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Conductometric Study of Ion-Ion and Ion-Solvent Interactions. I. Conductances of Silver Acetate in 0—50% (w/w) Methanol–Water Mixtures at 35 °C

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Conductances of the solutions of silver acetate in 0 to 50% (w/w) methanol–water mixtures were measured at 35 °C. The association constants and molar conductances at infinite dilution were calculated using the Shedlovsky extrapolation technique and the Fuoss-Hsia equation with Fernandez-Prini coefficients. The log K_A *vs.* $1/D$ plot passes through the origin in accordance with the Denison-Ramsey theory of ion-pair formation. The results were interpreted in terms of the equilibrium between the solvent separated ion-pairs (SSIP) and contact ion-pairs (CIP).

Ion-association increases from lithium to cesium in solutions of alkali metal halides, and from cesium to lithium in solutions of alkali metal acetates, hydroxides and fluorides.[1] Ion-pair formation in solutions of alkali metal halides and halides of small metal ions has been extensively investigated[2] conductometrically both in aqueous and aquo-organic solvents. However, such studies on acetates[3] of small metal ions are very few. The electrical conductances of silver acetate were thus measured in order to understand the reverse trend of ion-association in acetates *etc.*, as compared to that in halides. The conductance data was analysed using the Fuoss-Hsia equation[4] with Fernandez-Prini coefficients[5] to evaluate the association parameters. The results were interpreted in terms of the equilibrium between the solvent separated ion-pairs (SSIP) and contact ion-pairs (CIP). The applicability of various theories of ion-pair formation such as those of Bjerrum,[6] Fuoss,[7] Denison-Ramsey[8] (DR), and Ebeling-Kraeft-Yokoyama and Yamatera[9,10] (EKYY) has been discussed.

Experimental

Silver acetate (Fluka: purum) was used after repeated recrystallizations from ethanol and drying. Methanol (BDH, electrolytic grade) was used without further purification. The specific conductance was found to be within $2-5\times10^{-8}$ S cm^{-1}. Water with a specific conductance less than 5×10^{-7} S cm^{-1} was used. Due correction was made for the solvent conductance in the conductance values of all the salt solutions. All solutions were prepared freshly just before use and protected from light by covering with a thick dark cloth. The experimental arrangement was the same as reported earlier.[11] The overall accuracy of the measured molar conductances was better than ±0.05%.

Results and Discussion

The molar conductances of the solutions of silver acetate in water and 10, 20, 30, 40, and 50% (w/w) methanol–water mixtures at 35 °C are given in Table 1. The dielectric constants and viscosities of methanol–water mixtures were taken from literature.[12a,b]

The conductance data were first analysed using the Shedlovsky extrapolation technique,[13]

$$1/\Lambda S(Z) = 1/\Lambda_0 + (K_A/\Lambda_0^2)(c\Lambda y_\pm^2 S(Z)), \tag{1}$$

where Λ and Λ_0 are the molar conductances at concentrations c mol dm^{-3} and zero (infinite dilution), respectively.

$$S(Z) = 1 + Z + Z^2/2 + Z^3/8 + \cdots, \tag{2}$$

$$Z = s(\Lambda c)^{1/2}/\Lambda_0^{3/2}, \tag{3}$$

s is the limiting law slope and K_A is the association constant. The activity coefficient ($y_\pm$) was calculated using the Debye-Hückel limiting law.[14]

$$\log y_\pm = -A(\alpha c)^{1/2}, \tag{4}$$

where

$$A = 1.8246\times10^6/(DT)^{3/2}. \tag{5}$$

The degree of dissociation (α) is related to $S(Z)$ by

$$\alpha = \Lambda S(Z)/\Lambda_0. \tag{6}$$

The association parameters obtained by this method are given in Table 2.

The conductance data was then analysed using the Fuoss-Hsia equation[4] with Fernandez-Prini coefficients[5] as in the following.

$$\Lambda = \Lambda_0 - s(\alpha c)^{1/2} + E\alpha c\ln(\alpha c) + J_1(\alpha c) - J_2(\alpha c)^{3/2} - K_A\Lambda y_\pm^2\alpha c \tag{7}$$

where the various symbols have their usual meanings. The activity coefficients ($y_\pm$) were calculated by the equation,

$$-\log y_\pm = A(\alpha c)^{1/2}/\{1+Ba(\alpha c)^{1/2}\}. \tag{8}$$

Equation 7 was solved as originally described by Justice[15] and subsequently clarified by Pethybridge and Spiers,[16] and Kubota and Yokoi.[17] The procedure envisages the replacement of the distance of closest approach of ions (a) by the Bjerrum critical distance (q). The standard deviation (σ) values were calculated from the relation:

$$\sigma = \{\sum(\Lambda_{\mathrm{exp}}-\Lambda_{\mathrm{cal}})^2/(N-3)\}^{1/2}. \tag{9}$$

All the calculations were done on TDC-12 computer and the results are given in Table 3.

