2886 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (10), 2886—2891 (1979) [Vol. 52, No. 10

Vapor Pressure Osmometry and Conductance Studies of Solutions of Bis(tetraalkylammonium) Electrolytes in Methanol, Ethanol, and 2-Propanol

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(Received May 14, 1979)

Vapor-pressure depressions and electric conductivities have been measured for bis(tetraalkylammonium) electrolytes in methanol, ethanol, and 2-propanol. The analysis of the data of vapor pressure osmometry (VPO) of these bolaform salts was carried out taking into account the two-step dissociation equilibrium as follows.

$$M^{2+} + 2X^- \underset{K_d^{I}}{\rightleftarrows} MX^+ + X^- \underset{K_d^{II}}{\rightleftarrows} MX_2$$

In each solvent, the ionic association constants, K_a^{I} and K_a^{II} ($K_a = 1/K_b$), tend to decrease with increasing ionic size. This tendency is greater in K_a^{I} than in K_a^{II}. The K_a^{I} values of bis(tetraalkylammonium) electrolytes 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 solvent. Using the values of K_a^{I} and K_a^{II} in 2-propanol, the ultrasonic relaxation data were analyzed.

In a recent series of papers,[1-5] vapor pressure lowering data obtained by means of vapor pressure osmometer (VPO) measurements have been reported for a variety of electrolytes in nonaqueous solvents. The concentration dependence of the activities of the salts has been analyzed assuming the existence of a dissociation and/or association equilibrium. Vapor pressure osmometry is particularly useful in studying cases of neutral species where the use of conductance techniques is precluded.[5] As well, in the case where ionic equlibria are being studied, it provides a method of estimating equilibrium constants complementary to conductance studies.

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,[6-8] only a few results have been reported for these systems. A series of electrolytes that circumvent this solubility problem in nonaqueous solvents is the bis(tetraalkylammonium) 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 had been considered as model systems to examine the contribution of cation-cation ion pairing to the nonideal behavior of R_4N^+ ions in aqueous solutions. Conductance studies of several of these systems have been reported by Evans *et al.*[9]

In the present paper we report vapor pressure lowering and conductance measurements of some bis(tetraalkylammonium) salts in methanol, ethanol and 2-propanol in order to estimate the degree of ionic dissociation in these solvents. Also, the present results are compared with those previously obtained[10] by means of ultrasonic relaxation studies of these electrolytes in 2-propanol.

Theoretical

A salt, MX_2, dissolved in non-aqueous solvent can exhibit a two-step dissociation equilibrium, as follows:

$$\begin{aligned} &M^{2+} + 2X^- \underset{K_d^{I}}{\rightleftarrows} MX^+ + X^- \quad \text{step I} \\ &MX^+ + X^- \underset{K_d^{II}}{\rightleftarrows} MX_2 \qquad\quad \text{step II} \end{aligned} \tag{1}$$

The activity of the solvent is related to the activity coefficients of the undissociated salt and ions by an integrated form of the Gibbs-Duhem equation. For the reactions represented by equation 1 this expression is given as

$$\ln a_1 = -\frac{1}{N_1}\left(m_2 + m_3 + m_4 + m_5 + \int_0^{m_3} m_3 \,\mathrm{d}\ln\gamma_3 + \int_0^{m_4} m_4 \,\mathrm{d}\ln\gamma_4 + \int_0^{m_5} m_5 \,\mathrm{d}\ln\gamma_5\right) \tag{2}$$

where a_1 is the activity of the solvent,
N_1 is the mole number of the solvent ($=1000/M_1$; M_1 is the molecular weight of the solvent),
m is the molal concentration of the added solute,
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. 2

$$\begin{aligned} m_2 &= m[1-\alpha(1+\beta)] \\ m_3 &= m\alpha\beta \\ m_4 &= m\alpha(1+2\beta) \\ \text{and } m_5 &= m\alpha \end{aligned} \tag{3}$$

The dissociation equilibrium constants are obtained by curve fitting procedures using Eq. 2. In order to do this, values of the activity coefficients in terms on the right-hand side of Eq. 2 must be evaluated. We have assumed that the activity coefficients of the ions are represented by the Güntenberg-type equation:[11]

$$\ln \gamma_{\pm} = -\frac{A|z_1z_2|\sqrt{I}}{1+\sqrt{I}}, \quad A = \frac{1.825\times10^6}{(\varepsilon T)^{3/2}} \tag{4}$$

Numerical values of the density d_0 and the dielectric constant ε of the solvent used in calculations were obtained from Ref. 12.

