CHEMISTRY LETTERS, pp. 47-50, 1973. Published by the Chemical Society of Japan

SOLVATION OF BIS(2,9-DIMETHYL-1,10-PHENANTHROLINE)COPPER(I) CATION BY ACETONE

Katsuhiko MIYOSHI, Toshihiro TOMINAGA, and Yuroku YAMAMOTO
Department of Chemistry, Faculty of Science,
Hiroshima University, Hiroshima, Japan

Conductance of bis(2,9-dimethyl-1,10-phenanthroline)Cu(I) perchlorate was measured at 25°C in 1-propanol/acetone mixtures with about the same dielectric constants. The derived parameters have shown that addition of acetone to propanol decreases the ionic association of the chelate salt. This behavior can be interpreted in terms of the solvation of acetone to the chelate cation.

It appears worthwhile to investigate the association behavior of electrolytes in isodielectric mixtures,[1)] especially which are composed of protic and aprotic solvents in order to obtain the information about ion-solvent interaction since the electrostatic interaction energy between cations and anions in these mixtures may be regarded as constant for a given electrolyte.

Recently Evans et al.[2)] and Pistoia and Pecci[3)] have measured the conductance of tetraalkylammonium salts in alcohol-acetone mixtures and found that solvation of small ions by monomeric alcohols produced by addition of acetone gives rise to ionic association smaller than expected from the simple electrostatic theory[4)] despite the fact that these mixtures have about the same dielectric constants. They have also confirmed the weak tendency of ketones to solvate anions.[5)] However they have not referred to the solvation of tetraalkylammonium ions by acetone. We report here the experimental evidence suggesting the solvation of the chelate cation by acetone.

Experimental

Materials. Bis(2,9-dimethyl-1,10-phenanthroline)Cu(I) perchlorate (Dojin Chemicals Ltd.) was recrystallized from acetone solution. Its analytical data were as follows. Found: C, 58.05; H, 4.11; N, 9.67%. Calcd for $C_{28}H_{24}O_4N_4ClCu$: C, 58.03; H, 4.17; N, 9.67%. Acetone and 1-propanol were purified in the same manner as described previously.[6)] Specific conductance of thus purified solvents was 6.8×10^{-9} and 8.8×10^{-9} mho cm^{-1} for acetone and propanol, respectively. Water content was less than 0.01 wt% in both solvents. The density at 25°C was measured in a 50-ml single neck capillary pycnometer and was found to be 0.78462 and 0.79952 for acetone and propanol, respectively. The reported values in literature are 0.78453[3)] and 0.7843[2)] for acetone and 0.79960[7)] and 0.7995[2)] for propanol. The agreement is satisfactory for the present purpose. Solvent mixtures were prepared by weight just before use. The densities were 0.7967, 0.7936, 0.7905, 0.7875 and 0.7861 for the mixtures with 20, 40, 60, 80 and 90 mol% of acetone, respectively. The corresponding values reported[2)] are 0.7967, 0.7936, 0.7906, 0.7873 and 0.7859, respectively. The slight difference in acetone-rich mixtures is attributable to the difference in density of the starting acetones. Thus their physical constants necessary for the analysis of data were quoted from ref.2.

Apparatus and Procedure. All the equipment, cells and general techniques used for conductance measurements were the same as those previously reported6) and were similar to those used by Pistoia and Pecci.3) Briefly stated, flask type cells(200-ml) with lightly platinized electrodes were placed in a double water bath thermostated to 25 ± 0.01°C with a mercury-in-glass thermoregulator. A dilution method3) was applied to vary the salt concentration. Variation of resistance with time was not observed.

Results and Discussion

The measured conductance Λ and the corresponding concentration C in equivalents per liter are given in Table I. Code numbers are added for the identification of solvent mixtures.

Table I: The measured conductance and the corresponding concentration.

No. 2		No. 3		No. 4		No. 5		No.6	
Λ	C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ	C x 10^4
39.940	21.708	63.818	16.293	89.393	16.203	115.87	19.143	130.50	21.022
40.396	19.643	65.282	12.941	90.272	14.568	117.19	16.927	131.79	18.852
40.808	17.785	66.163	11.073	91.118	13.094	118.80	14.544	133.24	16.722
41.375	15.660	67.015	9.4912	91.941	11.742	120.18	12.666	134.65	14.794
41.848	13.952	67.881	8.1027	92.926	10.342	121.60	10.942	135.99	13.065
42.409	12.138	68.935	6.5368	93.934	9.0206	122.88	9.5329	137.54	11.299
42.958	10.552	69.818	5.3644	94.829	7.9020	124.02	8.2885	138.93	9.8068
43.474	9.1721			95.712	6.9007			140.27	8.5185
43.959	8.0141								

