BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (4), 1012—1015 (1978)

Study of Solutions of Tetraalkylammonium Salts in Acetone by Vapor Pressure Osmometry and Conductometry

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(Received July 12, 1977)

Vapor pressure depressions at 40.3 °C and electric conductivities at 25 and 40.3 °C have been measured for Bu_4NCl, Bu_4NBr, Bu_4NI, and Pr_4NI in acetone. Experiments were carried out with the greatest care to minimize the contact of salts and their solutions with air. A new representation of activity coefficients has been proposed for the undissociated species. Analysis by means of the representation gives better agreement between the dissociation constants and those obtained from electric conductivities. The very small dissociation constant of Bu_4NCl found previously has been corrected.

A number of papers[1,4,6,8] have appeared on the study of solutions of electrolytes in nonaqueous solvents by means of electric conductivity measurement. The dissociation of electrolyte salts is not complete in nonaqueous solvents. The dissociation constants have been determined by several authors. The activities in nonaqueous solutions of alkali halides[2] and tetraalkylammonium salts[3] were measured with a vapor pressure osmometer (VPO), and the dissociation constants of salts were estimated.

However, the dissociation constants of tetraalkylammonium salts were not in good agreement with those[4,8] determined conductometrically.

The present experiments have been undertaken in order to compare the dissociation constants obtained by two methods. The study of solutions of tetraalkylammonium salts, Bu_4NCl, Bu_4NBr, Bu_4NI, and Pr_4NI, in acetone by means of VPO has been repeated, measurements of the electric conductivities of the same solutions also being carried out.

In the calculation of dissociation constants from the VPO data, the activity coefficient of undissociated molecules has been taken into account.

Theoretical

It is well known that the tetraalkylammonium salts, MX, dissociate in acetone as

$$\mathrm{MX} \rightleftarrows \mathrm{M}^+ + \mathrm{X}^-. \tag{1}$$

Thus, the Gibbs-Duhem equation gives

$$N_1 \,\mathrm{d} \ln a_1 + m_2 \,\mathrm{d} \ln a_2 + m_3 \,\mathrm{d} \ln a_3 + m_4 \,\mathrm{d} \ln a_4 = 0, \tag{2}$$

where a_2, a_3, and a_4 are the activities of MX, M^+, and X^-, respectively, and a_1 is the activity of the solvent. N_1 is the moles of 1 kg of the solvent ($=1000/M_1$: M_1 the molecular weight of the solvent), and m_2, m_3, and m_4 are the molalities of MX, M^+, and X^-, respectively. Integration of Eq. 2 gives

$$\ln a_1 = -\frac{1}{N_1}\left(m_2 + 2m_4 + \int_0^{m_2} m_2 \,\mathrm{d} \ln \gamma_2 + 2\int_0^{m_4} m_4 \,\mathrm{d} \ln \gamma_4\right). \tag{3}$$

We assume that the activity coefficients of ions M^+ and X^- obey the Debye-Huckel (D-H) limiting law.[3] The integration of the last term of the right-hand side of Eq. 3 is, then, given by

$$2\int_0^{m_4} m_4 \,\mathrm{d} \ln \gamma_4 = -\frac{4.606A(\sqrt{m_4 d_0})^3}{3d_0}\sigma(X) - 2\left\{m_4 - \frac{\ln(1+0.001 m_4 M_2)}{0.001 M_2}\right\}, \tag{4}$$

$$X = Ba_0\sqrt{m_4 d_0},$$

$$\sigma(X) = \frac{3}{X^3}\left\{(X+1) - \frac{1}{X+1} - 2\ln(X+1)\right\},$$

where A and B are the constants in the D-H equation (see Eq. 9), and d_0 the density of the solvent. The second term in the right-hand side of Eq. 4 was omitted in Eq. 10 of the previous paper.[3]

The form of activity coefficient of the undissociated molecules, γ_2, should be duly considered. In the theory of Fuoss-Onsager, it has been assumed to be unity. We have attempted to determine the dissociation constant from the concentration dependence of the activity of the solvent by means of the curve-fitting. We start from the following two assumptions with respect to γ_2.

$$\text{I} \quad \ln \gamma_2 = 0 \tag{5}$$

$$\text{II} \quad \ln \gamma_2 = -\beta_2 m_2 + (\beta_3 m_2^2 + \cdots).$$

Integration of the third term in the right-hand side of Eq. 3 leads to

$$\int_0^{m_2} m_2 \,\mathrm{d} \ln \gamma_2 = -\frac{\beta_2}{2} m_2^2 + \left(\frac{2\beta_3}{3} m_2^3 + \cdots\right). \tag{6}$$

Assumption II shows that the deviation of γ_2 from unity caused by various unknown factors is compensated by introducing a parameter β_2.