As in previous work,[4] a function, h, defined as

$$h = \frac{N_1 \ln a_1}{m} + 1 \tag{5}$$

was used for the analysis of the experimental results.

Experimental

Materials. The bis(tetraalkylammonium) salts, 1,4-bis(triethylammonio) butane dibromide, 1,5-bis(triethylammonio) pentane dibromide, and 1,10-bis(triethylammonio) decane dibromide, abbreviated hereafter J4, J5, and J10, respectively, were prepared and purified as described eleswhere.[13] Before use, the salts were dried for a period of five days in a vacuum oven at 50 °C over molecular sieves 3A (1/8 in. pellet). Fresh molecular sieves were used each day.

Reagent grade methanol and 2-propanol (Kishida Chemical Co. Ltd.) were further purified by drying with anhydrous calcium sulfate and finally distilled in the presence of molecular sieves 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 was checked by Karl-Fisher analysis and found to be less than 0.0018, 0.028, and 0.009 wt % for methanol, ethanol, and 2-propanol, respectively.

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.

Vapor Pressure Osmometry and Conductance. The experimental method and equipment have been reported in a previous paper.[4]

Results

Vapor Pressure Osmometry. The proportionality constants K_s of the apparatus were determined using standard substances: benzil for methanol and ethanol and 1-octadecanol for 2-propanol. The values of the constants K_s and K_e ($=BrR/\Delta H$, see Ref. 3 for definition of terms), and their ratios are summarized in Table 1. Vapor pressure depression measurements were carried out at 45.0, 55.1, and 60.0 °C for methanol, ethanol, and 2-propanol, respectively.

Table 1. Proportionality constants of VPO in various solvents

T/°C	K_s/Ω	$K_e(=BrR/\Delta H)/\Omega$	K_s/K_e
		MeOH–Benzil	
45	−42100	−43200	0.974
50	−38000	−37200	1.022
		EtOH–Benzil	
55.1	−27600	−28300	0.973
		i-PrOH–1-Octadecanol	
60	−21800	−23900	0.911
70	−17300	−18200	0.951

Values of h, calculated by introducing the experimental values of activity coefficients a_1 in Eq. 5, are given in Table 2. Plots of h *vs.* the concentration in molality units are shown in Figs. 1—3. The behavior of the values of h ($h\leq0$) clearly shows the existence of a dissociation equilibrium.[3]

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. 1, the following procedures

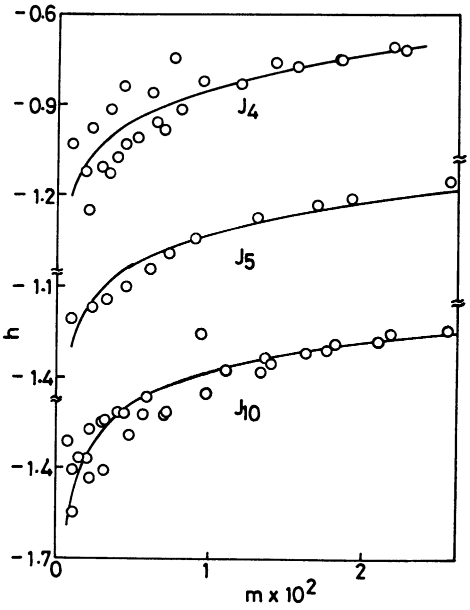


Fig. 1. Relationships between h and concentration for J4, J5, and J10 in methanol at 45 °C.

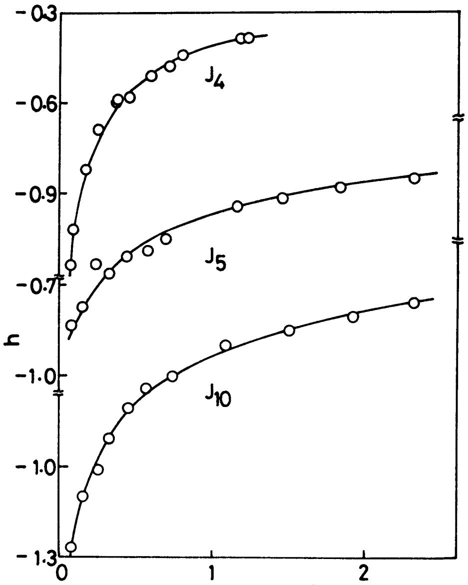


Fig. 2. Relationships between h and concentration for J4, J5, and J10 in ethanol at 55.1 °C.

