KOAc*
10	35.89	79.79	97.50	10.100	15.740	22.500
20	22.87	58.91	86.04	8.310	12.180	18.280
30	23.39	52.01	79.20	6.976	10.540	15.670
40	20.46	47.00	74.98	6.401	9.471	14.540
50	18.62	43.83	72.13	5.703	8.650	13.780
60	17.94	40.46	67.41	5.346	7.671	12.690
70	16.20	37.87	64.46	4.966	7.272	12.040
80	15.31	36.54	61.08	4.822	6.822	11.370
90	14.80	34.68	60.59	4.619	–	10.970
100	14.39	33.47	58.56	4.413	5.400	10.810
200	8.882	24.43	44.70	3.446	3.640	8.441
300	8.543	21.08	38.41	2.917	–	7.433
400	7.496	18.82	35.82	2.832	–	6.933
500	6.893	17.23	32.98	2.456	–	6.422
600	6.304	15.41	30.61	2.337	–	–
700	5.871	14.38	28.89	2.237	–	–
800	5.533	13.75	27.34	2.156	–	–
900	5.214	12.80	25.93	–	–	–
1000	4.991	12.41	24.04	2.003	–	–

Table 2 Λ_0 and K_A values obtained from Fuoss-Hsia, Fuoss-Kraus and Shedlovsky techniques at 35°.

	Fuoss-Hsia equation		*Fuoss-Kraus extrapolation technique*		*Shedlovsky technique*	
	Λ_0	K_A	Λ_0	K_A	Λ_0	K_A
			20% AcOH + 80% ACN			
LiOAC	56.38	1157.96	47.62	667.1	62.4	1494
NaOAc	124.90	1233.21	142.8	182.2	133.4	1480
KOAc	126.64	1310.43	119.1	288.6	131.58	361
			80% AcOH + 20% ACN			
LiOAc	—	—	—	—	32	7.313×10^3
NaOAc	—	—	43.48	5.91×10^5	50	8.930×10^3
KOAc	—	—	47.62	2.834×10^3	58.82	5.768×10^3

The conductance data of the three salts in 20% AcOH + 80% ACN is analysed by Fuoss-Hsia equation on TDC 12 computer, Osmania University, Hyderabad. The computer programme is similar to that developed by Kay[13] and subsequently supplimented by Fuoss[14]. Since this procedure is tedious and requires long computer times, the procedure described by Justice[15] is adopted. According to this method the ion-size parameter (a) in Fuoss-Hsia equation is replaced by 'q' and the Λ_0 and K_A values corresponding to $a = q = e^2/DkT$ were presented in Table 2.

Examination of these results shows that Λ_0 increases from lithium acetate to potassium acetate where as K_A values in case of lithium and sodium acetates are greater than potassium acetate. So it may be concluded that in the case of potassium acetate the probability of ion pair formation is less when compared to LiOAc and NaOAc.

The conductance data is also analysed on the basis of Fuoss-Kraus and Shedlovsky extrapolation techniques to get Λ_0 and K_A. These are presented in Table 2 along with the values got for 20% AcOH + 80% ACN for all the three salts for comparison. In both cases of extrapolation techniques the limiting Debye-Huckel law equation for the activity coefficients was made use of.

The Λ_0 values obtained from the extrapolation techniques differ from the values obtained from Fuoss-Hsia equation to different extents but the deviation in case of Fuoss-Kraus extrapolation is more than in the case of Shedlovsky technique. The K_A values obtained by all the techniques are agreeing with in reasonable limits except in case of lithium acetate from Fuoss-Kraus technique. This value is low when compared to the values of K_A from the other two techniques.

Inspite of the deviations between Fuoss-Hsia and Shedlovsky techniques, the Fuoss-Hsia equation is better to evaluate K_A values.

