

THERMODYNAMIC PROPERTIES OF IONS IN NONAQUEOUS SOLVENTS

—Application of Vapor Pressure Osmometry to
the Study of Nonaqueous Solution of Electrolyte—

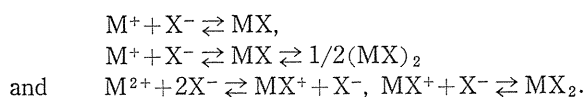
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Abstract

Vapor pressure depressions and electric conductivities have been measured for alkali halides, tetraalkylammonium salts and bis-(tetraalkylammonio) salts or bolaform electrolytes in various nonaqueous solvents. The analysis of data of vapor pressure osmometry (VPO) of these salts was carried out on the basis of one of the three models:



In these data analyses, the activity coefficient of the dissociated species was described by the Debye-Hückel limiting formula with sufficient accuracy. In most systems, the undissociated species have been assumed to behave ideally, but sometimes the activity of the undissociated species had to be taken into account.

Dissociation constants determined by the present work are generally in agreement with those obtained by conductivity measurements.

The relations of ionic dissociation constant with the dielectric constant of solvent and the ionic radius of solute have been discussed. The solvation number and the partial molar volume of some alkali halides in nonaqueous solvents were measured and the results were compared with the values in literature. The dissociation constants of bolaform salt obtained have been employed for the interpretation of ultrasonic relaxation data of this salt.

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1. General Introduction

Recently, much attention has been paid to the behavior of electrolyte ions in nonaqueous solvents. Physical properties of such solutions have an intimate relation to the problems of mechanism of organic catalytic reactions, where electrolytes are used as catalyst. The solvent extraction method used in the analytical chemistry also has direct bearing to the nonaqueous solution of electrolytes.

There have been numerous investigations of solution properties of electrolyte in nonaqueous solvents. However, most of these works have been carried out by

conductometry. In principle, this method is a measurement of the transport property in solution. The determination of such equilibrium quantities as association and dissociation constants from the data of the transport property is very peculiar. It should also be stressed that the ionic association constant obtained from the analysis of the conductometry data is nothing but a correction term for the Debye-Hückel theory. The view-point just mentioned above has been ignored by many chemists, consciously or unconsciously. For the study of the equilibrium in solution, methods based on the equilibrium thermodynamics are most preferable. The measurement of the vapor pressure depression is one of such methods. In the present work, the thermodynamic behavior of electrolyte ions in nonaqueous solutions was studied by the measurements of the vapor pressure depression. For the measurement, the vapor pressure osmometer, an apparatus of commercial product, was used, which is widely used for the determination of the molecular weight of polymer.

2. Theoretical

A salt, MX, dissolved in a solvent, dissociates to ions, M^+ and X^- , and an equilibrium is reached:



Then the Gibbs-Duhem equation

$$N_1 d \ln a_1 + m_2 d \ln a_2 + m_3 d \ln a_3 + m_4 d \ln a_4 = 0 \quad (2)$$

holds, where N_1 is the mole number of 1 kg of the solvent, m_i the molality of the dissolved species, a_i the activities, and the suffixes 2, 3 and 4 denote MX, M^+ , and X^- , respectively.

A function, h , is introduced, which is defined as

$$h = \frac{1000 \ln a_1}{M_1 m} + 1 \quad (3)$$

where M_1 is the molecular weight of the solvent and m , the molal concentration of the added solute. We derived the equation of h as a function of m under various assumptions.

[I] When the components, M^+ , X^- , and MX, behave as in ideal solution, we can put $a_2 = m_2$, $a_3 = m_3$, and $a_4 = m_4$, and as $m_3 = m_4$ and $m = m_2 + m_4$, we have

$$\ln a_1 = -\frac{1}{N_1} (m + m_4) \quad (4)$$

The equilibrium constant K_d is represented as

$$K_d = \frac{m\alpha}{1-\alpha} = \frac{m_4^2}{m-m_4} \quad (5)$$

where α is the degree of dissociation. From Eq. (5) we have

$$m_4 = \frac{-K_d + \sqrt{K_d^2 + 4mK_d}}{2}$$

Putting m_4 into Eq. (4), we obtain h as a function of K_d and m :

$$h = \frac{K_d - \sqrt{K_d^2 + 4mK_d}}{2m} \quad (6)$$

At infinite dilution, h becomes -1 .

$$\lim_{m \rightarrow 0} h = -1 \quad (7)$$

If an arbitrary value is assumed to the constant K_d , Eq. (6) can completely describe the variation of h as a function of the concentration. The relation between h and m calculated at various values of K_d is plotted in Fig. 1. It is seen from Fig. 1 that the profile of the variation of h with concentration is mainly determined by the value of K_d .

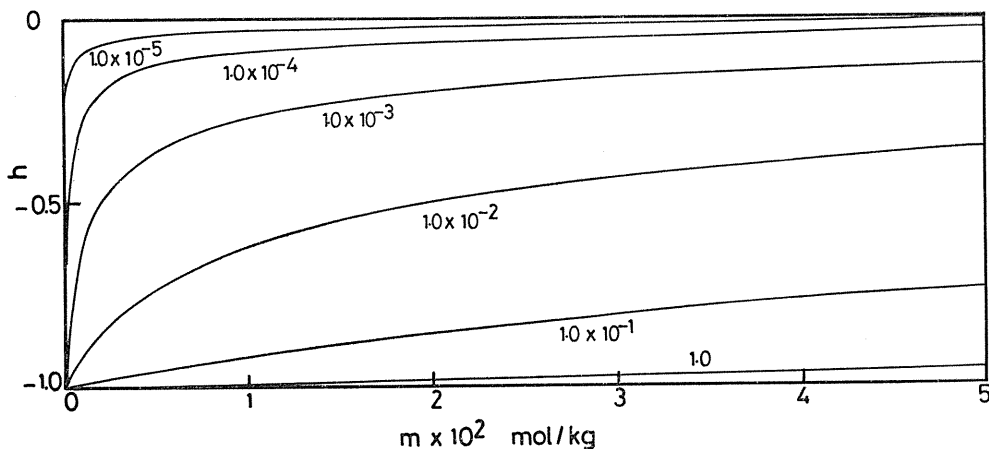


Fig. 1. Variation of function h calculated at various assumed values of K_d .

[II] The activity coefficient of the undissociated molecule, γ_2 , is unity, and the activity coefficients of ions obey the Debye-Hückel law. According to the Gibbs-Duhem relationship, we have

$$N_1 d \ln a_1 + dm_2 + 2dm_4 + 2m_4 d \ln \gamma_{\pm} = 0 \quad (8)$$

where $\gamma_{\pm} = (\gamma_3 \cdot \gamma_4)^{1/2}$, γ_3 and γ_4 , the activity coefficients. Integrating Eq. (8), we have

$$\ln a_1 = -\frac{1}{N_1} \left\{ m_2 + 2m_4 + 2 \int_0^{m_4} m_4 d \ln \gamma_{\pm} \right\} \quad (9)$$

According to the Debye-Hückel law, γ_{\pm} is represented as

$$\ln \gamma_{\pm} = -\frac{A \sqrt{m_4 d_0}}{1 + B a_0 \sqrt{m_4 d_0}} - \ln (1 + 0.001 m_4 M_1)$$

The integration of the last term of the right hand side of Eq. (9) leads to the equation:

$$2 \int_0^{m_4} m_4 d \ln \gamma_{\pm} = -\frac{2A}{3d_0} (\sqrt{m_4 d_0}) \sigma(x) - 2 \left\{ m_4 - \frac{\ln(1 + 0.001 m_4 M_1)}{0.001 M_1} \right\} \quad (10)$$

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

$$x = B a_0 \sqrt{m_4 d_0}$$

where a_0 , A , and B are the parameters in the Debye-Hückel theory, and d_0 is the density of the solvent. Then Eq. (9) reduces to

$$h = -\frac{1}{m} \left\{ m_4 - \frac{\ln(1 + 0.001 m_4 M_1)}{0.001 M_1} - \frac{2A (\sqrt{m_4 d_0})^3}{3d_0} \sigma(x) \right\} \quad (11)$$

$$m_4 = \frac{-K_d + \sqrt{K_d^2 + 4K_d m \gamma_{\pm}^2}}{2\gamma_{\pm}^2}$$

[III] We make further assumption that the activity coefficient of undissociated molecule, γ_2 , is represented as

$$\ln \gamma_2 = -\beta_2 m_2 + \beta_3 m_2^2 + \dots$$

Then h is represented as

$$h = \frac{1}{m} \left\{ \frac{1}{2} \beta_2 m_2^2 - \frac{2}{3} \beta_3 m_2^3 - m_4 + \frac{2A (\sqrt{m_4 d_0})^3}{3} \cdot \sigma(x) \right\} \quad (12)$$

and

$$m_4 = \frac{-K_d \gamma_2 + \sqrt{K_d^2 \gamma_2^2 + 4m \gamma_{\pm}^2 K_d}}{2\gamma_{\pm}^2}$$

3. Experimental

3. 1. Materials.

Tetraalkylammonium salts, Bu_4NCl , Bu_4NBr , Bu_4NI , and Pr_4NI were extra pure reagents supplied from Nakarai Chemical Co., Ltd. Alkali halide salts, LiCl , LiBr , NaI , KI , and RbI were extra pure reagents of products of Merck Co., Ltd. (West Germany). Before use the samples were dried in a vacuum oven at 50°C with molecular sieve 3\AA (1/8-in. pellet) for a week. The molecular sieve was renewed every day. The dryness reached by this method was much the same as that obtained by heating in an oven at temperatures as high as 400°C .

Bolaform salts, bis(triethylammonio) alkane dibromide used were 1, 4-bis(triethylammonio) butane dibromide (abbreviated hereafter as J4), 1, 5-bis(triethylammonio) pentane dibromide (J5), and 1, 10-bis(triethylammonio) decane dibromide (J10). These samples were prepared by professor R. E. Verrall of University of

Saskatchewan in Canada. The samples were dried following the similar procedures as above.

The solvents used were *N, N*-dimethylformamide (DMF), ethyl methyl ketone (EMK), acetone, methanol, ethanol, and 2-propanol. Spectral grade DMF was used without further purification, while reagent grade EMK was distilled after dehydration by anhydrous potassium carbonate. Reagent grade acetone, methanol, and 2-propanol were purified by drying with anhydrous calcium sulfate and finally distilled in the presence of molecular sieve in a nitrogen atmosphere. Reagent grade ethanol (Nakarai Chemical Co., Ltd.) was refluxed with magnesium metal and magnesium ethoxide in a dry nitrogen atmosphere for a period of 12 h and then distilled over molecular sieves in a dry nitrogen atmosphere. The water content of the purified solvents checked by Karl-Fischer analysis is shown in Table 1.