TABLE 2. h VALUES OF BIS-TETRAALKYLAMMONIUM SALTS IN VARIOUS SOLVENTS

$m\times10^2$	h	$m\times10^2$	h	$m\times10^2$	h	$m\times10^2$	h
MeOH-J4 at 45 °C		0.1083	−1.5454	1.2277	−0.3841	0.6614	−0.2234
0.0946	−1.0361	0.1110	−1.4028			0.7964	−0.2173
0.1021	−1.4673	0.1446	−1.3661	EtOH-J5 at 55.1 °C		0.8087	−0.2177
0.1242	−0.6932	0.2035	−1.3666	0.0824	−0.8349	0.8951	−0.1888
0.1855	−1.1250	0.2147	−1.2706	0.1566	−0.7703	1.1360	−0.1504
0.2058	−1.2533	0.2232	−1.4365	0.2421	−0.6328	1.2427	−0.1598
0.2173	−0·9836	0.2943	−1.2504	0.3315	−0.6625	1.2611	−0.1186
0.2882	−1.1181	0.3022	−1.4069	0.4456	−0.6079	1.6673	−0.0934
0.3345	−1.1303	0.3164	−1.2383	0.5831	−0.5879	1.7946	−0.1000
0.3461	−0.9222	0.3939	−1.2114	0.6965	−0.5487	2.0913	−0.0855
0.3895	−1.0805	0.4414	−1.2151	1.1706	−0.4435	2.0914	−0.0673
0.4334	−0.8423	0.4785	−1.2882	1.4653	−0.4187	2.4574	−0.1028
0.4490	−1.0324	0.5634	−1.2271	1.8362	−0.3834	2.4800	−0.0829
0.5147	−1.0150	0.5883	−1.1633	2.3225	−0.3507	2.5151	−0.0799
0.6153	−0.8636	0.6998	−1.2249				
0.6504	−0.9635	0.7158	−1.2126	EtOH-J10 at 55.1 °C		2-PrOH-J10 at 60 °C	
0.6993	−0.9893	0.8713	−1.0982	0.0833	−1.2691	0.1085	−0.5616
0.7616	−0.7487	0.9397	−0.9480	0.1574	−1.1006	0.1178	−0.6590
0.8037	−0.9208	0.9726	−1.1478	0.2548	−1.0086	0.1401	−0.4926
0.9526	−0.8288	1.0999	−1.0728	0.3287	−0.9069	0.2145	−0.5519
1.1904	−0.8382	1.3316	−1.0804	0.4579	−0.8055	0.2307	−0.4426
1.4087	−0.7658	1.3574	−1.0312	0.5746	−0.7404	0.2361	−0.4547
1.5599	−0.7779	1.3933	−1.0522	0.7409	−0.7068	0.3230	−0.4037
1.8301	−0.7542	1.6626	−1.0156	1.0913	−0.6018	0.3475	−0.4016
2.1927	−0.7121	1.7612	−1.0063	1.5030	−0.5559	0.4588	−0.3643
2.2599	−0.7261	1.8205	−0.9864	1.9196	−0.5087	0.4673	−0.3658
1.8366	−0.7521	2.0910	−0.9802	2.3156	−0.4655	0.4893	−0.3416
		2.1659	−0.9562			0.6049	−0.3225
MeOH-J5 at 45 °C		2.5414	−0.9441	2-PrOH-J5 at 60 °C		0.6244	−0.2838
0.0961	−1.2045	2.6814	−0.9238	0.1029	−0.4989	0.6696	−0.2951
0.2293	−1.1707			0.1118	−0.6119	0.8026	−0.2993
0.3236	−1.1469	EtOH-J4 at 55.1 °C		0.1138	−0.5295	0.9293	−0.2535
0.4556	−1.1039	0.0841	−1.1356	0.2001	−0.3353	0.9574	−0.2135
0.6087	−1.0421	0.0868	−1.0143	0.2004	−0.3102	0.9590	−0.2323
0.7265	−0.9942	0.1696	−0.8204	0.2330	−0.4087	1.4045	−0.1609
0.9031	−0.9455	0.2564	−0.6890	0.3121	−0.3207	1.4173	−0.1633
1.3085	−0.8704	0.3624	−0.6033	0.3264	−0.2862	1.7633	−0.1169
1.6969	−0.8282	0.3798	−0.5922	0.4304	−0.2735	1.7825	−0.1160
1.9320	−0.8082	0.4631	−0.5882	0.4427	−0.3105	2.2173	−0.0797
2.5625	−0.7500	0.6028	−0.5152	0.4731	−0.2263	2.2386	−0.0605
		0.7151	−0.4800	0.5553	−0.2647	2.6255	−0.0485
MeOH-J10 at 45 °C		0.7976	−0.4413	0.5646	−0.2547	2.6301	−0.0408
0.0680	−1.3111	1.1804	−0.3861	0.5767	−0.2337	2.6835	−0.0411