In case of solutions of three acetates in 80% AcOH + 20% ACN mixture, if the association parameters obtained by Fuoss-Kraus and Schedlovsky methods are examined, it shows that the Λ_0 values obtained by both methods are in reasonable agreement, in that they are of same order though differing in magnitude. If this is compared with the values in pure acetic acid[18], it may be concluded that when one

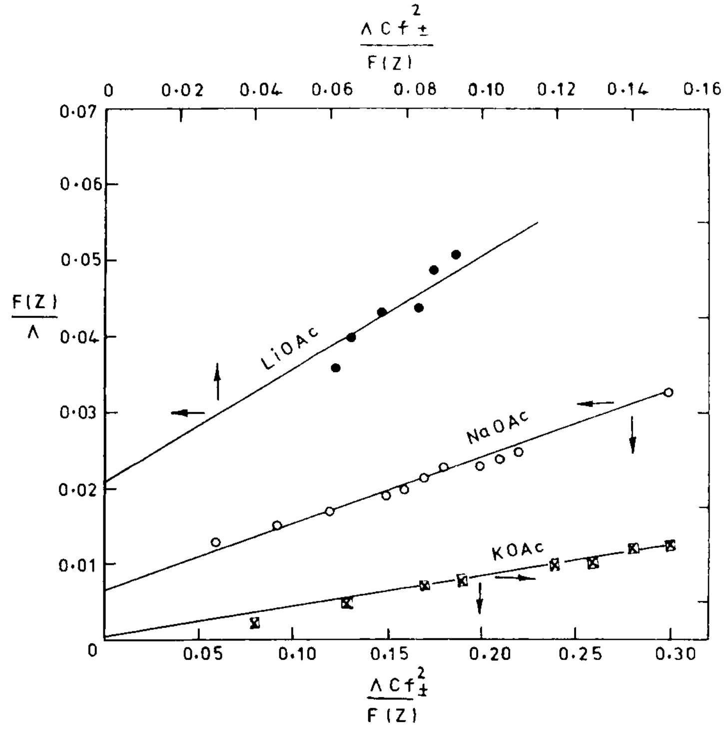

Figure 3 Fuoss–Kraus extrapolation (20% acetic acid + 80% acetonitrile).

changes the solvent from pure acetic acid to 20% AcOH + 80% ACN, there is an increase in Λ_0 values and decrease in K_A for all the three salts studied indicating that ion-association decreases with increase of solvent dielectric constant.

The ion size parameters required by various theories to predict experimentally obtained K_A values of LiOAc, NaOAc and KOAc in the two solvents were presented in Table 3. These values are compared with calculated ones. For this purpose the theoretical '*a*' values for the alkali acetates were calculated. The crystallographic radii

Table 3 '*a*' values (in Å) predicted by Bjerrum, Fuoss, DR and EKYY theories.

Solvent	*Salt*	*Bjerrum*	*Fuoss*	*DR*	*EKYY*	K_A
80% AcOH + 20% ACN	LiOAc	3.07	Very low values	4.20	0.3152	7.313×10^3
	NaOAc	2.99	Very low values	4.11	0.6255	8.93×10^3
	KOAc	3.12	Very low values	4.32	1.81	8.769×10^3
20% AcOH + 80% ACN	LiOAc	1.47	2.62	2.60	3.25	1.158×10^3
	NaOAc	1.44	2.39	2.58	5.7	1.233×10^3
	KOAc	1.76	2.28	3.20	4.69	3.10×10^2