Table 1. Water content in solvents determined by Karl-Fischer method.

solvent	water content %
DMF, EMK	not checked
acetone	<0.01
methanol	<0.018
ethanol	<0.009
2-propanol	<0.028

Most of the solutions used for the measurements were prepared in a dry-box filled with dried nitrogen gas and sealed in respective measuring cells in order to avoid the contamination of solutions by moisture in air.

3. 2. Vapor Pressure Osmometry.

The activity of the solvent is represented by the boiling point elevation of the solution by the equation:

$$-\ln a_1 = \frac{\Delta H \cdot \Delta T}{RT_0^2} + \dots \quad (13)$$

where a_1 is the activity of solvent, T_0 boiling point of pure solvent, ΔH heat of vaporization of pure solvent and R the gas constant. When the concentration of the solute is sufficiently low, the equation reduces to:

$$\Delta T = -\frac{RT_0^2}{\Delta H} \ln a_1 \quad (14)$$

In the vapor pressure osmometer (VPO), the boiling point depression is measured by the change of resistance of the thermistor.

$$\Delta r = \frac{BrR}{\Delta H} \ln a_1 = K_e \ln a_1 \quad (15)$$

where r is the resistance of the thermistor at T_0 , Δr its change, B the thermistor constant, and K_e a constant determined by the solvent and thermistor.

In our experiments, Hitachi-Perkinmeter vapor pressure osmometer, Type 115

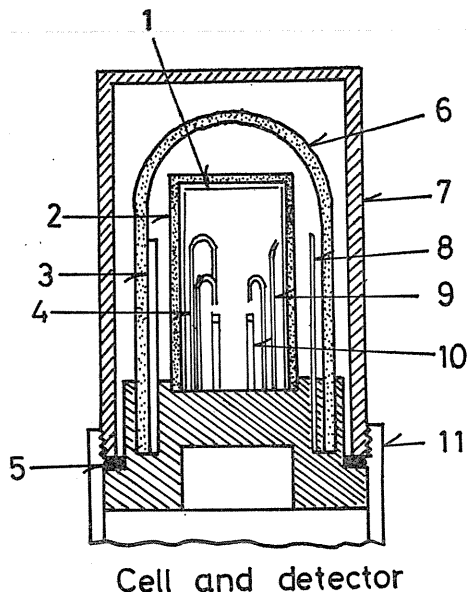


Fig. 2. Cell and detector of VPO apparatus.

- 1; filter paper, 2; inner cap,
 3; air pipe, 4; drop-pipe,
 5; gasket ring, 6; cap of filter paper,
 7; outer cap, 8, 9; inlet pipe,
 10; thermistor, 11; cap holder.

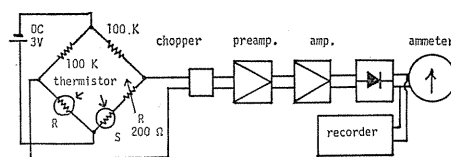


Fig. 3. Block diagram of amplifier of VPO apparatus.

was used. The arrangement of the cell and the detector of the VPO apparatus is illustrated schematically in Fig. 2. The block diagram of the amplifier of the apparatus is shown in Fig. 3. In the vapor pressure depression measurement using this type of apparatus, the thermodynamical equilibrium value of the boiling point elevation can not be measured. The measured temperature difference is of a steady state. The correction for the non-equilibrium is given by an equation:^{15,16,17)}

$$\Delta T = -\ln a_1 / \left\{ \frac{A_1 k_1 + A_2 k_2}{A_1 k_3 \Delta H P_0} + \frac{\Delta H}{RT_0^2} \right\} \quad (16)$$

where A_1 is the total surface area of the sample drop, A_2 area of the contact surface between sample drop and thermistor, k_1 and k_2 are the coefficients of the heat transfer of gas-liquid and liquid-solid, k_3 is the mass-transport coefficient and P_0 the vapor pressure of the pure solvent at T_0 . Then Eq. (15) becomes

$$\Delta r \simeq \ln a_1 / \left\{ \frac{(A_1 k_1 + A_2 k_2) T_0^2}{A_1 k_3 \Delta H P_0 Br} + \frac{\Delta H}{Br R} \right\} \quad (17)$$

$$K_s = 1 / \left\{ \frac{(A_1 k_1 + A_2 k_2)}{A_1 k_3 \Delta H P_0 Br} + \frac{\Delta H}{Br R} \right\} \quad (18)$$

where K_s is a constant which can not be determined from the heat of solution and the thermistor constant themselves only. Actually, K_s is determined by the measurement with a compound of known molecular weight.

As illustrated in Fig. 2, a highly complicated method is applied in order to establish the stable atmosphere of the saturated vapor of the solvent. However, additional attentions are also indispensable to operate the VPO apparatus. First, the steady state must be achieved within 2~5 minutes after dropping the solvent and the solution. Second, the value of K_s obtained with a standard sample of known

molecular weight does not differ much from the value of K_e calculated from the heat of vaporization and the physical property of the thermistor. The values of K_s and the ratio K_s/K_e in the solvent systems of the present work at appropriate temperatures are summarized in Table 2, where it is seen that the above requirements are satisfied. The effect of the second virial coefficient of the solute to the ratio K_s/K_e has been proved to be negligible.^{15,16,17)} The range of the concentrations in the present study was from 1×10^{-3} to 2.5×10^{-2} mol/kg.

Table 2. Proportionality constant K_s and the ratio K_s/K_e in various solvents.

Solvent	Standard solute	Molecular weight	K_s	K_s/K_e
Acetone (40.3°C)	Diphenyl	154.2	-57500	0.985
	Hexamethylbenzene	162.3	-57500	0.985
	Benzil	210.2	-58300	0.996
	1-Octadecanol	270.5	-58300	0.996
	Glycerol tribenzonate	404.4	-58300	0.996
Methanol (45°C) (50°C)	Benzil	154.2	-42100	0.974
	Benzil	154.2	-38000	1.022
Ethanol (55.1°C)	Benzil	154.2	-27600	0.973
2-Propanol (60°C) (70°C)	1-Octadecanol	270.5	-2180	0.911
	1-Octadecanol	270.5	-17300	0.951

3. 3. Conductometry.

The electric conductivity was measured by conductometer, a model CM-1DB, a product of Toa Denpa Co., Ltd. The conductometer was calibrated by a bridge, Type BD-30 of Shimadzu Co., Ltd. The conductivity water was prepared by the usual method by passing dried nitrogen gas. The cell constant was determined with KCl solution by the usual method. The measurements were made under the stream of dried nitrogen. The measuring temperatures were 25 and 40.3°C, and the highest concentration was 2.2×10^{-2} mol/kg. The preparation and handling of the salts and their solutions was carried out in a dry box under a nitrogen atmosphere in order to avoid contact with the moist air.

4. Analysis of Data

4. 1. Analysis of Data of VPO.

The empirical curves showing h as a function of m , the molal concentration of solute, can be obtained by VPO. From these curves, we obtained values of parameters K_d and β_2 by the curve-fitting. The value of a_0 , a parameter called ionic radius in Debye-Hückel equation, was fixed to some value before the analysis such as that determined from conductivity measurements or the crystal ionic radius.

The data analysis was done as follows. The objective function is defined as

$$\sigma = \sqrt{\frac{\sum (h_{\text{cal}} - h_{\text{exp}})^2}{N-1}} \quad (19)$$

where h_{cal} and h_{exp} are, the values of h calculated and obtained experimentally, respectively, and N the number of data.

(i) Determine the optimum value of K_d , which makes σ minimum on the basis of the assumption of ideal solution according to Eq. (6).

(ii) Determine the value of K_d , which makes σ minimum. The initial value of K_d was that determined in (i). Instead of Eq. (6), Eq. (11) is used, where some value is assigned to a_0 beforehand.

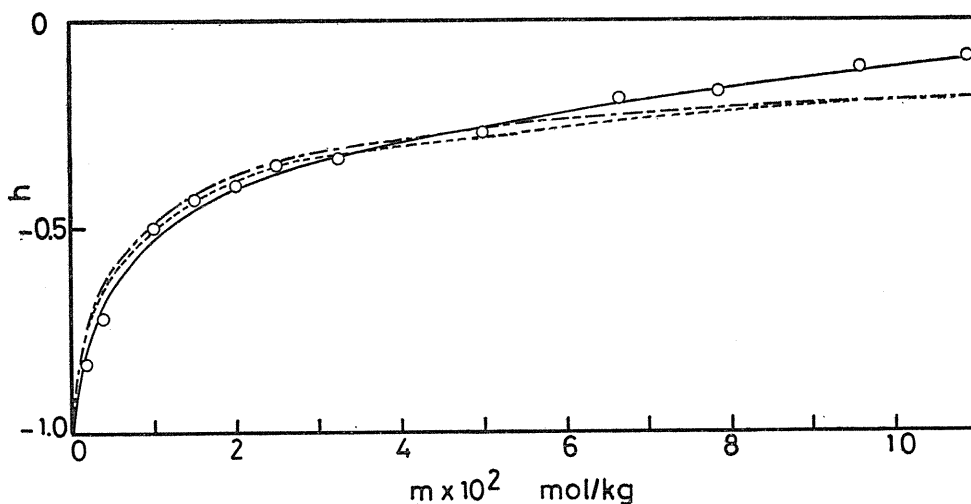


Fig. 4. Relationships between h and concentration for LiCl in DMF at 40°C. ---; assumption [I], - · - · -: assumption [II], —; assumption [III].

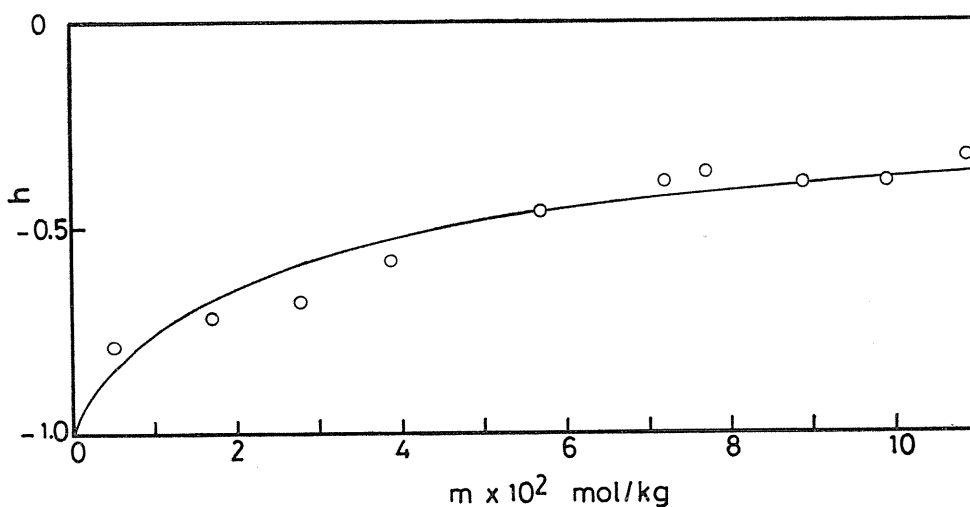


Fig. 5. Relationships between h and concentration for RbI in DMF at 40°C. The curve is obtained on the basis of assumption [II].

