Bull. Chem. Soc. Jpn., **55**, 293—296 (1982)

Conductometric Study of Ion-Ion and Ion-Solvent Interactions. III.[†] Conductances of Silver Acetate in Acetonitrile–Water Mixtures at 25 °C

U. G. Krishnam Raju, Bangalore Sethuram, and T. Navaneeth Rao*

Department of Chemistry, Osmania University, Hyderabad-500 007, India

(Received March 7, 1981)

Conductances of the solutions of silver acetate in 10 to 90% (w/w) acetonitrile–water mixtures were measured at 25 °C. The molar conductances at infinite dilution and association constants were calculated, using the Fuoss-Hsia equation with Fernandez-Prini coefficients. There was no association in 10 and 20% acetonitrile. The log K_A *vs.* $1/D$ plot was a straight line with negative intercept in accordance with the modified Denison-Ramsey theory of ion-pair formation. Walden products were also calculated. From these results it was concluded that silver ions are preferentially solvated by acetonitrile whereas acetate ion is hydrated in acetonitrile–water mixtures.

Existing literature indicates that in aqueous solutions of alkali metal halides ion-association increases from lithium to caesium whereas in solutions of their acetates, hydroxides and fluorides a reverse trend is observed *i.e.*, ion-association increases from caesium to lithium.[1] Eventhough ion-pair formation in solutions of alkali metal halides and halides of small metal ions have been extensively investigated[2] both in aqueous and aquo-organic solvents, such studies on acetates[3] of small metal ions are sporadic. The extended Fuoss-Hsia equation[4] with Fernandez-Prini coefficients,[5] which is based on the hard spheres model can be used for the analysis of the conductance data. A number of papers have been published by Lee and Wheaton[6] and Fuoss[7] proposing different models for ion-pair formation and new conductance equations. Beronius[8] comments that these equations based on solvent separated as well as contact ion-pairs are not exceptions to the Fuoss-Hsia conductance equation as they yield identical association constants when the values are above 15. Therefore in the present investigation, the electrical conductances of silver acetate in 10, 20, 40, 60, 80, and 90% (w/w) acetonitrile–water mixtures at 25 °C were measured and analysed using the Fuoss-Hsia equation[4] with Fernandez-Prini coefficients[5] with a view to calculate the association constants. The applicability of various theories of ion-pair formation such as those of Bjerrum,[9] Fuoss,[10] Denison-Ramsey (DR),[11] and Ebeling-Kraeft-Yokoyama-Yamatera(EKYY)[12,13] has also been discussed. The Walden products were calculated and the possible ion-solvent interactions were also discussed.

Experimental

Silver acetate (Fluka:Purum) was used after repeated recrystallisations from ethanol and drying. Acetonitrile (BDH) was purified as described by Vogel[14] and had a specific conductance of less than 1.0×10^{-7} S cm^{-1}. Water with a specific conductance less than 5.0×10^{-7} S cm^{-1} was used. Due correction was made for the solvent contribution to the conductance values of all the salt solutions. All the solutions were prepared freshly just before use and protected from light by covering the reaction vessel with a thick dark cloth. The experimental arrangement was the same as reported earlier.[15] 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 10, 20, 40, 60, 80, and 90% (w/w) acetonitrile–water mixtures at 25 °C are given in Table 1. The dielectric constants and viscosities of the solvent mixtures were taken from literature.[16]

The conductance data was analysed using the Fuoss-Hsia equation[4] with Fernandez-Prini coefficients[5]

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

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

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

Equation 1 was solved as originally described by Justice.[17] This procedure envisages the replacement of the distance of closest approach of ions (a) by the Bjerrum critical distance (q) term. The standard deviation (σ) values were calculated from the relation

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

All these calculations were carried out on a TDC-12 computer and the results are given in Table 2.