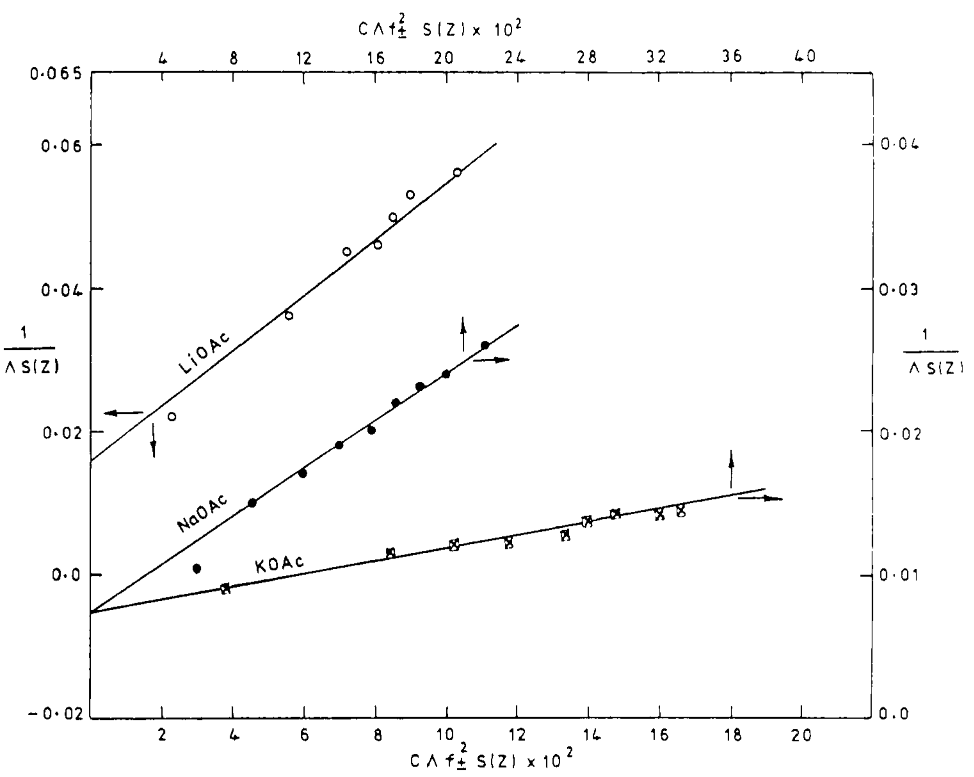

Figure 4 Shedlovsky extrapolation (20% acetic acid + 80% acetonitrile).

of Li$^+$, Na$^+$, K$^+$ ions were taken as 0.60, 0.95, 1.33 Å. Anantaswamy[16] has proposed the crystallographic radius of acetate ion equal to 1.27 Å. From this value of the crystallographic radius of acetate ion, the ion size parameters (a) for LiOAc, NaOAc and KOAc can be obtained as the sum of crystallographic radius of the constituent ions. The values worked out to be 1.87, 2.22 and 2.60 Å for LiOAc, NaOAc and KOAc respectively. From the results given in Table 3 it is evident that Bjerrum and DR theories predict higher values for all the salts in 80% AcOH + 20% ACN system where as Fuoss theory predicts very low values for all of them. These values are very low when compared with the minimum expected value of 1.87, 2.22 and 2.60 Å. But in case of 20% AcOH + 80% ACN system the Fuoss and DR theories predict slightly higher values than minimum expected, whereas the Bjerrum theory predicts values which are less than the minimum expected. In view of the above discussion it can be concluded that none of the theories predict correctly the state of the salts in the solvent systems studied.

The experimental K_A values together with theoretical K values for different theories of ion-pair formation are given in Table 4. An examination of the results shown that in case of 80% AcOH + 20% ACN the K_A is less than the theoretical K value. It implies that in this solvent the ion solvent interactions are very strong (The same was observed in case of pure acetic acid[18] also). Kay *et al.*,[17] pointed out that in such

Table 4 Theoretical values of association constants according to different theories along with the experimental K_A values at 35°C.

Salt	K_A	K_B	K_F	K_{DR}	K_{EKYY}
			80% *AcOH* + 20% *ACN*		
LiOAc	7.313×10^3	1.538×10^6	7.543×10^{18}	4.571×10^{20}	6.956×10^4
NaOAc	8.930×10^3	1.538×10^5	6.866×10^{15}	2.512×10^{17}	7.228×10^3
KOAc	5.768×10^3	3.691×10^4	3.215×10^{13}	7.244×10^{14}	1.874×10^3
			20% *AcOH* + 80% *ACN*		
LiOAc	1153.0	217.5	2.385×10^8	1.445×10^{10}	9.7
NaOAc	1283.0	117.4	2.011×10^6	3.589×10^8	4.864
KOAc	310.4	74.67	1.324×10^5	2.818×10^7	2.397

systems, all the ion pairs will be solvent separated ion pairs (SSP) and the distance of closest approach will be considerably greater than the sum of crystallographic radius of the ions. This indicates that ion-solvent interactions are stronger than ion-ion interactions in this system.

In case of 20% AcOH + 80% ACN system experimental K_A values are greater than theoretical K_A values obtained by Bjerrum theory. This type of behaviour encountered, can occur for several reasons. The most obvious explanation is dielectric saturation, but this explanation gives wrong size dependence. Another explanation is the existance of two types of ion-pairs i.e., contact ion pairs (CIP) and solvent separated ion-pairs (SSIP). This formation can be regarded like this—

$$\begin{tikzcd}
M^+S_{(m)} + A^-(S)_n \arrow[r, shift left, "k_1"] & M^+SA^-S_{(m+n)-1} \arrow[l, shift left] \arrow[d, shift left, "k_2"] \\
 & M^+A^-S_{(m+n)-1} + S \arrow[u, shift left]
\end{tikzcd}$$

where S is the solvent.