(iii) Start from the K_d obtained in (ii) and determine the optimum values of K_d and β_2 simultaneously, which make σ minimum. In order to do this, vary K_d and β_2 independently, and the two-dimensional grid-research method was used.

As an illustrating example, the results of analysis for the solution of LiCl in DMF are shown in Fig. 4. As is seen in Fig. 4, the analysis taking into account of assumption [III] of chapter 2 can give the best result. The value of σ is minimum and the fitting is satisfactory for whole concentration range. The similar results for RbI-DMF systems are shown in Fig. 5. The application of the Debye-Hückel equation to the ionic species can sufficiently describe the observed variation of h as a function of concentration, and assumption [III] is unnecessary in this case. However, the comparison between Fig. 1 and Figs. 4, 5 leads to the conclusion that the introduction of various types of assumptions concerning the dissolved species plays rather a minor role on the general features of the relation observed between h and m . The most important factor is K_d .

4. 2. Analysis of Data of Conductivity Measurements.

The data analysis of conductivity measurements was made on the basis of Fuoss-Onsager equations. According to Fuoss and Onsager,⁷⁾ the conductivity of solution is represented by the following equations;

$$A = A_0 - (AA_0 + B\sqrt{C}) + EC \log C + JC \quad (20)$$

where C is the concentration in molarity scale. When there is an ion-association equilibrium,

$$A = A_0 - (AA_0 + B)\sqrt{C\alpha} + EC\alpha \log (C\alpha) + JC - K_A C\alpha f^2 A \quad (21)$$

where E is a parameter determined by A_0 and the physical properties of the solvent, while J is a function of ion-size parameter, a_0 . The analysis was made by the Kay's method.¹⁸⁾ Kay assumed that three parameters, A_0 , K_A , and a_0 were independent of each other, and also put $\partial A/\partial A_0 = 1$. He also linearized the equation with respect to these three parameters, and applied the method of least squares.

5. Tetraalkylammonium Salts in Acetone and Solvent Dependence of Ionic Association Constant

5. 1. Introduction.

A number of papers^{1,4,6,23)} have appeared on the study of solutions of electrolytes in nonaqueous solvents by means of electric conductivity measurement and the dissociation constants have been determined. However, there have been no thermodynamical investigations for nonaqueous solutions of electrolytes, because of the low solubility of electrolytes in nonaqueous solvents. Vapor pressure osmometry is a very useful technique to measure the activity of solvent in very low concentration regions of solute in solutions.

The present experiments have been undertaken in order to compare the dissociation constants obtained by two methods, namely VPO and conductometry. For this purpose, the solutions of tetraalkylammonium salts Bu_4NCl , Bu_4NBr , Bu_4NI , and Pr_4NI , in acetone have been studied by means of VPO at 40.3°C, measurements

of electric conductivities of the same solutions also being carried out at 25°C and 40.3°C. To discuss the dependence of the dissociation constant, K_d , on the dielectric constant of solvent, the VPO and conductometry measurements were also carried out on solutions of Et_4NBr in three kinds of alcohols, namely methanol, ethanol, and 2-propanol

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

5. 2. VPO.

The plots of Δr against the concentration, m , for the tetraalkylammonium salts in acetone, are given in Fig. 6. The profile of plots of h against the concentration clearly shows the existence of a dissociation equilibrium in the solution.¹¹⁾

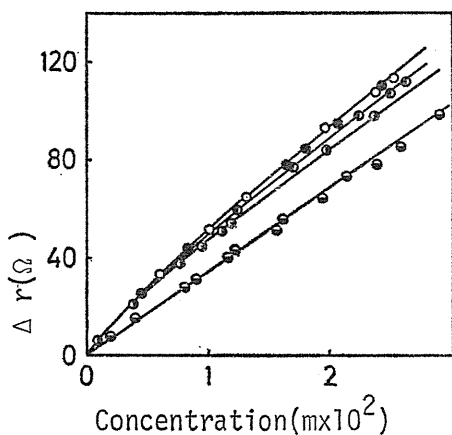


Fig. 6. Relationships between Δr and m for benzil and tetraalkylammonium salts in acetone at 40.3°C.
 ●; Bu_4NCl , ○; Bu_4NBr ,
 ○; Bu_4NI , ●; Pr_4NI
 ○; benzil

Numerical analysis of function h was carried out. Two parameters, K_d and β_2 , were determined on assumptions [II] and [III] 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 [II] and [III] is not highly significant, but the values obtained from assumption [III] seem more favorable.

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

	Assump. [II]		Assump. [III]		
	$K_d \times 10^3$	σ	$K_d \times 10^3$	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

5. 3. Conductometry.

The concentration dependence of the conductivities obtained at 25 °C by the present measurements is compared in Fig 7 with that found in literature.⁶⁾ The results obtained were analyzed by means of the Fuoss-Onsager theory⁷⁾ (Eq. (21) of chapter 4). The parameters in the Fuoss-Onsager equation were determined by the method of least squares. The values of conductivity parameters, K_A , a_0 and Λ_0 at 25 °C obtained are given in Table 4, the values in literature^{6,23)} 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 ⁶⁾	20.56 ⁶⁾
40.3	0.7667 ¹⁾	0.00263 ⁶⁾	19.24 ¹⁾

Here ϵ is the dielectric constant of the solvent.

Analysis of the conductivity data at 40.3 °C was made by the same procedure. However, the values of a_0 used were

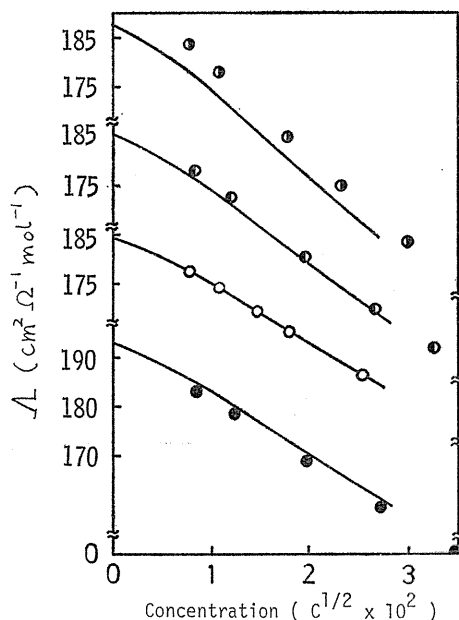
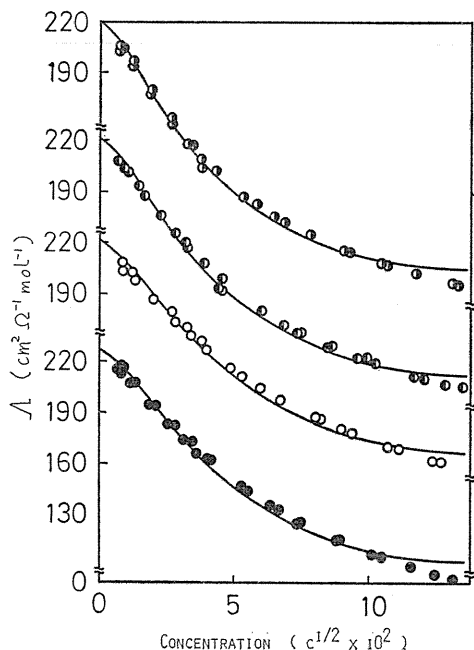


Fig. 7. Relationships between Λ and \sqrt{C} for tetraalkylammonium salts in acetone at 25 °C. Lines show the results in literature.⁶⁾
 ●; Bu₄NCl, ○; Bu₄NBr,
 ○; Bu₄NI, ●; Pr₄NI.

Table 4. Conductivity parameters of tetraalkylammonium salts in acetone at 25°C. ($\overset{\circ}{\text{A}}=0.1 \text{ nm}$)

	This research			Literature ^{6, 23)}		
	K_A	$a_0(\overset{\circ}{\text{A}})$	Λ_0	K_A	$a_0(\overset{\circ}{\text{A}})$	Λ_0
Bu ₄ NCl	437.4	5.69	193.4	430.0	5.7	187.6 ³⁾
Bu ₄ NBr	309.0	5.78	186.9	285.0	5.0	185.3 ⁶⁾
Bu ₄ NI	164.4	5.61	184.7	155.0	5.1	184.4 ⁶⁾
Pr ₄ NI	138.5	3.28	191.3	174.0	5.1	193.1 ⁶⁾
				164.2	5.24	1907.2 ³⁾

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 value contains some ambiguity and is not unique. The temperature change of a_0 seems to be negligible. The value of a_0 for Pr₄NI at 25 °C, 3.28 $\overset{\circ}{\text{A}}$, was lower than the other values. Thus, the value 5.24 $\overset{\circ}{\text{A}}$ in literature was used in this case. The data of the concentrations up to $1 \times 10^{-3} \text{ mol/dm}^3$ were analyzed by the Fuoss-Onsager equation.⁷⁾ The results are



shown in Table 5. The data of concentrations up to 20×10^{-3} mol/dm³ were analyzed by the Fuoss-Hisa equation.⁸⁾ The results are shown in Fig. 8. No tendency of the formation of poly-ions at high concentrations was observed.

Fig. 8. Relationships between Λ and \sqrt{c} to very high concentration for tetraalkylammonium salts in acetone at 40.3°C. Lines show the values calculated from Fuoss-Hisa equation.⁸⁾

5. 4. Comparison of VPO and Conductometry.

In a previous work,¹¹⁾ 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 assumption [III], and (2) by conductometry using the Fuoss-Onsager equation from the data of concentrations less than 1×10^{-3} mol/dm³ 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.

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

	VPO	Conductometry	VPO ¹¹⁾
	Assump. [III]	up to 1×10^{-3} mol/dm ³	our previous work
Bu ₄ NCl	3.33×10^{-3}	2.50×10^{-3}	0.55×10^{-3}
Bu ₄ NBr	7.10×10^{-3}	3.56×10^{-3}	4.5×10^{-3}
Bu ₄ NI	10.00×10^{-3}	7.39×10^{-3}	4.0×10^{-3}
Pr ₄ NI	9.07×10^{-3}	5.97×10^{-3}	4.4×10^{-3}

The difference between the results obtained by assumptions [II] and [III] is not serious (Table 3). However, the introduction of parameter β_2 may be reasonable, since it compensates various errors due to the assumption of ideality of the undissociated species.

5. 5. Solvent Dependence of Ionic Association Constant.