These data were analyzed with the Fuoss-Onsager-Skinner(1965) conductance theory8) in the form,

$$\Lambda = \Lambda_o - SC^{1/2} + E'C \ln(6E'_1C) + L C$$

for unassociated electrolytes and in the form,

$$\Lambda = \Lambda_o - S(C\gamma)^{1/2} + E'C\gamma \ln(6E'_1C\gamma) + L C\gamma - K_A C\gamma\Lambda f_{\pm}^2$$

for associated electrolytes. Symbols used here have their usual meaning.8) No viscosity correction was made. All calculations were performed on a TOSBAC 3400 electronic computer using the least squares method proposed by Kay.9) The derived conductance parameters are summarized in Table II together with those obtained previously in pure acetone and 1-propanol,6) where a is a contact distance between ions and σ_Λ is a standard deviation at each concentration.

It is clearly seen in Table II that addition of acetone to propanol decreases the ionic association of the chelate salt despite the fact that propanol, acetone and their mixtures all have approximately the same dielectric constant D. (Slight decrease in D on adding acetone was attributed to the depolymerization of propanol hydrogen-bonded chains by Evans et al.2)) It is also seen that no ionic association is detectable when the content of acetone is increased to more than 40 mol%. This association behavior is quite similar to that observed for Bu_4NClO_4, the cation of which was confirmed to be hydrodynamically equivalent to this chelate cation by the comparison of the ionic Walden products in several alcohols.6) However, the association constant K_A is considerably larger for Bu_4NClO_4 than for this chelate perchlorate, that is,769 ± 67) in propanol and 90 ± 22) in acetone. This difference in

K_A values was attributed in part to the difference in charge density on the two cations and in part to the solvation of acetone to the chelate cation.[6)] In this respect, it is meaningful to compare the conductance behavior of the two salts in acetone-propanol mixtures.

Table II: Derived conductance parameters.

	mol%	D	Λ_o	L	a(Å)	K_A	σ_Λ
No.1	0	20.45	26.90 ± 0.04	248 ± 84	3.98 ± 0.35	82 ± 10	0.008
No.2	20	19.02	51.00 ± 0.07	647 ± 60	4.47 ± 0.12	19 ± 5	0.009
No.3	40	18.47	78.67 ± 0.02	1118 ± 20	4.64 ± 0.02	0	0.020
No.4	60	18.64	109.27 ± 0.02	1863 ± 17	4.90 ± 0.02	0	0.016
No.5	80	19.37	142.41 ± 0.06	2268 ± 42	4.76 ± 0.03	0	0.043
No.6	90	19.96	160.25 ± 0.05	2380 ± 33	4.66 ± 0.02	0	0.041
No.7	100	20.56	176.74 ± 0.02	2929 ± 13	4.87 ± 0.01	0	0.041

Two factors may be assumed that govern the association behavior of the chelate salt seen in Table II. The first is that as Kay et al.[10)] suggested, bulky ion pairs are stabilized by the hydrogen bond chains in alcohols (a kind of structure-enforced ion-pairing[11)]) and that as the content of acetone is increased, propanol chains are ruptured and therefore the stabilization of the ion pair by the structure of propanol disappears. Such structural effects are expected to be clarified by the study on the temperature coefficient of K_A since the electrostatic interaction energy between the cation and the anion is predicted to vary as a function of the product D T. However the lack of such data prevents further discussions.

The second is the stabilization of the chelate cation by the solvation of acetone. It is not plausible for acetone to solvate ClO_4^- ion since the negative end of its dipole is in an exposed position[5)] and the charge density on ClO_4^- ion is relatively low. It also seems unreasonable to assume the solvation of propanol to large size ions with low charge density such as the ions in question. Therefore it is useful to examine the difference of the Walden product(limiting equivalent conductance-viscosity product) between Bu_4NClO_4 and this chelate perchlorate in these mixtures in order to obtain the information about the solvation of cations by acetone, since it necessarily represents the difference between the two cations which are hydrodynamically equivalent to each other in alcohols as mentioned above. In Figure 1 the Walden products for the two salts[2)] and their differences are plotted vs. the mol% of acetone. If the classical Stokes law holds strictly for this system, the difference will directly correspond to the retardation of ionic migration by solvation of acetone. The hydrodynamic conditions for the Stokes law to hold may be assumed to be satisfied approximately in this system because of the large size of the two cations.[12)] It is seen in the figure that the difference increases as the content of acetone is raised and that at 40 mol% of acetone, it becomes nearly constant and ionic association disappears. If the solvation by acetone is strong, an abrupt increase in the difference will be observed at lower acetone content. Therefore the solvation does not seem so strong. Instead, an abrupt increase in the difference is observed when the content of acetone is considerably increased. Since the effect of dipole relaxation of the solvents on the Walden product will be small owing to the large size of the cations,[13)] and will be constant owing to the approximate constancy of D,[13] this increase will be probably due to the structural effect of the solvent mixtures with much higher acetone content but not to the increased solvation by acetone in acetone-rich mixtures. It is well known that propanol is extensively self-associated through the hydrogen bonding, while acetone is not. Thus the structural change of the solvent mixtures is expected to be much stronger in acetone-rich mixtures than in propanol-rich mixtures. A study on this chelate salt in MeOH-methylethyl ketone and EtOH-acetone mixtures is under way in the hope of ascertaining above assumption.