All over association constant (K) for this process may be defined by

$$K = \frac{\sum C(\text{ion-pairs})}{C(M^+) + C(A^-)}$$

$$= \frac{C(M^+SA^-) + C(M^+A^-)}{C(M^+) + C(A^-)}$$

which can be written as $K = k_1[1 + k_2/C_s]$.

Where C_s is the molar concentration of the solvent. Since K involves the product of two association constants, very large values can be obtained if k_2 is appreciable. K can be identified with the measured association constant K_A assuming that neither type of ion pair is conducting. So in case of 80% AcOH + 20% ACN system, the high values of the association constant are due to the formation of contact ion-pairs. This behaviour is also observed in pure acetic acid[18] and in case of 20% AcOH + 80%

Table 5 Hydrodynamic radii $[1/r_s^+ + 1/r_s^-]^{-1}$ values for LiOAc, NaOAc and KOAc at 35°.

Salt	*in* 80% *AcOH* + 20% *ACN*	*in* 20% *AcOH* + 80% *ACN*
LiOAc	3.559	3.121
NaOAc	2.278	1.409
KOAc	1.936	1.390

ACN the higher experimental K_A values are due to the formation of both SSIP and CIP.

The hydrodynamic radius values calculated were presented in Table 5. If we compare these values with pure acetic acid[18] the values decrease from pure acetic acid to 20% AcOH + 80% ACN. The higher values of hydrodynamic radii in pure acetic acid[18] indicates that ions are more solvated in AcOH than in mixed solvents. This may be concluded that addition of acetonitrile causes in the decrease of solvation of ions.

From the study of conductance behaviour it may be concluded that, the behaviour of lithium, sodium and potassium acetates in 80% AcOH + 20% ACN and 20% AcOH + 80% ACN the salts are present as ion-pairs, and if we compare this behaviour with pure acetic acid[18]. This tendency decreases when one changes the dielectric constant of the medium by mixing acetic acid with acetonitrile.

References

1. A. D. Aprano, D. I. Donato and E. Caponetli, *Ann. Chim. (Rome)*, **66**, 185, (1976).
2. C. W. Jones and C. M. Cunningham, *Adv. Chem. Ser.*, **155**, 244, (1976).
3. D. F. Evans and M. I. Mcelroy, *J. Soln. Chem.*, **4**, 413, (1975).
4. A. D. Aprano *et al.*, *J. Chem. Soc. Faraday Trans I*, **72**, 79, (1976).
5. K. K. Bose and K. K. Kundu, *Indian J. Chem.* **17A**, 122, (1979).
6. R. M. Fuoss and K. L. Hsia, *Proc. Natl. Acad. Sci. U.S.A.* **57**, 1550, (1967); **58**, 1818, (1967).
7. R. Fernandez-Prini Trans, *Faraday Soc.*, **65**, 3311, (1969).
8. N. K. Bjerrum. Danske Vidensk selsk. 7, Part 9, (1926).
9. R. M. Fuoss, *J. Amer. Chem. Soc.*, **80**, 5059, (1958).
10. J. T. Denison and J. B. Ramsey, *J. Amer. Chem. Soc.*, **77**, 2615, (1955).
11. H. Falkenhagen, W. Ebeling and W. D. Kraft, *Ionic Interactions*, Vol. I. P. 104, (Academic Press, New York, 1971).
12. H. Yokoyama and H. Yamatera, *Bull. Chem. Soc.*, *(Japan)* **48**, 1770, (1975).
13. R. L. Kay, *J. Amer. Chem. Soc.*, **82**, 2099, (1960).
14. R. M. Fuoss, *J. Phys. Chem.*, **79**, 525, (1975).
15. J. C. Justice, *Electro. Chim. Acta*, **16**, 701, (1971).
16. J. Anantaswamy Ph.D. Thesis, Osmania University (1978).
17. R. L. Kay, D. F. Evans and M. A. Matesich, *Solute-Solvent Interactions* (Marcel Dekker Inc., New York, 1976) Chapter 10.
18. T. Srinivasa Murthy and K. Lakshminarayana Paper communicated to J. Electrochem. Soc. India.
19. J. Narahari and K. Lakshminarayana, *Bull. Electro. Chem.*, Vol. 2 (5) 525-27, (1986).