The VPO measurements were carried out for solutions of Et_4NBr in methanol, ethanol, and 2-propanol. The experimental temperatures were different because of the different optimum experimental conditions of the three solvents. The values of K_a and β_2 were determined by the similar procedure as mentioned above. In order to compare K_a values on a certain base, it is necessary to estimate K_a values at 25°C from VPO data obtained at different temperatures. The apparent activation energy, ΔH of ionic association has been estimated to be 1.8 kcal/mol for Bu_4NBr in 2-propanol.³⁵⁾ The ionic association constant in nonaqueous solvent depends mainly on the dielectric constant and its temperature derivative. The activation energies in methanol and ethanol were estimated from the values in 2-propanol taking into consideration the difference in dielectric constant of the solvents. The estimated values for the VPO method at 25°C are converted to those of K_A by the relation $K_A = 1/K_a d_0$ and are shown in brackets in Table 6.

Table 6. Ionic association constant K_A of Et_4NBr in alcohols by VPO and conductometry (in terms of molality).

solvent	$t/^\circ\text{C}$	$K_A \times 10^3$ (VPO)	β_2	$K_A \times 10^3$ (conduct.)
MeOH	45	0.9 (1.03 ₃)	124.1	9.8
EtOH	55.1	200.0 (206)	0.62	99
2-PrOH	60	1488.1 (1085)	11.1	1110

The values in the brackets show the corrected values at 25°C .

The relationships between $\log K_A$ and $100/\epsilon$, where ϵ refers to dielectric constant of solvent at 25°C is shown in Fig. 9. As is seen in Fig. 9, in VPO $\log K_A$ does not increase linearly with increasing values of $100/\epsilon$, but in the case of conductometry, this relation is linear. This discrepancy may come from the differences in the treatment of the activity coefficient of the undissociated molecules in the two method. In conductometry, it is neglected.

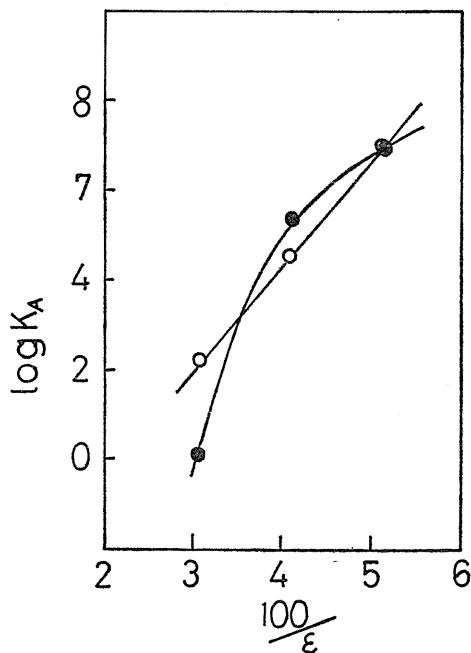


Fig. 9. Relationships between $\log K_A$ and $100/\epsilon$ for Et_4NBr at 25°C .

●; VPO, ○; conductometry.

6. Alkali Halides in Various Solvents

6. 1. Introduction.

In chapter 5, the vapor pressure depression of tetraalkylammonium salts in acetone was reported and the data were analyzed assuming the existence of an ionic dissociation equilibrium.¹⁹⁾ The dissociation constants obtained from VPO were in good agreement with those obtained from conductivity measurements within an experimental error.

In our earlier papers,^{27,28)} the vapor pressure depression of LiCl, LiBr, NaI, KI, and RbI in various solvents was measured. However, it has been reported that some lithium salts show an anomalous behavior in solutions of acetone. Later, the vapor pressure depression of these salts in acetone was re-examined, the great care being taken to prevent moisture from coming in contact with the samples and their solutions, and measurements of the electric conductivities were also carried out in order to examine the existence of the dissociated ions.²⁰⁾

In order to account for the data of VPO for lithium salts in acetone, an assumption of the existence of dissociation-association equilibria was proposed. And the studies of VPO and conductometry were made for such salts as NaI, KI, and RbI for the sake of comparison.

Results of the re-analysis of the data obtained in our early work^{27,28)} are summarized in this chapter.

6. 2. VPO.

For the solutions of alkali halides in ethanol, the plots of h vs. the molality, m , are represented in Fig. 10. Similar relations for solutions of NaI, KI, and RbI in acetone are given in Fig. 11. The general feature of these two figures is resembling each other.

Numerical analysis of function h was carried out by the method of non-linear least squares. Two parameters, K_a , and β_2 were determined on assumptions [I], [II], and [III] described in chapter 3. The best values of K_a and β_2 and their standard deviation, σ , are given in Table 7. As is seen in Table 7, in whole system, assumption [II] shows the smaller deviation than in the case of assumption [I]. However, the differences of the

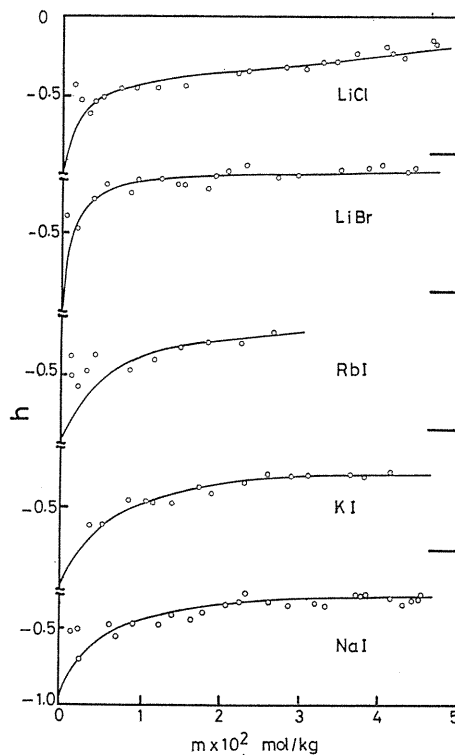


Fig. 10. Relationships between h and concentration for alkali halides in EtOH at 40 °C.

Table 7. Dissociation constants of alkali halides in various solvents (in acetone, at 40 or 40.3°C).

	E M K		Acetone		EtOH		MeOH		D M F	
	$K_d \times 10^3$	$\beta_2 \quad \sigma$	$K_d \times 10^3$	$\beta_2 \quad \sigma$	$K_d \times 10^3$	$\beta_2 \quad \sigma$	$K_d \times 10^3$	$\beta_2 \quad \sigma$	$K_d \times 10^3$	$\beta_2 \quad \sigma$
LiCl	I				3.672	0.1412	24.104	0.111	4.516	0.3758
	II				3.485	0.0418	23.180	0.0683	4.880	0.0535
	III								6.111	2.68 0.0217
LiBr	I				0.527	0.3092				
	II				0.535	0.0456				
	III				0.570	0.95 0.0448				
NaI	I	1.052	0.8048	5.897	0.0220	5.137	0.1073	24.249	0.0592	19.107
	II	1.300	0.0786	5.889	0.0113	3.975	0.0889	25.000	0.0387	19.448
	III	1.338	6.24 0.0468							19.444 0.12 0.0409
KI	I			4.714	0.0188	4.692	0.0747	31.452	0.0514	20.440
	II			5.166	0.0136	4.816	0.0388	35.402	0.0327	19.277
	III									0.0574
RbI	I			5.204	0.0242	3.845	0.0642	31.127	0.0546	23.054
	II			4.681	0.0113	3.882	0.0230	33.025	0.0377	22.822
	III					4.259	4.94 0.0154			26.646 1.67 0.0437

* I; Assumption [I], II; Assumption [II], III; Assumption [III]

results based on [II] and [III] are not highly significant, except for the cases of LiCl-DMF, NaI-EMK, and RbI-EtOH.

In Figs. 10 and 11, the solid curves are those calculated using the values of K_d given in Table 7.

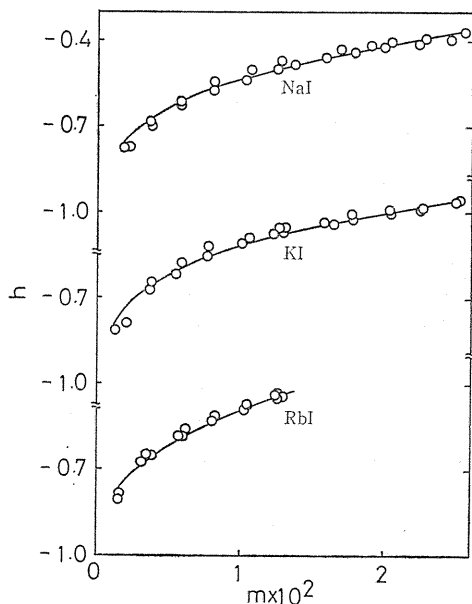


Fig. 11. Relationships between h and concentration for NaI, KI, and RbI in acetone at 40.3°C

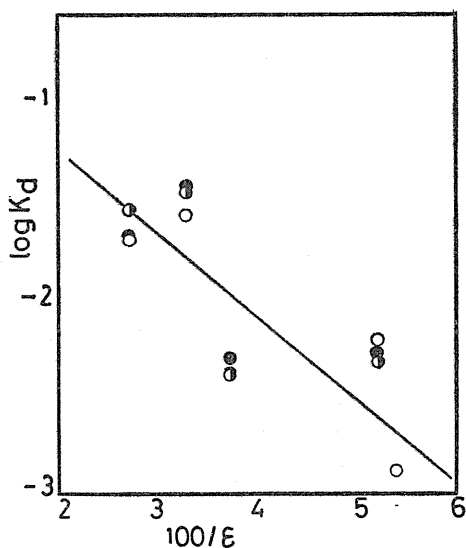


Fig. 12. Relationships between $\log K_d$ and $100/\epsilon$ for alkali halides.

○; NaI, ●; KI, ⊖; RbI.

6. 3. Solvent Dependence of Dissociation Constant.

The values of K_d based on assumption [II] were adopted. The relationship between $\log K_d$ and the dielectric constant of the solvents in Table 7 is shown in Fig. 12. As seen in Fig. 12, the relationship between $\log K_d$ and $100/\epsilon$ can not be represented by a straight line. Roughly speaking, however, $\log K_d$ decrease with increasing values of $100/\epsilon$. This fact indicates that the interactions of simple ions M^+ and X^- with nonaqueous solvent are mainly governed by the dielectric constant of solvent, but the dielectric constant only is insufficient to describe the solution properties of these systems.

6. 4. Solvation Number and Partial Molar Volume.²⁴⁾

To determine the solvation number of ions in nonaqueous solutions, the measurements of ultrasonic velocity and density were carried out by 1 MHz ultrasonic interferometer and 20 cm^3 Ostwald type pycnometer. The detailed experimental procedures and data reductions have been described elsewhere.²⁹⁾

Solvation numbers obtained from the ultrasonic measurement and partial molar volumes of alkali halides in nonaqueous solvents are summarized in Tables 8 and 9. In Table 8, our values of the solvation number are compared with those found in literature. Two sets of values are in excellent agreement with each other.