were carried out; From Eq. 1, one can write the following equations:

$$K_d^{I} = m\alpha\beta(1+2\beta)\frac{\gamma_{M^{2+}}\gamma_{X^-}}{\gamma_{MX^+}}$$
$$K_d^{II} = \frac{m\alpha^2(1+2\beta)}{1-\alpha(1+\beta)}\,\frac{\gamma_{MX^+}\gamma_{X^-}}{\gamma_{MX_2}} \qquad (6)$$

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

$$h = -\alpha(1+2\beta) \qquad (7)$$

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

$$\sigma^2 = \sum\left(\frac{h_{exp}-h_{cal}}{h_{exp}}\right)^2 \qquad (8)$$

is minimized.

In the second step, using the values of $K_d{}^{I}$ and $K_d{}^{II}$ obtained and Eq. 4 for $\gamma_\pm$, the values of α and β in Eq. 6 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 3. The solid lines in Figs. 1—3 are the results obtained using these "best fit" values. It can be seen that there is good agreement between experimental and calculated values.

Conductometry.[14] The concentration dependence of the equivalent conductivities of J5 and J10 in 2-

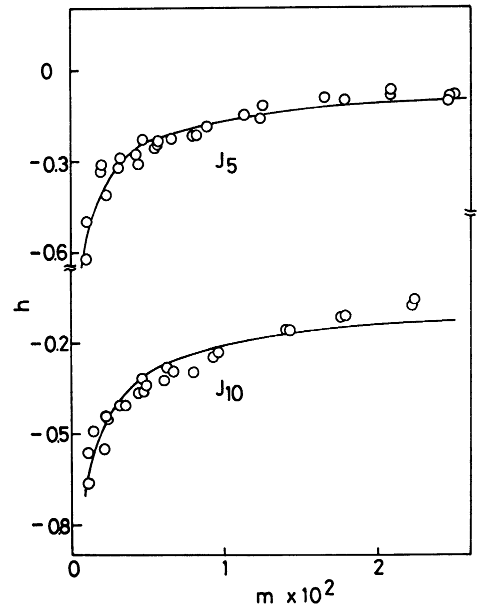


Fig. 3. Relationships between h and concentration for J5, and J10 in 2-propanol at 60 °C.

Table 3. Dissociation constants obtained by VPO and conductometry

Solute	$K_d^I \times 10^4$	$K_d^{II} \times 10^4$	Standard deviation for the function h	$K_d^I \times 10^4$
		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	
		i-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.

propanol obtained at 25 °C is shown in Fig. 4. Conductance data have been analyzed by the treatment proposed by Davis[6] and Monk,[7] 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. 1 can be disregarded and the solution contains three species: M^{2+}, MX^-, and X^-. If α is the fraction of intermediate product, MX^-, defined in Eq. 2 (neglecting the difference between m (mol/kg) and c (mol/l), this α is consistent with that defined in Eq. 2. This assumption can be acceptable in these experimental conditions.), the equivalent conductivity will be given by:

$$\Lambda = (1-\alpha)\Lambda_{M^{2+}} + \frac{1}{2}\Lambda_{MX^-} + \left(1-\frac{\alpha}{2}\right)\Lambda_{X^-}$$
$$\Lambda = (1-\alpha)(\Lambda_{M^{2+}}+\Lambda_{X^-}) + \frac{\alpha}{2}(\Lambda_{MX^-}+\Lambda_{X^-}) \tag{9}$$