The functional dependence of log K_A *vs.* $1/D$ was used to test the applicability of various theories of ion-pair formation. Figure 1 shows that the association constants of silver acetate in water is very high and far off from the values in the other solvent mixtures. It is observed that there is no association in 10 and 20% acetonitrile–water mixtures. Strechlow and Koepp[18] have shown that silver ions are preferentially solvated by acetonitrile molecules than water. The solubility of silver acetate is more in acetonitrile–water mixtures than in pure solvents. Further the solubility is least in pure acetonitrile. This could be due to the non-solvation of acetate ion in acetonitrile. When small amounts of acetonitrile were added to aqueous solutions of silver acetate, Ag^+ ion gets heavily solvated by acetonitrile and prevents the acetate ions from reaching the Ag^+ ions so that no association could be found in 10 and 20% acetonitrile–water

---

[†] Part II: *Rev. Roum. Chim.* (Communicated).

Table 1. Conductances of silver acetate in acetonitrile-water mixtures at 25 °C

$\frac{10^5 c}{\text{mol dm}^{-3}}$	S cm^2 mol^{-1}	$\frac{10^5 c}{\text{mol dm}^{-3}}$	S cm^2 mol^{-1}
10% Acetonitrile		20% Acetonitrile	
649.41	69.688	950.06	66.120
556.64	69.875	814.33	66.441
487.06	69.984	712.54	66.676
389.65	70.256	570.03	66.990
324.71	70.354	475.03	67.307
278.32	70.352	415.65	67.566
243.53	70.536	332.52	67.714
194.82	70.648	277.10	67.930
162.35	70.726	237.51	68.096
139.16	70.790	207.82	68.195
121.76	70.847	166.26	68.423
97.410	70.904	138.53	68.574
81.180	70.941	103.91	68.755
65.820	70.959	83.130	68.898
		71.660	69.024
40% Acetonitrile		60% Acetonitrile	
708.42	70.993	940.57	75.806
566.74	71.913	806.20	76.886
472.28	72.516	705.42	77.880
404.81	73.145	564.34	79.367
354.21	73.606	470.29	80.313
283.37	74.216	403.10	81.094
257.61	74.563	352.71	81.722
220.81	74.847	282.17	82.814
192.25	75.180	235.14	83.556
154.57	75.638	201.55	84.118
128.80	76.035	176.36	84.642
110.40	76.240	141.09	85.322
96.600	76.559	117.57	85.797
85.870	76.747	88.180	86.558
64.400	77.087	75.050	86.907
80% Acetonitrile		90% Acetonitrile	
940.20	86.643	689.95	72.300
806.20	88.584	591.39	74.140
705.42	90.206	517.46	75.869
564.34	92.659	413.97	78.669
470.29	93.617	344.98	80.631
403.10	95.886	295.69	81.883
352.71	96.989	258.73	83.009
282.17	98.819	206.99	84.899
235.14	100.05	172.49	86.297
201.55	101.12	147.85	87.289
176.36	102.10	129.37	88.219
141.09	103.14	103.49	89.398
117.57	104.16	86.240	90.330
88.160	105.41	67.080	91.630
75.050	106.97	54.880	92.212

Table 2. Association parameters for silver acetate obtained using Fuoss-Hsia equation in acetonitrile-water mixtures for $a=q$ at 25 °C

Solvent	Λ_0	K_A	σ
Water[a]	102.4	32.90	0.304
40% AN	79.75	4.347	0.054
60% AN	91.24	10.17	0.077
80% AN	113.7	25.43	0.338
90% AN	100.2	43.76	0.335

a) Ref. 20.