Table 8. Solvation number determined from the compressibility of solution at 30°C.

	Acetone	EtOH		MeOH	
LiCl	—	2.8 ₅ ,	2.7 ^{a)}	4.4 ₈ ,	4.2 ^{a)}
LiBr	3.3 ₀	—	3.4 ^{a)}	—	5.0 ^{a)}
NaI	3.8 ₄	3.8 ₁ ,	3.2 ^{a)}	6.1 ₀ ,	6.2 ^{a)}
KI	—	—	—	5.7 ₀ ,	6.0 ^{a)}

a) D.S. Allam and W. H. Lee, *J. Chem. Soc., A*, 5 (1966)

Table 9. Partial molar volumes of alkali halides in organic solvents (cm³/mole).

	Acetone	EtOH		MeOH	
LiCl	—	-5.0,	-6.7 ^{b)}	-1.2,	-4.9 ^{a)}
LiBr	-4.9 ₆	—	-4.1 ^{b)}	—	0.4 ^{a)}
NaI	-6.9 ₀	19.3 ₅ ,	16.9 ^{b)}	13.6,	11.1 ^{a)}
KI	—	—	26.3 ^{b)}	22.5 ₈ ,	20.9 ^{a)}

Values with sign a) or b) are obtained from the additivity of ionic partial molar volumes found in a) F. Kawaizumi and R. Zana, *J. Phys. Chem.*, **78**, 627 (1974), and b) F. Kawaizumi and R. Zana, *J. Phys. Chem.*, **78**, 1099 (1974)

Table 9 include the values obtained by the additivity rule of the ionic partial molar volumes (30 °C). The determination of partial molar volume of electrolytes in organic solvents is a very difficult work, and sometimes the differences among the reported values of \bar{V}_2^0 amount to more than 5 cm³/mol. Considering these facts, our values of \bar{V}_2^0 are sufficiently in good agreement with the most plausible values reported lately. As is see in Table 8, the solvation number of alkali halides in these nonaqueous solvents increases slightly with increasing ionic radius of salts but it is almost independent of the dielectric constant of solvents.

In the case of aqueous solutions of electrolytes, Hepler¹⁰⁾ has presented the following equation

$$\bar{V}_{\text{ion}}^0 = Ar_c^3 + \frac{BZ^2}{r_c} \quad (22)$$

where, \bar{V}_{ion}^0 is the partial molar volumes of ions at infinite dilution, and Z and r_c refer to the electric charge and ionic (in crystalline state) radius, respectively and A and B are constants. Mukerjee²⁶⁾ has modified this equation taking into account the electrostrictive effects, then using the Drude and Nernst equation⁵⁾ as follows.

$$\left. \begin{aligned} \bar{V}_{\text{ion}}^0 &= 2.51(1+K)^3 r_c^3 - \frac{BZ^3}{r_c(1+K)} \\ 1+K &= r_s/r_c \end{aligned} \right\} \quad (23)$$

where, r_s refers to the ionic radius of ions in solution. In aqueous solution of electrolytes, it has been shown²⁶⁾ that Eq. (23) can well describe ionic partial molar volumes by assuming that $K=0.213$ and $B=9.7$.

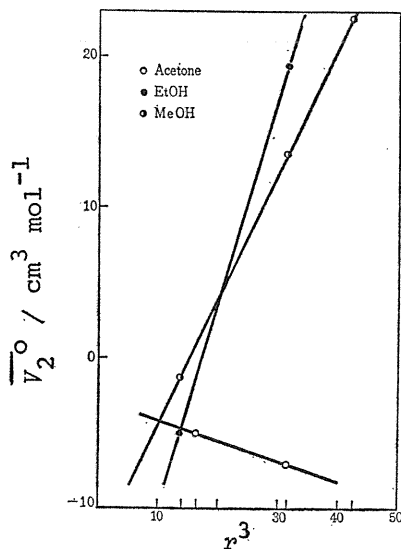
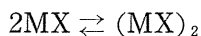


Fig. 13. Relationships between \bar{V}_2^0 and r^3 in acetone, EtOH, and MeOH at 30°C.

6. 5. LiCl and LiBr in Acetone.

The plots of h vs. the molality m are shown in Fig. 14. As shown in Fig. 14, it should be noted that the values of h for LiCl are positive at concentrations higher than 3×10^{-3} mol/kg

In the earlier paper,²⁷⁾ the values of h/m (not h) were plotted against m , and the curves obtained for LiCl and LiBr showed a tendency for h/m to increase with decrease in m at low concentrations. To account for this result we assumed that an equilibrium:



prevails at these concentrations. According to this assumption,

$$\lim_{m \rightarrow 0} \frac{h}{m} = K_a^{20)}$$

On the contrary, in Fig. 14, h tends to -1 at $m \rightarrow 0$. This discrepancy is probably due to the incomplete drying of the lithium salts in the previous experiments.²⁷⁾

In order to represent the experimental curves for LiCl and LiBr, we assume the following model:

In Fig. 13 the values of the partial molar volumes of LiCl, LiBr, NaI, and KI shown in Table 9 are plotted against r^3 ($r = r_c(M^+) + r_c(X^-)$), where $r_c(M^+)$ and $r_c(X^-)$ are the Pauling ionic radii for cation and anion, respectively. As is seen in Fig. 13, in MeOH and EtOH, \bar{V}_2^0 increases linearly with r^3 , while in acetone this relation does not hold. In addition, the value of K in Eq. (23) obtained in acetone is negative, that is $r_s/r_c < 1$. This fact contradicts the general rule that solvated radii of ions in nonaqueous solution are larger than crystallographic ones.²⁵⁾ The present paucity of the data available for \bar{V}_2^0 values in acetone prevents the interpretation of the discrepancies observed in alcohols and acetone.

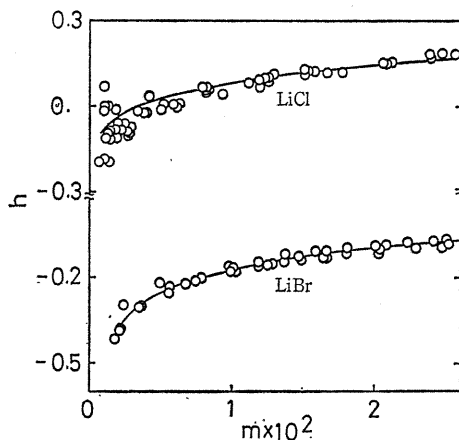
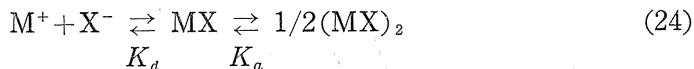


Fig. 14. Relationships between h and concentration for LiCl and LiBr in acetone at 40.3°C.



The dissociation equilibrium of the left-hand side is necessary in order to represent the shape of curves at low concentrations, and the association equilibrium is inevitable to account for the fact that h is positive at moderate concentrations. The application of the Gibbs-Duhem equation to the above association-dissociation equilibria gives;

$$\ln a_1 = -1/N_1(m_2 + 2m_4 + m_a + 2 \int_0^{m_4} m_4 d \ln \gamma_4) \quad (25)$$

$$m_3 = m_4 = m\gamma$$

$$m_2 = m(1 - \alpha - 2\beta) \quad (26)$$

$$m_a = m\beta$$

where: m_a , the molality of the dimer, $(MX)_2$
 α, β the degrees of dissociation and association respectively,
 γ_4 the mean activity coefficient of the ions,
 K_d the equilibrium constant of ionic dissociation,
 K_a the equilibrium constant of association,

and other parameters have been defined in chapter 2. In Fig. 14, the activity coefficients of MX and $(MX)_2$ are assumed to be unity for the simplicity of analysis. On the other hand, activity coefficients of the ions are assumed to be represented by the Debye-Hückel limited law, assumption [II].

We have tried to estimate the most probable values of K_a and K_d by means of the same curve-fitting procedures as for NaI , KI and RbI . The results are shown in Table 10. The curves in Fig.

Table. 10. K_a and K_d for $LiCl$ and $LiBr$ in acetone at $40.3^\circ C$. (in molality scale)

	$K_a \times 10^3$	$K_d \times 10^3$	Standard deviation
$LiCl$	0.00952	18.8	0.047
$LiBr$	0.432	4.19	0.015

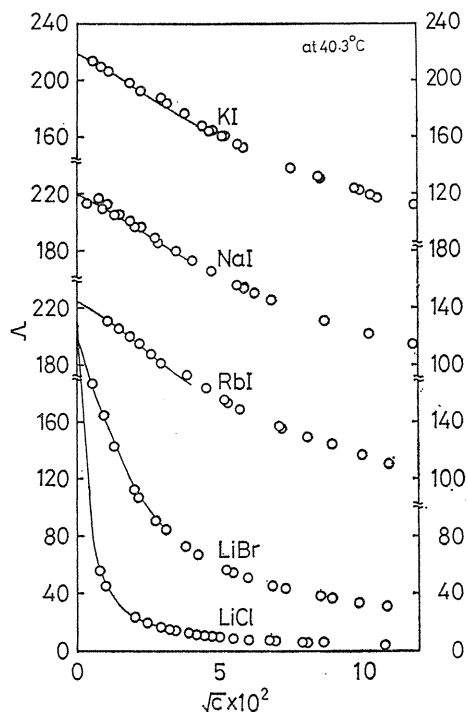


Fig. 15. Plots of A vs. \sqrt{C} for alkali halides in acetone at $40.3^\circ C$.

Table 11. Conductance parameters for acetone-alkali halide systems. (in molality scale)

	This Research (40.3°C)		Literature (25°C)	
	K_A	A_0	K_A	A_0
LiCl	2114×10^2	227.1	3030×10^2	214 (33)
LiBr	5146	219.6	4570	194 (33)
NaI	157	218.7	160	184.4(13)
KI	153.5	218.0	110	197.3(13)
			179.5	197.5(33)
RbI	254.8	224.3		

14. are theoretical ones calculated by the use of the parameters shown in Table 10. The agreements with the experimental values are satisfactory.

The electric conductances of solutions of LiCl, LiBr, NaI, KI and RbI in acetone were measured at 40.3°C. The concentration dependence of the conductivities of alkali halides in acetone are compared in Fig. 15. The results were analyzed by the use of Shedlovsky's equation.⁹⁾ The parameters, K_A and A_0 in Shedlovsky's equation, as obtained from our experimental results are shown in Table 11, where those at 25°C found in literature^{13,33)} are also given for comparison. Shedlovsky's equation is:

$$\frac{1}{AS(z)} = \frac{1}{A_0} + \frac{CAf_{\pm}^2 S(z) K_A}{A_0^2} \quad (27)$$

$$S(z) = \left\{ \frac{S\sqrt{CA}}{2A_0^{3/2}} + \left[1 + \left(\frac{S\sqrt{CA}}{2A_0^{3/2}} \right)^2 \right] \right\}^2 \quad (28)$$

$$\log f_{\pm} = -\frac{4.606A\sqrt{C\alpha}}{1 + Ba_0\sqrt{C\alpha}} \quad (29)$$

where A_0 is the equivalent conductance at infinite dilution.