In this equation, the solution is regarded as a mixture

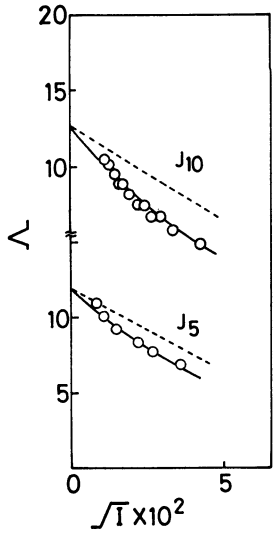


Fig. 4. Relationships between Λ and concentration for J5, and J10 in 2-propanol at 25 °C.

of a completely dissociated uni-bivalent salt of concentration c, where c refers to the molar concentration of the solution (mol/l).

In solving the equation for α, the equivalent conductivity at infinite dilution of the intermediate ion is indespensable. The equivalent conductivity of intermediate product, Λ_{MX^+}, is assumed to be 0.6 times of $\Lambda_{M^{2+}}$, similarly to that of Monk *et al.* Using the values of λ_{Br^-} in the literature,[15] the values of $\lambda^\circ_{M^{2+}}$ were determined by the extrapolating procedure in the plots of Λ *vs.* $I^1/^2$. Using the limiting Onsager equation, the empirical equations were obtained:

$$\begin{aligned}\Lambda &= 12.0-111.13I^{1/2}-\alpha(6.11-74.07I^{1/2}) \text{ for J5,}\\ \Lambda &= 15.6-125.23I^{1/2}-\alpha(8.61-86.18I^{1/2}) \text{ for J10}\end{aligned} \tag{10}$$

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

$$K_d^I = \frac{c(2-\alpha)(1-\alpha)}{\alpha}\,\frac{\gamma_{M^{2+}}\gamma_{X^-}}{\gamma_{MX^+}} \tag{11}$$

By means of the usual computer method, using Eqs. 10 and 11, the dissociation constant $K_d{}^I$ was determined so that the standard deviation

$$\sigma^2 = \sum\left(\frac{\Lambda_{exp}-\Lambda_{cal}}{\Lambda_{exp}}\right)^2 \tag{12}$$

is minimized.

The values obtained for J5 and J10 are summarized in the 5 th column of Table 3; In Fig. 4, solid lines show the best fitting ones. In Fig. 4, the dashed lines show the limiting Onsager's law.

Discussion

The VPO measurements were carried out at different temperatures because of the different optimum experimental conditions 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,[10] 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 3. It is seen that the agreement between K_d^{I} values at 25 °C derived from VPO and conductance data is within an order of magnitude. Figures 1—4 also show that there is no apparent evidence of micell formation in these systems.

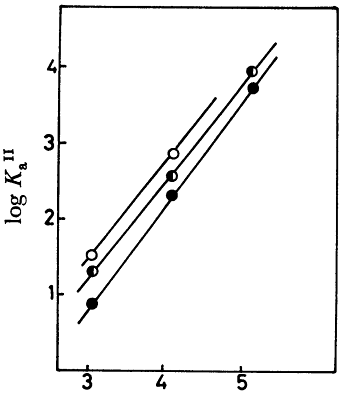
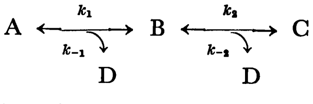


Fig. 5. Relationships between log K_a^{II} and 100/ε
○; J4, ◐; J5, ●; J10.

Solvent and Ionic Dependence of Ionic Accosiation Constants. 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(tetraalkylammonium) 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 100/ε, where ε refers to the dielectric constant of solvent, is shown in Fig. 5. As is seen in Fig. 5, log K_a^{II} increases linearly with increasing values of 100/ε. This behavior is in good agreement with that of tetraalkylammonium ions in nonaqueous solvents.[15] This result indicates that the ionic association in step II (in Eq. 1) 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.*[15] and discussed in our previous paper,[10] 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 value 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 conductometry[15] and 5.05×10^{-4} by VPO. 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.