An increase in a on adding acetone is observed in Table II and seems to be attributable to the increase of the chelate cation radius by the solvation of acetone to it. However, the increase in a cannot be a strong support for the assumption of the solvation since a-values derived from conductance measurements do not necessarily represent the distances between cations and anions owing to the incompleteness of the conductance theory.[10,14]

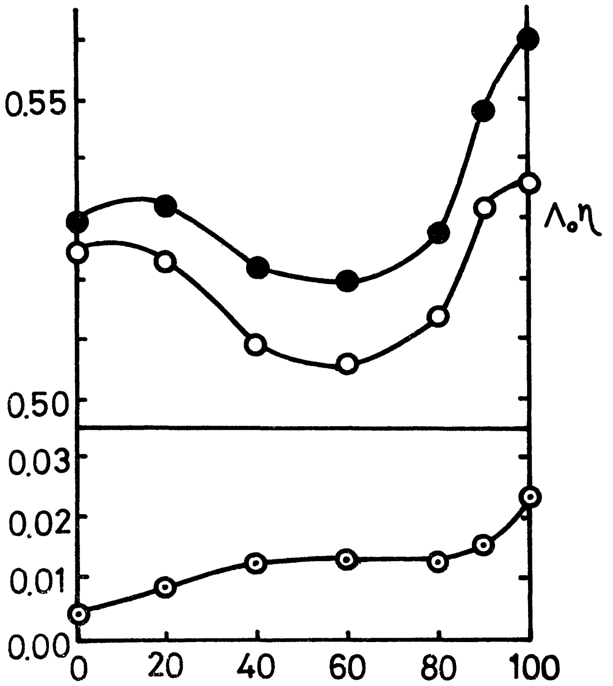

Fig.1.

●; Bu_4NClO_4
O; Complex salt
⊙; Difference between the two

References

1)For example: H.Sadek and R.M.Fuoss,J.Amer.Chem.Soc.,72,301(1950); F.M.Sacks and R.M.Fuoss,ibid.,75,5172(1953); A.D'Aprano and R.M.Fuoss,ibid.,91,211(1969),J.Phys. Chem.,67,1704(1963),73,400(1969); M.A.Coplan and R.M.Fuoss,ibid.,68,1181(1964); F. Conti and G.Pistoia,ibid.,72,2245(1968). 2) D.F.Evans,J.Thomas,A.J.Nadas and S.M.A. Matesich,ibid.,75,1714(1971). 3) G.Pistoia and G.Pecci,ibid.,74,1450(1970). 4) R.M. Fuoss,J.Amer.Chem.Soc.,80,5058(1958). 5) A.Parker,Quart.Rev.(London),16,163(1962). 6) K.Miyoshi,J.Phys.Chem.,76,3029(1972). 7) D.F.Evans and p.Gardam,ibid.,72,3281 (1968). 8) R.M.Fuoss,L.Onsager and J.F.Skinner,ibid.,69,2581(1965). 9) R.L.Kay,J. Amer.Chem.Soc.,82,2099(1960). 10) R.L.Kay,C.Zawoyski and D.F.Evans,J.Phys.Chem., 69,4208(1965). 11) R.M.Diamond,ibid.,67,2513(1963). 12) H.R.Frank,"Chemical Physics of Ionic Solutions",ed. by B.E.Conway and R.G.Barradas,John Wiley and Sons, Inc., New York,N.Y.(1966),p.61. 13) R.M.Fuoss,Proc.Nat.Acad.Sci.,45,807(1959); D.S.Berns and R.M.Fuoss,J.Amer.Chem.Soc.,83,1321(1961); R.Zwanzig,J.Chem.Phys.,38,1603(1963), 52,3625(1970). 14) J.E.Lind and R.M.Fuoss,J.Phys.Chem.,65,999,1415(1961),66,1722 (1962); C.Treiner and R.M.Fuoss,Z.Physik.Chem.(Leip.),228,343(1965); K.Miyoshi, Bull. Chem.Soc.Japan(in press).

(Received November 13, 1972)