The values of K_A thus obtained are converted to K_d and are shown in Table 11, together with the values from VPO. In the table, the agreement between the values from VPO and conductometry is really satisfactory for LiCl, NaI, and KI. For LiBr and RbI, the agreement is not satisfactory, but it is still within a factor of ten.

In order to account for the profiles of the h - m plots for LiCl and LiBr the equilibrium of the monomer-dimer at higher concentration is indispensable. The conductometry data can tell nothing about the presence of the dimer because of its electrically neutral nature. It should be emphasized at this point that the study with VPO is essentially necessary for the study of the solution properties of nonaqueous solutions.

7. Bolaform Electrolyte in Methanol, Ethanol, and 2-Propanol

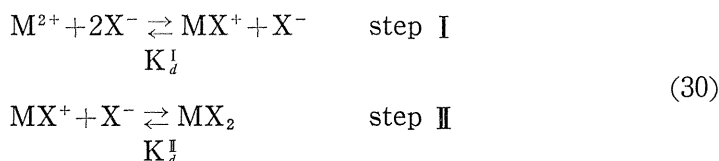
7. 1. Introduction.

There have been numerous investigations of solution properties of 1 : 1 electrolytes in nonaqueous solutions. However, because of the low solubility of 2 : 1 electrolytes in nonaqueous solvents, only a few results^{3,14,30)} have been reported for these systems. A series of electrolytes that circumvent this solubility problem in nonaqueous solvents is the bis-(tetraalkylammonio) or bolaform type of electrolyte. Their moderately high solubility is due to the rather large portion of hydrocarbon moieties in their elemental composition. These salts have been considered as model systems to examine the contribution of cation-cation ion pairing to the non-ideal behavior of R_4N^+ ions in aqueous solutions. Conductance studies of several of these systems have been reported by Evans *et al.*^{3,4)}

In this chapter we report vapor pressure lowering and conductance measurements of three kind of bis-(tetraalkylammonio) salts, J4, J5, and J10 in methanol, ethanol and 2-propanol in order to estimate the degree of ionic dissociation in these solvents. Measurements of VPO were carried out for methanol at 45°C, for ethanol at 55.1°C, and for 2-propanol at 60°C, while those of conductometry were at 25°C. Also, the present results are compared with those previously obtained^{3,5)} by means of ultrasonic relaxation studies of these electrolytes in 2-propanol.

7. 2. Theoretical.

An electrolyte, MX_2 , dissolved in nonaqueous solvent can exhibit a two-step dissociation equilibrium, as follows ;



For the reaction represented by Eq. (30), the integrated form of the Gibbs-Duhem equation is given as

$$\begin{aligned} \ln a_1 = & -\frac{1}{N_1} (m_2 + m_3 + m_4 + m_5 \\ & + \int_0^{m_3} m_3 d \ln \gamma_3 + \int_0^{m_4} m_4 d \ln \gamma_4 + \int_0^{m_5} m_5 d \ln \gamma_5) \end{aligned} \quad (31)$$

where m_2 is the molality of undissociated salt MX_2 ,

m_3 is the molality of cation M^{2+} ,

m_4 is the molality of anion X^- ,

m_5 is the molality of cation MX^+ ,

α is defined as $\alpha = m_5/m$ ($0 < \alpha < 1$),

β is defined as $\beta = m_3/m_5$ ($\beta > 0$),

γ_i is the mean activity coefficients of the ions, suffixes 3, 4, and 5 referring to M^{2+} , X^- , and MX^+ , respectively, and γ_2 , the activity coefficient of the undissociated salt, is assumed to be unity.

From these definitions it follows that in Eq. (30)

$$\begin{aligned} m_2 &= m[1 - \alpha(1 + \beta)] \\ m_3 &= m\alpha\beta \\ m_4 &= m\alpha(1 + 2\beta) \end{aligned} \quad (32)$$

$$\text{and } m_5 = m\alpha$$

The dissociation equilibrium constants are obtained by the same curve fitting method as for R_4NX and MX . For this purpose values of the activity coefficients on the right-hand side of Eq. (31) must be evaluated. We have assumed that the activity coefficients of the ions are represented by the Güntenberg type equation:*)

$$\ln \gamma_{\pm} = -\frac{A|Z_1Z_2|\sqrt{I}}{1 + \sqrt{I}}, \quad A = \frac{1.825 \times 10^6}{(\epsilon T)^{3/2}} \quad (33)$$

Numerical values of the density d_0 and the dielectric constant ϵ of the solvent used in calculations were obtained from Ref. 31.

7. 3. Results.

7. 3. 1. Vapor Pressure Osmometry.

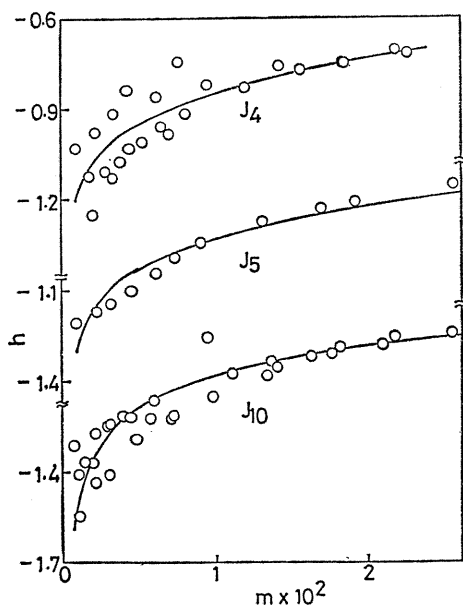


Fig. 16. Relationships between h and concentration for J4, J5, and J10 in MeOH at 45°C.

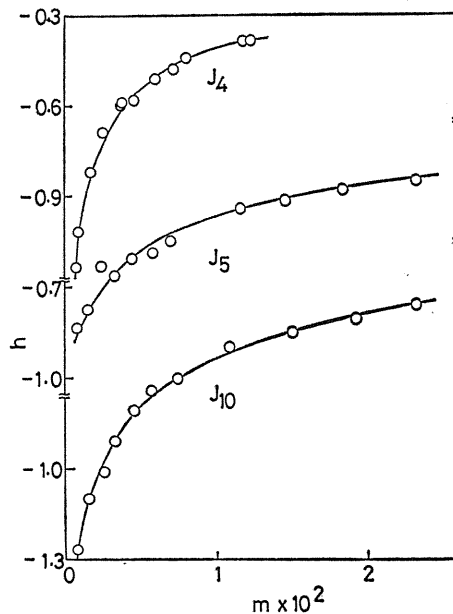


Fig. 17. Relationships between h and concentration for J4, J5, and J10 in EtOH at 55.1°C.

*) Güntenberg, E, *Z. Phys. Chem.*, 123, 199 (1926)

Unfortunately, at this stage, we have no experimental values of ionic radii of bis-(tetraalkylammonio) electrolytes in nonaqueous solvents, and so we have used Eq. (33) to calculate values of γ_{\pm} . However, as seen in Ref. 31, in the very low concentration regions, as in this work, the difference between observed and calculated ones from Eq. (33) can be negligible small.

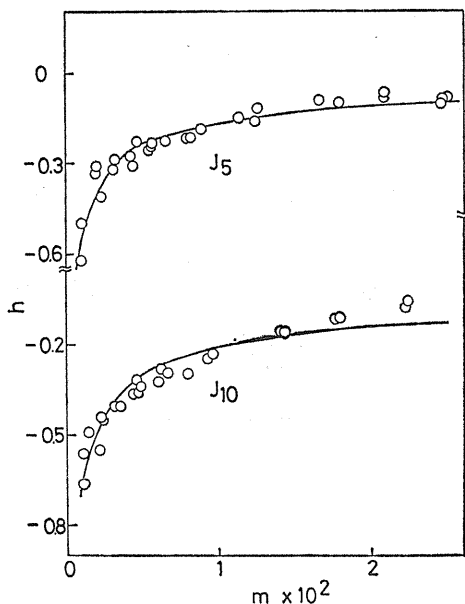


Fig. 18. Relationships between h and concentration for J5 and J10 in 2-PrOH at 60°C.

Plots of h vs. the concentration in molality units are shown in Figs. 16–18. The behavior of the values of h ($h \leq 0$) clearly shows the existence of a dissociation equilibrium.¹¹⁾

Attempts to fit the profiles of h vs. concentration using the procedures of one-step dissociation equation such as R_4NX in acetone did not give good fitting in this case. In order to estimate the two-step dissociation constants K_d^I and K_d^{II} in Eq. (30) the following procedures were carried out; From Eq. (30) one can write the following equations:

$$K_d^I = m\alpha\beta(1+2\beta) \frac{\gamma_{M^{2+}}\gamma_{X^-}}{\gamma_{MX^+}} \quad (34)$$

$$K_d^{II} = \frac{m\alpha^2(1+2\beta)}{1-\alpha(1+\beta)} \frac{\gamma_{MX^+}\gamma_{X^-}}{\gamma_{MX_2}}$$

In the first approximation, to simplify the calculations, assume the values of $(\gamma_{M^{2+}}\gamma_{X^-}/\gamma_{MX^+})$ and $(\gamma_{MX^+}\gamma_{X^-}/\gamma_{MX_2})$ to be unity. The function h can be expressed as

$$h = -\alpha(1+2\beta) \quad (35)$$

By means of the complete grid search techniques, the dissociation constants, K_d^I and K_d^{II} , were estimated so that the standard deviation

$$\sigma^2 = \sum \left(\frac{h_{\text{exp}} - h_{\text{cal}}}{h_{\text{exp}}} \right)^2 / (N-1) \quad (36)$$

is minimized, where N is the number of data.

In the second step, using the values of K_d^I and K_d^{II} obtained and Eq. (31) for γ_{\pm} , the values of α and β in Eq. (34) are corrected, then the computer method used in the first step was repeated, still assuming the γ_{MX^+} and γ_{MX_2} to be unity, because of their very low concentration.

The values of K_d^I and K_d^{II} obtained using this method are summarized in Table 12. The solid lines in Figs. 16–18 are the results obtained using these “best fit” values. It can be seen that there is a good agreement between experimental and calculated values.