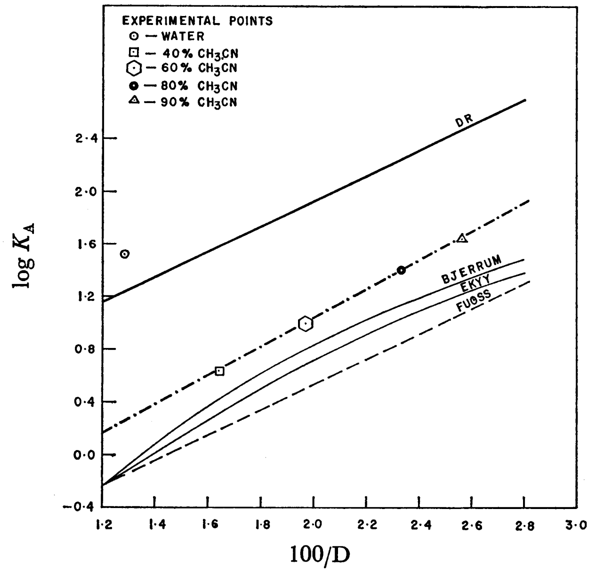

Fig. 1.

mixtures. At higher percentages of acetonitrile, the decrease in the dielectric constant dominates the solvation and hence association is observed from 40% acetonitrile onwards. Leaving the K_A value for water the rest of the values at 40, 60, 80, and 90% acetonitrile exhibit a good linear trend, (drawn as a chained line in Fig. 1) with a correlation coefficient of 0.999. The linearity of the plot suggests the applicability of either DR theory or Fuoss theory excluding Bjerrum and EKYY theories from consideration. From the slope and intercept values of the log K_A *vs.* $1/D$ plot, the relative merits of the DR and Fuoss theories can be elucidated. Both DR and Fuoss theories predict the same slope *i.e.*, $|Z_+Z_-|e^2/(2.303\,akT)=96.23$ whereas the experimentally obtained line is having a slope of 109.33 and intercept −1.1472. But DR theory predicts zero intercept and Fuoss theory predicts $\log(4\pi Na^3/3000)$ as intercept. Equating the experimental slope of 109.33 to $|Z_+Z_-|e^2/(2.303\,a\,kT)$ the average ion-size parameter (a) for silver acetate in these solvents was obtained as 2.23 Å. However, when experimentally obtained intercept was equated to $3\log a+\log(4\pi N/3000)$, the '$a$' value calculated form there had a value 3.05 Å. Thus Fuoss theory predicts contradictory and different 'a' values of 2.23 Å and 3.05 Å from the slope and intercept values respectively 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

$$K_A = K_A^\circ \exp(|Z_+Z_-|e^2/aDkT). \qquad (4)$$

The experimental results could be fitted into this expression as

$$\log K_A = -1.1472 + 109.33/D, \tag{5}$$

$$\text{or } K_A = 0.0713\exp(251.7/D), \tag{6}$$

$$\text{and } a = 2.23\,\text{Å}.$$

This is slightly less ($\approx 12\%$) than the crystallographic value of 2.53 Å (The ionic radius of Ag^+ is 1.26 Å and the effective radius of CH_3COO^- is 1.27 Å). Similar results are reported in the literature.[19] Bodenseh and Ramsey[19] reported that 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. These deviations may be due to the fact that each ion in an isolated ion-pair whether in solution or in the vapour state is bound or coordinated with only one ion of opposite charge whereas in the crystalline state it will be coordinated with more than one oppositely charged ions. This explanation conforms to the fact that the smaller the number of nearest neighbours of oppositely charged associated ions in the crystal, the smaller will be the minimum distance between the oppositely charged ions in the salt. Figure 1 also shows the theoretical log K_A *vs.* $1/D$ plots corresponding to Bjerrum, Fuoss, DR, and EKYY theories using a=2.53 Å.

The ion-size parameter (a) values required by different theories to predict the experimental K_A values are compared with the '*a*' values calculated from crystallographic data *i.e.*, 2.53 Å. In the solvent mixtures containing acetonitrile it is evident that the Bjerrum, EKYY, and Fuoss theories predict very low values of '*a*' in the range of 1.45 to 1.88 Å which are unreasonable. The DR theory predicts meaningful '*a*' values of 3.79 to 6.25 Å. In water[20] the DR theory predicts 2.04 Å which is much better than the values predicted by other theories *i.e.*, 0.61 to 0.67 Å. Getting higher '*a*' values than the crystallographic value can be explained by considering the solvent separated ion-pairs.