We see from Table 2 that Λ_0 values obtained by the Shedlovsky method are higher than those obtained by use of the Fuoss-Hsia equation by 0.1—1.4%. The deviations in K_A values are 7.7—16.4% (50% methanol). Thus, the Λ_0 values obtained by the Shedlovsky method deviate to a lesser extent than the corresponding K_A values. Therefore, the Shedlovsky method may be used as a rapid first hand tool for evaluating Λ_0 values, even though the K_A values obtained by this method are not so reliable.

The functional dependence of $\log K_A$ on $1/D$ was used to test the applicability of the various theories

Table 1. Molar conductivities of silver acetate in methanol-water mixtures at 35 °C

$10^4 c$ / mol dm^{-3}	Λ / S cm^2 mol^{-1}	$10^4 c$ / mol dm^{-3}	Λ / S cm^2 mol^{-3}
50% Methanol		40% Methanol	
D=53.21		D=57.720	
η=0.01129 poise		η=0.01143 poise	
49.708	53.537	49.200	58.197
42.607	55.514	42.172	60.101
37.281	57.301	36.900	61.654
33.139	58.993	32.800	63.003
29.825	59.956	29.500	64.082
27.114	61.007	26.837	65.006
24.854	62.002	24.600	65.901
22.942	62.805	22.708	66.702
21.304	63.588	21.086	67.385
19.883	64.391	19.680	67.977
18.641	64.951	18.450	68.535
30% Methanol		20% Methanol	
D=62.20		D=66.52	
η=0.01119 poise		η=0.01005 poise	
48.230	65.709	48.956	74.754
41.340	66.472	41.654	76.773
36.173	68.963	36.447	78.214
32.153	70.002	32.398	79.425
28.938	71.221	29.158	80.418
26.307	72.143	26.507	81.325
24.115	73.001	24.298	82.101
22.260	73.616	22.429	82.802
20.670	74.302	20.827	83.417
19.292	74.861	19.439	84.001
18.086	75.259	18.224	85.487
10% Methanol		Water	
D=70.68		D=75.03	
η=0.00866 poise		η=0.00725 poise	
48.335	87.302	21.094	114.524
41.430	88.998	18.080	115.532
36.251	90.471	15.820	116.426
32.223	91.532	14.063	117.157
29.001	92.506	12.656	117.783
26.365	93.321	11.506	118.301
24.168	94.077	10.547	118.785
22.309	94.701	9.735 (6)	119.202
20.715	95.325	9.040 (2)	119.629
19.334	95.833	8.437 (5)	119.938
18.126	96.316		

of ion-pair formation. A linear plot passing through the origin is expected according to the Denison-Ramsey (DR) theory whereas Bjerrum and EKYY theories predict curves which are concave downwards. The Fuoss theory predicts a straight line with a finite intercept. The least square regression line required by the experimental points has a correlation coefficient of 0.997 with slope and intercept values of 120.4 and −0.0453 respectively (Fig. 1). When we neglect the small intercept (−0.0453), the plot of $\log K_A$ *vs.* $1/D$ becomes a straight line passing through the origin. The following simple expression of DR theory closely reproduces the association constant data for silver acetate in 0—50% (w/w) methanol–water mixtures at 35 °C.

Table 2. Λ_0 and K_A values calculated according to the Shedlovsky method and their deviations from the corresponding values obtained by use of the Fuoss-Hsia equation

Solvent	Λ_0 / S cm^2 mol^{-1}	Deviation in Λ_0/%	K_A / dm^3 mol^{-1}	Deviation in K_A/%
50% MeOH	80.888	1.36	132.0	16.4
40% MeOH	81.453	0.963	93.36	14.8
30% MeOH	86.438	0.704	68.71	13.6
20% MeOH	95.667	0.595	57.05	12.8
10% MeOH	105.84	0.377	37.93	11.8
Water	125.81	0.111	31.89	7.70

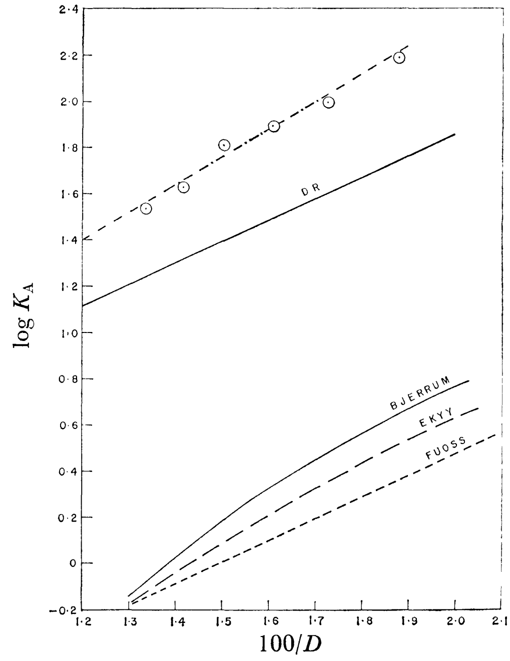

Fig. 1. log K_A *vs.* 100/D.