Table 12. Dissociation constants of J4, J5, and J10 obtained by VPO and conductivity

Solute	$K_a^I \times 10^4$	$K_a^{\text{II}} \times 10^4$	Standard deviation for the h function	$K_a^I \times 10^4$
MeOH at 45°C				
J4	3.33 (2.71)	375.9 (305.6)	0.135	
J5	5.84 (4.75)	611.1 (496.8)	0.047	
J10	15.56 (12.2)	1944.4 (1521.7)	0.078	
EtOH at 55.1°C				
J4	5.00 (3.32)	20.58 (13.7)	0.030	
J5	0.034 (—)	40.53 (26.9)	0.028	
J10	6.67 (4.11)	77.78 (48.0)	0.016	
2-PrOH at 60°C at 25°C				
J5	4.12 (2.30)	2.12 (1.18)	0.037	6.25
J10	4.67 (2.33)	3.76 (1.88)	0.054	7.23

The values in the brackets show the corrected values at 25°C.

7. 3. 2. Conductometry.*)

The concentration dependence of the equivalent conductivities of J5 and J10 in 2-propanol obtained at 25°C is shown in Fig. 19. Conductance data have been analyzed by the treatment proposed by Davis³⁰⁾ and Monk,¹⁴⁾ in which deviations from the limiting Onsager equation are interpreted in terms of ion-association. At concentrations where the extent of association is small, the second step of Eq. (30) can be disregarded and the solution contains three species: M^{2+} , MX^+ , and X^- . If α is the fraction of intermediate product, MX^+ , (neglecting the difference between m (mol/kg) and C (mol/l), this α is consistent with that defined in Eq. (31). This assumption can

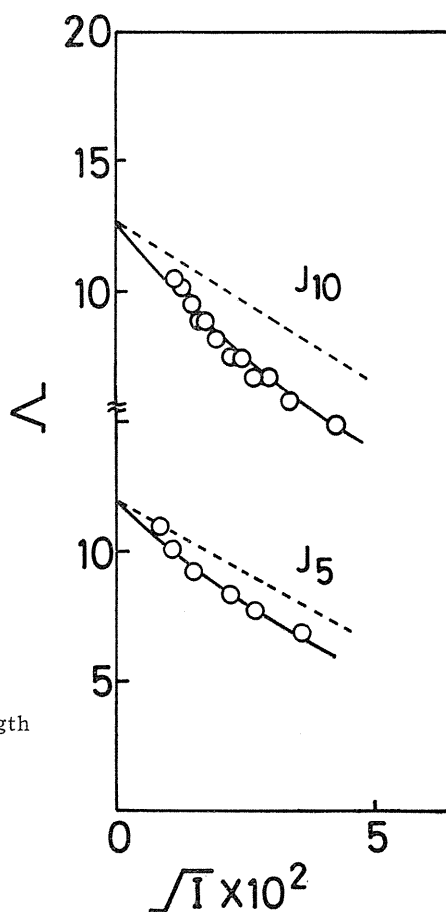


Fig. 19. Relationships between Λ and ionic strength for J5 and J10 in 2-PrOH at 25°C.

*) As seen in Ref. 27, the only reason to use Monk and Davis method is that it does not need the values of the ionic radii.

be acceptable in these experimental conditions. The equivalent conductivity will be given by;

$$A = (1 - \alpha) A_{M^{2+}} + \frac{1}{2} A_{MX^+} + \left(1 - \frac{\alpha}{2}\right) A_{X^-} \quad (37)$$

$$A = (1 - \alpha) (A_{M^{2+}} + A_{X^-}) + \frac{\alpha}{2} (A_{MX^+} + A_{M^-})$$

In this equation, the solution is regarded as a mixture of a completely dissociated uni-bivalent salt of concentration C , the molar concentration of the solution.

In solving the equation for α , the equivalent conductivity at infinite dilution of the intermediate ion is indispensable. The equivalent conductivity of intermediate product, A_{MX^+} , is assumed to be 0.6 times of $A_{M^{2+}}$, similarly to that of Monk *et al.*¹⁴⁾ Using the values of $\lambda_{Br^-}^0$ in the literature,¹⁸⁾ the values of $\lambda_M^{0,2+}$ were determined by the extrapolating procedure in the plots of A vs. $I^{1/2}$. Using the limiting Onsager equation, the empirical equations were obtained:

$$A = 12.0 - 111.13 I^{1/2} - \alpha(6.11 - 74.07 I^{1/2}) \quad \text{for J5,} \quad (38)$$

$$A = 15.6 - 125.23 I^{1/2} - \alpha(8.61 - 86.18 I^{1/2}) \quad \text{for J10}$$

The dissociation constant K_d^I can be obtained *i.e.*

$$K_d^I = \frac{C(2 - \alpha)(1 - \alpha)}{\alpha} \frac{\gamma_{M^{2+}} \gamma_{X^-}}{\gamma_{MX^+}} \quad (39)$$

By means of the usual computer method, using Eqs. (38) and (39), the dissociation constant K_d^I was determined so that the standard deviation

$$\sigma^2 = \sum \left(\frac{A_{\text{exp}} - A_{\text{cal}}}{A_{\text{exp}}} \right)^2 / (N - 1) \quad (40)$$

is minimized.

The values obtained for J5 and J10 are summarized in the 5th column of Table 12. In Fig. 19, solid lines show the best fitting ones, while the dashed lines show the limiting Onsager's law.

7. 4. Discussion.

The VPO measurements were carried out at different temperatures because of the different optimum experimental temperatures for the three solvents. In order to compare the K_d values obtained from the two techniques it was necessary to estimate the K_d^I and K_d^{II} values from VPO measurements for 25 °C. In a previous paper,³⁵⁾ the apparent activation energy ΔH of ionic association was estimated to be 3.3 and 3.9 kcal/mol for J5 and J10, respectively, in 2-propanol. As well, the ionic association constants in nonaqueous solvent depend mainly on the dielectric constant and its temperature dependence. Assuming the temperature dependence of K_d^I and K_d^{II} to be equivalent the activation energies in methanol and ethanol were estimated from the values in 2-propanol, taking into consideration the difference in dielectric constants of the solvents. The estimated values for the VPO method at

25°C are shown in brackets in Table 12. It is seen that the agreement between K_A^I values at 25°C derived from VPO and conductance data is within an order of magnitude. Figures 16-19 also show that there is no apparent evidence of micelle formation in these systems.

7. 4. 1. Solvent and Ionic Size Dependence of Ionic Association Constant.

In each solvent, the ionic association constant, K_A^I and K_A^{II} , defined as $K_A = 1/K_d$, tends to decrease with increasing ionic size. (As usual, the equilibrium properties of electrolytes in nonaqueous solvents are discussed using the ionic association constant, K_A , rather than K_d . We will talk about K_A instead of K_d .) This tendency is greater in K_A^{II} than in K_A^I . The K_A^I values of bis(tetraalkylammonio) electrolyte show virtually no dependence on the dielectric constant of solvent. On the contrary, the values of K_A^{II} strongly depend on the dielectric constant of the solvent. The relationship between $\log K_A^{II}$ and the dielectric constant of solvent is shown in Fig. 20. As is seen in Fig. 20, $\log K_A^{II}$ increases linearly with increasing values of $100/\epsilon$. This behavior is in good agreement with that of tetraalkylammonium ions shown in Fig. 9. This result indicates that the ionic association in step II (in Eq. (30)) is a solvent-separated type. It looks strange that in 2-propanol, the values of K_A^{II} are greater than that of K_A^I for both J5 and J10. However, as pointed by Evans *et al*²²⁾ and discussed in our previous paper³⁵⁾ the Et_4N^+ , Br^- ions and Et_4NBr in 2-propanol are strongly solvated with 2-propanol. It may be considered that J5 and J10 are also strongly solvated with 2-propanol as solvent. At this stage, the solvent effects on the dissociation equilibria of J5 and J10 in 2-propanol can not be explained completely, but it may be roughly considered as follows: The values of K_A^I and K_A^{II} for J10 in 2-propanol are comparable and also of the same order of magnitude as K_a for Et_4NBr in 2-propanol, 8.45×10^{-4} by conductometry¹⁸⁾ and 9.22×10^{-4} by VPO (see section 5.5, Table 6.). This fact clearly indicates that in a solvent of low dielectric constant, the ionic sites of J10^{2+} ion act independently because of the long distances between them.

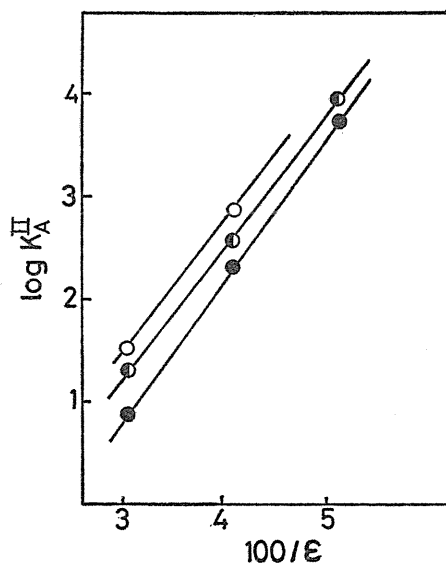


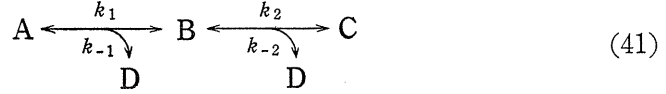
Fig. 20. Relationships between $\log K_A^{II}$ and $100/\epsilon$
○; J4, ◐; J5, ●; J10.

7. 4. 2. Interpretations for Dynamic Data by Means of Ultrasonic Method.

In a previous paper³⁵⁾, ultrasonic absorption data obtained over the frequency range 5-95 MHz by the pulse method were reported for tetraethylammonium bromide, J5, and J10 in 2-propanol in the temperature range 0-25°C. A single relaxation curve was observed under all experimental conditions. However, because of the lack of thermodynamic and conductance data for J5 and J10, a complete kinetic analysis

could not be carried out.