The main effect of ion-association on ion-pair formation is either to decrease K_A due to increase in contact distance for the formation of 'solvent separated ion-pairs' (SSIP) or to increase K_A due to the formation of the additional associated species such as 'contact ion-pairs' (CIP). Earlier work[21] shows that silver acetate exists mostly as CIP in water. Whereas in acetonitrile–water mixtures the preferential solvation of Ag^+ ions by acetonitrile and CH_3COO^- ions by water suggests the formation of SSIP. The crystallographic radius of AgOAc is 2.53 Å. For this '*a*' value the expected association constants are 37.64, 77.59, 174.7, and 287.7 $dm^3\,mol^{-1}$ for 40, 60, 80, and 90% (w/w) acetonitrile–water mixtures respectively. But the corresponding experimental values are 4.343, 10.17, 25.43, and 43.76 $dm^3\,mol^{-1}$. These low values of experimental association constants compared to the theoretical values indicate that there might be a large contribution of weakly bound solvent separated ion-pairs. Therefore, SSIP and CIP may be in equilibrium as shown below.

$$\begin{array}{ccc} M^+S + S'A^- & \rightleftharpoons & M^+SS'A^- \text{ or } M^+SA^-S' \text{ or } SM^+S'A^- \\ & & \Big\upharpoonleft\!\Big\downharpoonright \\ & & SM^+M^-S' \text{ or } [M^+A^-]S[M^+A^-]S' \end{array}$$

By assuming perfect 'Stick' of the solvent at the surface of the ion, Walden[22] modified the Stokes law and obtained the relation

$$\lambda_0^{\pm}\eta = 0.820|Z_{\pm}|\,1/r_s^{\pm}, \tag{7}$$

$$\begin{aligned} \text{or } \Lambda_0\eta &= 0.820(|Z_+|\,1/r_s^+ + |Z_-|\,1/r_s^-), \\ &= \text{constant}, \end{aligned} \tag{8}$$

where $\lambda_0{}^{\pm}$ is the limiting ionic conductances of hydrodynamic entity of radius $r_s{}^{\pm}$ and charge $Z_{\pm}$ in a medium of viscosity η. The Walden product $\Lambda_0\eta$ is expected to be constant for a given electrolyte in a series of solvents/solvent mixtures in which ion-solvent interactions are uniform. It is evident from the Walden products calculated (Table 3) that $\Lambda_0\eta$ decreases with increasing percentage of acetonitrile in acetonitrile–water mixtures indicating that the total solvation increases with increasing percentage of acetonitrile.

TABLE 3. WALDEN PRODUCTS AND STOKES LAW RADII FOR SILVER ACETATE AT 25 °C

Solvent	$\Lambda_0\eta$	λ_0^+	λ_0^-	r_s^+/Å	r_s^-/Å
Water	0.9114	61.92	40.41	1.49	2.27
40% AN	0.6771	45.64	34.11	2.12	2.83
60% AN	0.6040	56.83	34.41	2.18	3.60
80% AN	0.5266	70.90	42.84	2.50	4.13
90% AN	0.3877	78.52	21.66	2.70	9.78