A function h defined by

$$h = \frac{N_1 \ln a_1}{m} + 1 \tag{7}$$

was used for the analysis of the experimental results, where m is the molality of salt.

Experimental

Material. Tetraalkylammonium salts, Bu_4NCl, Bu_4NBr, Bu_4NI, and Pr_4NI, and acetone (guaranteed grade, Nakarai Chemical Co., Ltd.) were used. Before use, the salts were dried for five days in a vacuum oven at 50 °C with molecular sieves 3 Å (1/8-in. pellets). Fresh molecular sieves were used each day. Acetone was dried with anhydrous calcium sulfate and distilled in the presence of the molecular sieves. The water content was confirmed to be less than 0.01 wt % by the Karl-Fischer analysis. The molecular sieves and anhydrous calcium sulfate were dried, before use, over a period of 12 h in an electric oven at 360 and 250 °C, respectively. KCl was dried by a similar way to that for the tetraalkylammonium salts. The conductivity water was prepared by the usual method by passing dried nitrogen gas. Great care was taken to minimize the contact of the salts and their solutions with air. A dry box filled with nitrogen gas was used.

Vapor Pressure Osmometer. A vapor pressure osmometer Hitachi-Perkinelmer 115 was used. The experimental procedures were reported.[2] The temperature of measurement was 40.3 °C.

Conductometry. The conductometer, a model CM-1DB, Toa Denpa Co., Ltd., was calibrated with a Wheatstone Bridge, Type BD-30 of Shimadzu Co., Ltd. The cell constants were determined with KCl solutions in the usual way. Temperature of measurements were 25 and 40.3 °C.

Results and Discussion

Vapor Pressure Osmometry. Proportionality constants K_S, of the apparatus obtained for several compounds of known molecular weight is given in Table 1. The plots of Δr, the change of resistance of a bridge in the apparatus, against the concentration, m, for the tetraalkylammonium salts in acetone, are given in Fig. 1. The values of h, calculated from Eq. 7 are given in Table 2. The profile of plots of h against the concentration clearly shows the existence of a dissociation equilibrium in the solutions.[3]

Table 1. Proportionality constant of VPO in acetone solutions at 40.3 °C

	Molecular weight	$-K_s \times 10^{-4}$
Biphenyl	154.2	5.75
Hexamethylbenzene	162.3	5.75
Benzil	210.2	5.83
1-Octadecanol	270.5	5.83
Glycerol tribenzoate	404.4	5.83

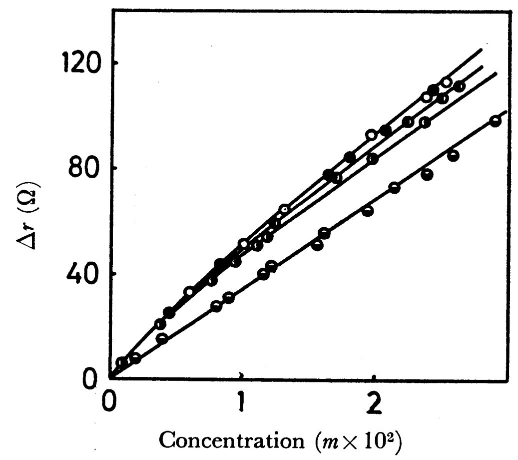

Fig. 1. Relationships between Δr and m for benzil and tetraalkylammonium salts at 40.3 °C.
◑: Bu_4NCl, ◐: Bu_4NBr, ○: Bu_4NI, ●: Pr_4NI, ◒: benzil.