$$\log K_A = 120.4/D \tag{10}$$

or

$$K_A = \exp(277/D). \tag{11}$$

By comparing Eq. 10 with DR theory expression, we have

$$\log K_A = |Z_+Z_-|e^2/aDkT. \tag{12}$$

The distance of the closest approach of ions was found to be 2.02 Å. The ion-size parameters (a_K) required by various theories to give the experimental K_A values were also calculated. While the Fuoss, Bjerrum and EKYY theories require the a values to lie in the range 0.6—0.8 Å, the DR theory requires thom to be 2.01± 0.03 Å. Since the ionic radii of Ag^+ itself is 1.26 Å, an a value of 0.8 Å for silver acetate is incompatible. The DR theory is in better agreement with experimental results.

The ion-size parameter of the silver acetate was calculated[18] to be 2.53 Å from the known crystallographic data. The theoretical association constant

TABLE 3. ASSOCIATION PARAMETERS OF SILVER ACETATE OBTAINED BY USE OF THE FUOSS-HSIA EQUATION

Solvent	q/Å	Λ_0 / S cm^2 mol^{-1}	K_A / dm^3 mol^{-1}	σ	$\Lambda_0\eta$
50% Methanol	5.095	82.006	157.9	0.121	0.9267
40% Methanol	4.697	82.245	109.6	0.072	0.9376
30% Methanol	4.358	87.051	79.49	0.097	0.9750
20% Methanol	4.075	96.240	65.40	0.382	0.9672
10% Methanol	3.835	106.24	43.01	0.054	0.9200
Water	3.613	125.95	34.55	0.091	0.9131

values for silver acetate according to Bjerrum, Fuoss, Denison-Ramsey (K_{DR}) and EKYY theories were calculated for various dielectric constants using the crystallographic ion-size parameter value, *i.e.* 2.53 Å. The plots of the logarithms of these theoretical association constants against $1/D$ are also shown in Fig. 1. It is evident that all the theories predict lower association constants than those obtained experimentally. However, K_{DR} values are comparatively nearer to the experimental values. The experimental results are in better agreement with the DR theory than the other theories. The same was concluded above from the nature of log K *vs.* $1/D$ plots. The experimental values are higher than the theoretical values, *i.e.* K_{DR}. This could be explained[19] by assuming the existence of two types of ion-pairs *i.e.* solvent separated ion-pairs (SSIP) and contact ion-pairs (CIP) in equilibrium. This involves a two step process:

$$\begin{array}{c} M^+(S)_m + A^-(S)_n \overset{K_1}{\rightleftharpoons} \begin{array}{c} M^+SA^-(S)_{m+n-1} \\ \text{(SSIP)} \\ \Big\updownarrow {\scriptstyle K_2} \\ M^+A^-(S)_{m+n-1} + S, \\ \text{(CIP)} \end{array} \end{array}$$

where S denotes a solvent molecule and m and n are the solvation numbers of ions. The overall association constant K_t for this process could be related to K_1 and K_2 by

$$K_t = K_1(1+K_2/[S]). \qquad (13)$$

The values of K_2 were calculated by substituting the association constant values calculated using the DR theory with an a value of 2.53 Å for K_1 and experimentally obtained K_A values for K_t in Eq. 13. The results are given in Table 4. In Eq. 13, S was taken as the concentration of water in methanol–water mixtures since the medium activity coefficient data[20] shows that both Ag^+ and CH_3COO^- are preferentially hydrated in methanol–water mixtures.

The association constants of silver acetate increased from 34.55 in water (D=75.03) to 157.9 dm^3 mol^{-1} in 50% methanol (D=53.21). The values are unusually high as compared to those of alkali metal halides in these solvent systems. In a recent study[16] the K_A values of alkali metal fluorides in water at 25 °C were found to be 0.07 (CsF), 0.16 (RbF), 0.14 (KF), 0.47 (NaF) and 1.78 (LiF). In aqueous solutions[21] potassium, rubidium and cesium hydroxides are completely dissociated whereas lithium hydroxide (K_A= 0.81 dm^3 mol^{-1}) shows clear evidence of association. An unusually high association constant of 200 dm^3 mol^{-1} was reported[22] for silver hydroxide. Similarly silver nitrate was found to be more associated than alkali metal nitrates in both methanol and ethanol.[23] This shows that ion-pair formation is higher in silver salts than in the corresponding alkali metal salts.

TABLE 4. EQUILIBRIUM CONSTANTS FOR THE CONVERSION OF SSIP INTO CIP

Solvent	$K_1=K_{DR}$ / dm^3 mol^{-1}	$K_2=[S](K_t/K_1-1)$ / dm^3 mol^{-1}
50% Methanol	56.12	50.38
40% Methanol	40.97	55.87
30% Methanol	31.36	59.69
20% Methanol	25.06	71.54
10% Methanol	20.74	53.69
Water	17.40	54.76

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