Interesting results could be obtained by splitting the salt conductance (Λ_0) into its ionic conductances. The limiting single ion conductances of Ag^+ ion were taken from the plot of $\lambda_0{}^+\eta$ *vs.* mole fraction of acetonitrile. By subtracting this from Λ_0 value, the limiting ionic conductance of acetate ion were obtained. The hydrodynamic radii of the Ag^+ and acetate ions were calculated by substituting these $\lambda_0{}^+$ and $\lambda_0{}^-$ in Eq. 7 and the values thus obtained are presented in Table 3. The $r_s{}^+$ values for Ag^+ increase from 2.12 Å in 40% acetonitrile to 2.70 Å in 90% acetonitrile whereas it is only 1.49 Å in water which clearly indicates that in the acetonitrile–water mixtures Ag^+ is preferentially solvated by acetonitrile. The $r_s{}^-$ values for acetate ion go on increasing from 2.27 to 9.78 Å. These odd values for acetate ion could be attributed to the unsymmetrical shape and distribution of the charge between the two oxygen atoms of the carboxylate group. This could also be the reason for the departure from the Stoke's law in the polarizable solvent. From these results one can conclude that Stoke's law may be applicable to the simple ions like Ag^+ and not to the ions in which charge is distributed.

One of the authors (UGKR) is thankful to CSIR-(New Delhi) for the award of a postdoctoral fellowship.

References

1) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," Reinhold, N. Y. (1950), pp. 369, 562, and 563.

2) L. G. Sillen and A. E. Martell, "Stability Constants of Metal–Ion Complexes, Supplement No. 1." ed by The Chemical Society, London (1971), Special Publication No. 25.

3) F. H. MacDougall and L. E. Topol, *J. Phys. Chem.*, **56**, 1090 (1952).

4) R. M. Fuoss and K. L. Hsia, *Proc. Natl. Acad. Sci. U.S.A.*, **57**, 1550 (1966); **58**, 1818 (1967).

5) R. Fernandez-Prini, *Trans. Faraday Soc.*, **65**, 3311 (1969).

6) W. H. Lee and R. J. Wheaton, *J. Chem. Soc., Faraday Trans. 2*, **74**, 743, 1456 (1978); **75**, 1128 (1979); *Acta Chem. Scand.*, **A34**, 307 (1980).

7) R. M. Fuoss, *J. Phys. Chem.*, **78**, 1383 (1974); **79**, 525 (1975); **80**, 2091 (1976); **82**, 2427 (1978); *J. Solution Chem.*, **7**, 771 (1978).

8) P. Beronius, *Acta Chem. Scand.*, **A34**, 309 (1980).

9) N. K. Bjerrum, *Danske Vidensk. Selsk.*, **7**, No. 9 (1926).

10) R. M. Fuoss, *J. Am. Chem. Soc.*, **77**, 2615 (1958).

11) J. T. Denison and J. B. Ramsey, *J. Am. Chem. Soc.*, **77**, 2615 (1955).

12) H. Falkenhagen, W. Ebeling and W. D. Kraeft, "Ionic Interactions," ed by S. Petrucci, Academic Press, N. Y. (1971), Vol. I. p. 104.

13) H. Yokoyama and H. Yamatera, *Bull. Chem. Soc. Jpn.*, **48**, 1770 (1975).

14) A. I. Vogel "A Textbook of Practical Organic Chemistry," Longmans, London (1955), p. 407.

15) J. Ananthaswamy, B. Sethuram, and T. N. Rao, *Indian J. Chem.*, **15A**, 9 (1977).

16) A. D. Aprano and R. M. Fuoss, *J. Phys. Chem.*, **73**, 400 (1969).

17) J. C. Justice, *J. Chim. Phys.*, **65**, 353 (1968); *Electrochim. Acta*, **16**, 701 (1971).

18) H. Strechlow and H. M. Koepp, *Z. Electrochem. Ber. Bunsenges. Phys. Chem.*, **62**, 373 (1958).

19) H. K. Bodenseh and J. B. Ramsey, *J. Phys. Chem.*, **69**, 543 (1965).

20) J. Ananthaswamy, B. Sethuram, and T. N. Rao, *J. Inorg. Nucl. Chem.*, **42**, 735 (1980).

21) J. Ananthaswamy, B. Sethuram, and T. N. Rao, *Bull. Chem. Soc. Jpn.*, **52**, 3076 (1979).

22) P. Walden and E. Birr, *Z. Phys. Chem.*, **153A**, 1 (1931).