Numerical analysis of function h was carried out. Two parameters, K_d and β_2, were determined on assumptions I and II by the method of least-squares. A HITAC 10 computer was used for the curve fitting of function h. The best values of K_d and β_2 and their standard deviations, σ, are given in Table 3. The difference between assumptions I and II is not highly

Table 2. h values of tetraalkylammonium salts in acetone at 40.3 °C

	Concentration $m\times 10^3$	h	Concentration $m\times 10^3$	h	Concentration $m\times 10^3$	h
Bu_4NCl	0.4824	-0.899_3	0.9741	-0.790_3	1.0234	-0.761_8
	3.915	-0.600_5	4.128	-0.546_8	7.604	-0.457_6
	8.026	-0.417_9	9.388	-0.404_2	11.100	-0.366_0
	11.842	-0.345_2	19.702	-0.257_1	23.641	-0.219_0
Bu_4NBr	1.0490	-0.802_9	1.2291	-0.827_6	2.1590	-0.765_8
	2.3396	-0.793_9	3.9354	-0.652_5	4.224	-0.623_3
	4.389	-0.629_9	8.302	-0.488_2	8.588	-0.459_3
	8.805	-0.480_4	12.188	-0.406_6	12.300	-0.422_6
	13.264	-0.379_4	16.479	-0.352_4	16.992	-0.332_4
	17.858	-0.337_3	18.729	-0.325_7	21.779	-0.297_4
	22.321	-0.296_4	24.190	-0.283_0	24.908	-0.268_5
Bu_4NI	1.3526	-0.857_4	1.5432	-0.781_2	2.3971	-0.750_9
	2.9316	-0.713_9	5.0524	-0.626_3	6.005	-0.579_9
	8.817	-0.538_6	9.976	-0.508_1	10.551	-0.495_8
	12.618	-0.461_7	12.803	-0.472_9	17.299	-0.401_1
	17.505	-0.389_6	19.588	-0.389_7	19.800	-0.373_3
	21.154	-0.365_1	22.959	-0.351_8	23.787	-0.334_5
	25.000	-0.340_4	25.163	-0.334_4		
Pr_4NI	1.0792	-0.807_6	1.2115	-0.903_0	1.9850	-0.741_9
	2.1886	-0.701_6	4.5469	-0.612_1	8.3093	-0.533_1
	8.8329	-0.522_5	9.1678	-0.521_7	13.039	-0.448_5
	13.717	-0.443_6	15.948	-0.412_2	16.415	-0.397_3
	17.958	-0.380_9	20.609	-0.352_4	20.757	-0.367_0
	24.271	-0.323_7	24.315	-0.329_9		

Table 3. Dissociation constants obtained by VPO at 40.3 °C (in terms of molality)

	Assump. I		Assump. II		
	$K_d\times10^3$	σ	$K_d\times10^3$	β_2	σ
Bu_4NCl	2.88	0.054	3.33	12.5	0.040
Bu_4NBr	4.32	0.062	7.10	41.7	0.036
Bu_4NI	6.33	0.041	10.00	41.7	0.023
Pr_4NI	6.00	0.044	9.07	38.9	0.031

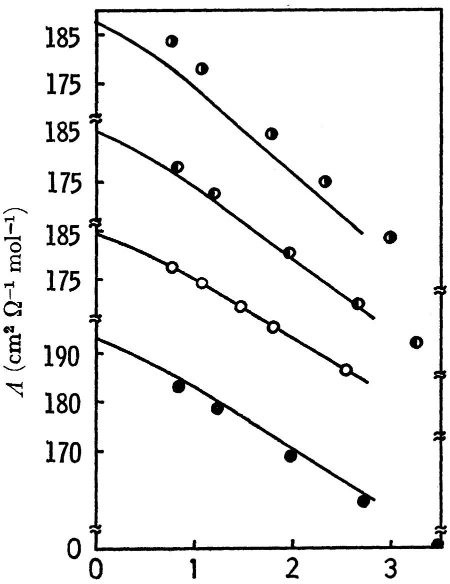

Fig. 2. Relationships between Λ and $\sqrt{C}$ for tetraalkylammonium salts at 25 °C. Lines show the results in literature.[4]

◑: Bu_4NCl, ◐: Bu_4NBr, ○: Bu_4NI, ●: Pr_4NI.

significant, but the values obtained from assumption II seem more favorable.

Conductometry. The concentration dependence of the conductivities obtained at 25 °C by the present measurements is compared in Fig. 2 with that found in literature.[4] The results obtained were analyzed by means of the Fuoss-Onsager theory.[5] The parameters in the Fuoss-Onsager equation where C is the concentration in molarity scale, were determined by the method of least squares.[9]

$$\Lambda = \Lambda_0 - S(C\alpha)^{1/2} + EC\alpha\log_{10}(C\alpha) + JC\alpha - K_A f_\pm^2 C\alpha\Lambda, \tag{8}$$

$$\ln f_\pm^2 = -\frac{4.606A\sqrt{C\alpha}}{1+Ba_0\sqrt{C\alpha}}. \tag{9}$$

The values of conductivity parameters, K_A, a_0 (ion-size parameter), and Λ_0 at 25 °C obtained are given in Table 4, the values in literature[4,8] being given for comparison. The physical constants of acetone used in the present calculation are as follows.