The equilibria, Eq. (30), can be symbolized as



where A, B, C, and D refer to MX_2 , MX^+ , M^{2+} , and X^- in Eq. (30) respectively, and the equilibrium concentration of them is shown as \bar{A} , \bar{B} , \bar{C} , and \bar{D} , respectively. As shown by the VPO data, this two-step reaction should be closely coupled. Under such conditions, the reciprocal relaxation terms can be expressed as^{11,32)}

$$\left. \begin{aligned} 2\pi f_{r1} &= \frac{1}{\tau_1} = \frac{a_{11} + a_{22}}{2} [1 + (1-b)]^{\frac{1}{2}} \\ 2\pi f_{r2} &= \frac{1}{\tau_2} = \frac{a_{11} + a_{22}}{2} [1 - (1-b)]^{\frac{1}{2}} \end{aligned} \right\} \quad (42)$$

and

$$b = \frac{4(a_{11}a_{22} - a_{12}a_{21})}{(a_{11} + a_{22})^2}$$

where

$$a_{11} = k_1 + k_{-1}(\bar{B} + \bar{C})$$

$$a_{12} = -k_1(\bar{B} - \bar{C})$$

$$a_{21} = -(k_2 + k_{-2}\bar{C})$$

$$a_{22} = -k_2 + k_{-2}(\bar{C} + \bar{D})$$

and the maximum excess absorption per wavelength is in this case represented by

$$\left. \begin{aligned} \mu_{\max 1} &= \frac{\pi(\Delta V_1 + X\Delta V_2)^2}{2\beta_0 RT} \left\{ \left(\frac{1}{\bar{A}} + \frac{1}{\bar{B}} + \frac{1}{\bar{C}} \right) + 2X \left(\frac{1}{\bar{D}} - \frac{1}{\bar{B}} \right) \right. \\ &\quad \left. + X^2 \left(\frac{1}{\bar{B}} + \frac{1}{\bar{C}} + \frac{1}{\bar{D}} \right) \right\}^{-1} \end{aligned} \right\} \quad (43)$$

and

$$\left. \begin{aligned} \mu_{\max 2} &= \frac{\pi(Y\Delta V_1 + \Delta V_2)^2}{2\beta_0 RT} \left\{ \left(\frac{1}{\bar{A}} + \frac{1}{\bar{B}} + \frac{1}{\bar{C}} \right) Y^2 + 2Y \left(\frac{1}{\bar{D}} - \frac{1}{\bar{B}} \right) \right. \\ &\quad \left. + \left(\frac{1}{\bar{B}} + \frac{1}{\bar{C}} + \frac{1}{\bar{D}} \right) \right\}^{-1} \end{aligned} \right\}$$

where

$$X = \frac{-k_2 - k_{-2}\bar{C}}{a_{11} + 1/\tau_2}$$

$$Y = \frac{k_{-1}(\bar{D} - \bar{B})}{a_{22} + 1/\tau_1}$$

Using the ionic association constants for J5 and J10 reported here, we can estimate the experimental relaxation frequencies. Since the kinetic constants, k_{-1} and k_{-2} , can be considered to represent diffusion control processes, their values are of the order of $10^{-10} \text{ M}^{-1}\text{s}^{-1}$. Assuming the values of k_{-1} and k_{-2} to be 2.35×10^{-10} , which is obtained for Et_4NBr in 2-propanol,³⁵⁾ the values of k_1 and k_2 can be estimated from the values of K_1^{II} and K_2^{II} .

Figure 21 shows the relaxation frequencies estimated by the above method for J5 and J10 in 2-propanol at 25°C. For J5 in 2-propanol, the agreement between the estimated and experimental values of higher relaxation frequencies is good. However, for J10 the agreement is not so good, but still within an order of magnitude. Considering the assumptions used for VPO data analysis and the method of obtaining these estimates, this difference is acceptable.

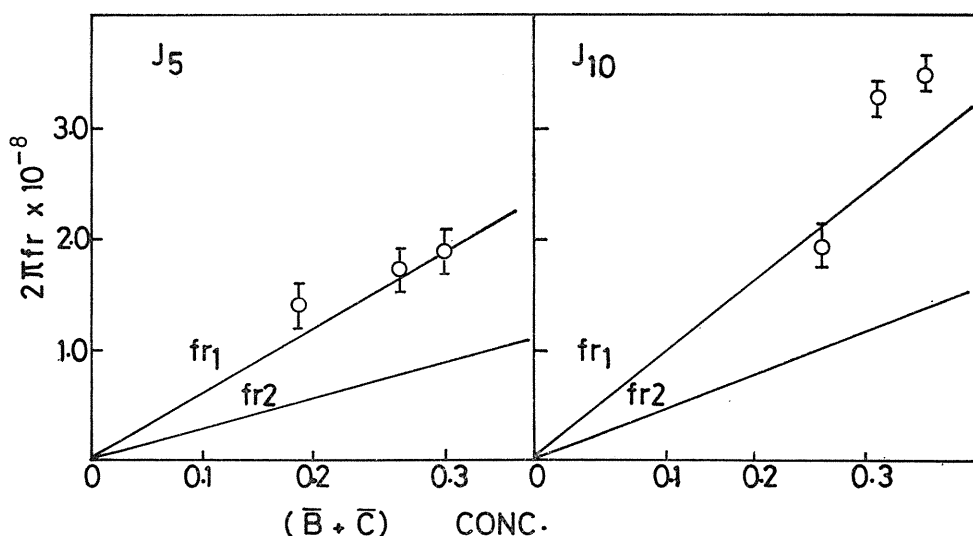


Fig. 21. Relationships between $2f_r$ and $(\bar{B} + \bar{C})$ in Eq. (42) (solid lines show the estimated one) for J5 and J10 in 2-PrOH.

For the case of J5 in 2-propanol, the maximum excess absorption per wavelength should be expressed by Eq. (43). In Eq. (43), the value of Y is almost zero and from a plot of $\mu_{\text{max}2}$ against $\left(\frac{1}{\bar{B}} + \frac{1}{\bar{C}} + \frac{1}{\bar{D}}\right)$ one can estimate the value of ΔV_2 to be $52.9 \text{ cm}^3/\text{mol}$. This value is of a reasonable magnitude and compares with that for malonic acid in aqueous solution, $50.3 \text{ cm}^3/\text{mol}$.³²⁾

Conclusion

Vapor pressure osmometry was applied to the study of the nonaqueous solution of electrolyte. The method of data analysis was established on the basis of one of

three models: i) $M^{+} + X^{-} \rightleftharpoons MX$, ii) $M^{+} + X^{-} \rightleftharpoons MX \rightleftharpoons (MX)_2$, and iii) $M^{2+} + 2X^{-} \rightleftharpoons MX^{+} + X^{-}$, $MX^{+} + X^{-} \rightleftharpoons MX_2$. In the data analysis, the activity coefficients of the dissociated species and the undissociated species were taken into account. The ionic dissociation constants determined by the present work are generally in good agreement with those obtained by conductivity measurements. Conductometry has been widely applied to the physicochemical study of the nonaqueous solution, but it can not be free from the following disputations; 1), it can not tell nothing about the presence of the dimer (for example, LiCl in acetone) because of the electrically neutral nature of the dimer. 2), for two-step dissociation equilibrium it can not give the dissociation equilibrium constant of each step simultaneously. 3), the activity coefficient of the undissociated species has been discarded. 4), it is a measurement of transport property, which is irrelevant to the discussion of thermodynamic equilibrium constant. It is therefore highly questionable to the discussion of the dissolved state of solute in nonaqueous solution to rely solely on the results of conductometry. The study of VPO is essentially necessary and very useful for the study of the physical properties of nonaqueous solutions. The method of VPO has just open a new way for the elucidation of the solution properties of nonaqueous solutions of electrolytes.

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References

- 1) Adams. W. A. and K. J. Laidler, *Can. J. Chem.*, **46**, 1977 (1968).
- 2) Broadwater. T. L. and D. F. Evans, *J. Phys. Chem.*, **73**, 3985 (1969).
- 3) Broadwater. T. L, T. J. Murphy and D. F. Evans, *J. Phys. Chem.*, **80**, 753 (1976).
- 4) Darbari. G. S. and S. Petrucci, *J. Phys. Chem.*, **74**, 268 (1970).
- 5) Drude, P. and W. Nernst, *Z. Phys. Chem.*, **15**, 79 (1894).
- 6) Evans. D. F, J. Thomas, J. A. Nadas, and S. M. A. Matesich, *J. Phys. Chem.*, **75**, 1714 (1971).
- 7) Fuoss. R. M. and F. Accasciana, "Electrolytic Conductance" Interscience Publishers, Inc. New York. N. Y. (1959).
- 8) Fuoss. R. M. and K. L. Hisa, *Proc. Natl. Acad. Sci. U. S. A.* **57**, 1550 (1967).
- 9) Fuoss. M. R. and T. Shedlovsky, *J. Am. Chem. Soc.*, **71**, 1496 (1949).
- 10) Hepler, L. G, *J. Phys. Chem.*, **61**, 1426 (1957).
- 11) Imura. M, H. Nomura, F. Kawaizumi, and Y. Miyahara, *Bull. Chem. Soc, Jpn.*, **47**, 2559 (1974).
- 12) Jackopin L. G. and E. Yeager, Technical Report No. 35. ONR Contract No. 1430 (04), Project No. 384-305, Western Reserve University, 1969.
- 13) Janz, G. J. and M. J. Tait, *Can. J. Chem.*, **45**, 1101 (1967).
- 14) Jenkins. I. L, and C. B. Monk, *J. Am. Chem. Soc.*, **72**, 2695 (1950).
- 15) Kamide, K, *Kobunshi-Kagaku* **25**, 648 (1968).

- 16) Kamide, K, *Kobunshi* **17**, 1144 (1968).
- 17) Kamide, K and M. Sanada, *Kobunshi-Kagaku*, **24**, 751 (1967).
- 18) Kay, R. L, *J. Am. Chem. Soc.*, **82**, 2099 (1960).
- 19) Lee, H. C. and Y. Miyahara, *Bull. Chem. Soc. Jpn.*, **51**, 2101 (1978).
- 20) Lee, H. C. and Y. Miyahara, *Bull. Chem. Soc. Jpn.*, **51**, 3140 (1978).
- 21) Lee, H. C, H. Nomura, Y. Miyahara, and R. E. Verrall, *Bull. Chem. Soc. Jpn.*, **52**, 2886 (1979).
- 22) Matesich, M. A, J. Nadas and D. F. Evans, *J. Phys. Chem.*, **74**, 4568 (1970).
- 23) McDowell, M. J. and C. A. Kraus, *J. Am. Chem. Soc.*, **73**, 3293 (1951).
- 24) Miyahara, Y, Annual Report on the Asahi Glass Foudation for the Contribution to Industrial Technology, **17**, 37 (1970).
- 25) Monica, M. D. and L. Senatore, *J. Phys. Chem.*, **74**, 205 (1970).
- 26) Mukerjee, P, *J. Phys. Chem.*, **65**, 740 (1961).
- 27) Nomura, H, M. Ando and Y. Miyahara, *Nippon Kagaku Zasshi*, **90**, 1222 (1969).
- 28) Nomura, H, M Ando, Y. Miyahara, *Nippon Kagaku Zasshi*, **91**, 840. (1970).
- 29) Nomura, H. and Y. Miyahara, *J. Appl. Polym. Sci.*, **8**, 1643 (1964).
- 30) Righellate, E.C. and C. W. Davis, *Trans. Faraday Soc.*, **26**, 592 (1930).
- 31) Robinson, R. A. and R. H. Stokes, "Electrolyte Solutions" 2nd. ed. Butterworth, London (1965).
- 32) Sano, T and T. Yasunaga, *J. Phys. Chem.*, **77**, 2031 (1973).
- 33) Savedoff, L. G, *J. Am. Chem. Soc.*, **88**, 664 (1966).
- 34) Thomas, J and D. F. Evans, *J. Phys. Chem.*, **76**, 3812 (1972).
- 35) Verrall, R. E. and H. Nomura, *J. Solution Chem.*, **6**, 541 (1977).