Interpretations for Dynamic Data by Means of Ultrasonic Method: In a previous paper,[10] 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. 1, can be symbolized as



$$\mathrm{A} \underset{k_{-1}\,\searrow\,\mathrm{D}}{\overset{k_1}{\rightleftarrows}} \mathrm{B} \underset{k_{-2}\,\searrow\,\mathrm{D}}{\overset{k_2}{\rightleftarrows}} \mathrm{C} \tag{13}$$

where A, B, C, and D refer to MX_2, MX^+, M^{2+}, and X^- in Eq. 1 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[16,17]

$$\left.\begin{aligned} 2\pi f_{r1} &= \frac{1}{\tau_1} = \frac{a_{11}+a_{22}}{2}[1+(1-b)]^{1/2} \\ 2\pi f_{r2} &= \frac{1}{\tau_2} = \frac{a_{11}+a_{22}}{2}[1-(1-b)]^{1/2} \end{aligned}\right\} \tag{14}$$

and

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

where

$$\begin{aligned} a_{11} &= k_1 + k_{-1}(\bar{B}+\bar{C}) \\ a_{12} &= -k_1(\bar{B}-\bar{C}) \\ a_{21} &= -(k_2+k_{-2}\bar{C}) \\ a_{22} &= -k_2 + k_{-2}(\bar{C}+\bar{D}) \end{aligned}$$

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

$$\left.\begin{aligned} \mu_{\max 1} &= \frac{\pi(\Delta V_1+X\Delta V_2)^2}{2\beta_0 RT}\left\{\left(\frac{1}{\bar{A}}+\frac{1}{\bar{B}}+\frac{1}{\bar{C}}\right) + 2X\left(\frac{1}{\bar{D}}-\frac{1}{\bar{B}}\right) + X^2\left(\frac{1}{\bar{B}}+\frac{1}{\bar{C}}+\frac{1}{\bar{D}}\right)\right\}^{-1} \\ &\text{and} \\ \mu_{\max 2} &= \frac{\pi(Y\Delta V_1+\Delta V_2)^2}{2\beta_0 RT}\left\{\left(\frac{1}{\bar{A}}+\frac{1}{\bar{B}}+\frac{1}{\bar{C}}\right)Y^2 + 2Y\left(\frac{1}{\bar{D}}-\frac{1}{\bar{B}}\right) + \left(\frac{1}{\bar{B}}+\frac{1}{\bar{C}}+\frac{1}{\bar{D}}\right)\right\}^{-1} \end{aligned}\right\} \tag{15}$$

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} $M^{-1}\,s^{-1}$. Assuming the values of k_{-1} and k_{-2} to be 2.35×10^{-10}, which is obtained for Et_4NBr in 2-propanol, the values of k_1 and k_2 can be estimated from the values of $K_a{}^{I}$ and $K_a{}^{II}$.

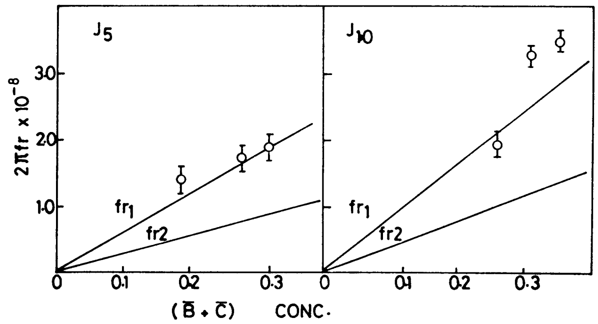


Fig. 6. Relationships between $2f_r$ and $(\bar{B}+\bar{C})$ in Eq. 14 (solid lines show the estimated one) for J5 and J10 in 2-propanol.

Figure 6 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.

For the case of J5 in 2-propanol, the maximum excess absorption per wavelength should be expressed by Eq. 15. In Eq. 15, the value of Y is almost zero and from a plot of $\mu_{\max 2}$ against $(1/\bar{B}+1/\bar{C}+1/\bar{D})$. One can estimate the value of ΔV_2 to be 52.9 ml/mol. This value is of a reasonable magnitude and compares with that for malonic acid in aqueous solution, 50.3 ml/mol.[17)]

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Unfortunately, at this stage, we have no experimental values of ionic radii of bis(tetraalkylammonium) electrolytes in nonaqueous solvents, and so we have used Eq. 4 to calculate values of $\gamma_{\pm}$. However, as seen in Ref. 12, in the very low concentrations, as in this work, the difference between observed and calculated ones from Eq. 4 can be negligible small.

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