t/°C	d_0/(g cm^{-3})	η/(g cm^{-1} s^{-1})	ε
25	0.7844	0.00303[4]	20.56[4]
40.3	0.7667[6]	0.00263_6[6]	19.24[6]

Analysis of the conductivity data at 40.3 °C was made

Table 4. Conductivity parameters of tetraalkylammonium salts in acetone at 25 °C (Å=0.1 nm)

	This research			Literature[4,8]		
	K_A	a_0(Å)	Λ_0	K_A	a_0(Å)	Λ_0
Bu_4NCl	437.4	5.69	193.4	430.0	5.7	187.6[4]
Bu_4NBr	309.0	5.78	186.9	285.0	5.0	185.3[4]
Bu_4NI	164.4	5.61	184.7	155.0	5.1	184.4[4]
Pr_4NI	138.5	3.28	191.3	174.0	5.1	193.1[4]
				164.2	5.24	190.7[8]

by the same procedure. However, the values of a_0 used were those obtained at 25 °C (Table 4) for the sake of consistency. If the value of a_0 is determined independently by curve-fitting the best value contains some ambiguity and is not unique. The temperature change of a_0 seems to be negligible. The value of a_0 for Pr_4NI at 25 °C, 3.28 Å, was lower than the other values. Thus, the value 5.24 Å in literature was used in this case. The data of the concentrations up to 1×10^{-3} mol/dm^3 were analyzed by the Fuoss-Onsager equation. The results are shown in Table 5. The data of concentrations up to 20×10^{-3} mol/dm^3 were analyzed by the Fuoss-Hisa Equation.[7] The results are shown in Fig. 3. No tendency of the formation of poly-ions at high concentrations was observed.

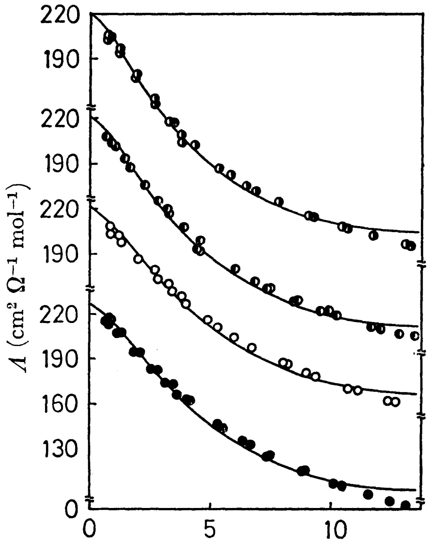

Fig. 3. Relationships between Λ and $\sqrt{C}$ to very high concentration for tetraalkylammonium salts at 40.3 °C. Lines show the values calculated from Fuoss-Hisa equation.

◑: Bu_4NCl, ◐: Bu_4NBr, ○: Bu_4NI, ●: Pr_4NI.

Comparison of VPO and Conductometry. In a previous work,[3] the dissociation constants of the tetraalkylammonium salts in acetone obtained by VPO were compared with those found in literature. The agreement between them was not satisfactory. The results of the present study are summarized in Table 5, where the dissociation constants were obtained (1) by VPO on the assumption II, and (2) by conductometry

Table 5. Comparison of dissociation constants by VPO and conductometry at 40.3 °C (in terms of molality)

	VPO	Conductometry	VPO[3]
	Assump. II	up to 1×10^{-3} mol/dm^3	Our previous work
Bu_4NCl	3.33×10^{-3}	2.50×10^{-3}	0.55×10^{-3}
Bu_4NBr	7.10×10^{-3}	3.56×10^{-3}	4.5×10^{-3}
Bu_4NI	10.00×10^{-3}	7.39×10^{-3}	4.0×10^{-3}
Pr_4NI	9.07×10^{-3}	5.97×10^{-3}	4.4×10^{-3}

using the Fuoss-Onsager equation from the data of concentrations less than 1×10^{-3} mol/dm^3 at 40.3 °C. The previous data are also given for the sake of comparison. Concentrations in terms of molality were used. The agreement is satisfactory.

The difference between the results obtained by assumptions I and II was not serious (Tables 3 and 5). However, introduction of parameter β_2 seems reasonable, since it compensates various errors due to the assumption of ideality.

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