

전해질 수용액의 구조와 성질

Ethanol—물 혼합용매에서의 Tetraalkylammonium Halides 의 점도에 관한 연구

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Structures and Properties of Electrolytes Aqueous Solutions

Viscosity studies of tetraalkylammonium halides in ethanol-water mixtures

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Abstract

The relative viscosities of a series of homologous tetraalkylammonium halides Me_4NBr , Me_4NCl , Me_4NI , $n\text{-Pr}_4\text{NCl}$, $n\text{-Pr}_4\text{NBr}$, $n\text{-Pr}_4\text{NI}$, Et_4NI and $n\text{-Bu}_4\text{NI}$ in a series of ethanol-water mixtures have been determined at 30, 35 and 40°C. The viscosity data have been interpreted in terms of viscosity A- and B-coefficients calculated from the Jones-Dele equation, $\eta_r = 1 + A\sqrt{C} + B \cdot C$. The energies and entropies of activation for viscous flow have also been calculated for a number of ionic species.

The results indicate that the structure breaking effect of halide ions are maximum at 0.1–0.2 mole fraction ethanol. Structure breaking effects decrease in the order $\text{I}^- > \text{Br}^- > \text{Cl}^-$.

The viscosity B-coefficients of these salts are all positive and increase in the order $\text{Me}_4\text{N}^+ < \text{Et}_4\text{N}^+ < n\text{-Pr}_4\text{N}^+ < n\text{-Bu}_4\text{N}^+$ and decrease in the order for the halide $\text{Cl}^- > \text{Br}^- > \text{I}^-$. The B-coefficient of Me_4NX increases and that of Pr_4NX decreases with increase in temperature. The energy and entropy of activation of these salts are calculated and the influence of such ions upon the binary solvent structure is discussed.

Introduction

In 1945, Frank and Evans¹⁾ proposed that symmetrical tetraalkylammonium ions should promote water structure as the hydrophobic nature of the ions increases with the size. Since then, numerous studies have shown that the idea was essentially correct. For example activity coefficient,^{2,3,4)} enthalpy and entropy of dilution,^{5,6)} heat capacity,^{7,8,9)} partial molal volume,^{9–16)} partial molal expansibility,^{17–20)} partial molal compressibility^{21–24)} ionic conductance,^{25–38)} viscosity,^{39–43)} infra-red absorption of water,

^{44–47)} X-ray diffraction,⁴⁸⁾ ultrasonic relaxation⁴⁹⁾ and solubility.⁵⁰⁾

Kay et al.⁵¹⁾ reported viscosity B-coefficient for the tetraalkylammonium bromides and iodides in aqueous solutions. They have shown that the Pr_4N^+ and Bu_4N^+ ions are excellent structure makers and the Me_4N^+ ion is a structure breaker, while for Et_4N^+ ion the two effects appear to cancel. Temperature dependence of the B-coefficients have been measured in water, D_2O , methanol and acetonitrile solutions, and Cho and Lee⁴³⁾ have been determined the B-coefficient of R_4NCl in isopropanol-water mixtures. The results of these authors also indicated that in aqueous and water-rich solutions the larger $n\text{-Pr}_4\text{N}^+$

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and $n\text{-Bu}_4\text{N}^+$ ions appear to be excellent structure-formers. Viscosity B-coefficients are characteristic of each salt and in principle each B-coefficient can be divided into individual ionic B-coefficient. These ionic B-coefficients reflect the effect of the ion upon solvent structure.

Since K^+ and Cl^- are approximately the same size and isoelectronic, it was suggested that in water at 298°K ,⁽²⁾ over the range $288\text{--}318^\circ\text{K}$ ⁽⁵⁵⁾ and in ethanol-water mixtures at $303\text{--}313^\circ\text{K}$,⁽⁵⁶⁾ $B(\text{K}^+)$ equals $B(\text{Cl}^-)$. Such ionic coefficients can be used to calculate other ionic quantities. No systematic investigation of the ionic B-coefficient of R_4NX in non-aqueous and ethanol-water mixtures have been performed.

In this work we have determined viscosities of ethanol-water mixtures containing R_4NI ($\text{R}=\text{Me}$, Et , $n\text{-Pr}$, and $n\text{-Bu}$), Me_4NX and $n\text{-Pr}_4\text{NX}$ ($\text{X}=\text{Cl}$, Br and I) at 30 , 35 and 40°C . The influence of electrolytes upon the viscosity of the solvent is interpreted as a rate process,⁽⁵⁷⁾ and energy, free energy and entropy of activation for viscous flow have been calculated for a number of salts. From these data the influence of the individual ions upon the energy and entropy of activation for viscous flow have been estimated. The aim of this work was to gain information on the individual ion-solvent interaction in dilute ethanol-water mixtures.

Experimental

Merk's reagent grade tetraalkylammonium salts were purified by recrystallization and dried in vacuum as described in the literature.^(12,41,58)

Merk's absolute ethanol was used without further purification (water content, 0.2%) throughout the course of experiment. In all measurements, water was redistilled twice and was equilibrated with atmospheric carbon dioxide. The conductivity was less than 1 meg-ohm. All solutions were made by weight (corrected to vacuum) and converted to molarities from the known densities.⁽⁵⁹⁾ For all measurements the temperature was controlled to better than $\pm 0.01^\circ\text{C}$.

Densities were measured in a 25ml. capacity pycnometer calibrated with distilled water for 0.05–0.0016 M solutions of salt. For each salt solution and solvent, at least three measurements were taken and the average value was reported. Average reproducibility of density was ± 0.00003 . All weighings were done to fifth decimal place with Mettler H 20-T semi-micro balance and compensated to values in vacuum by removing buoyancy by air. Compensation of buoyancy was performed by our previous treatment.⁽⁵⁶⁾ Computer IBM 1130, at the computing center, S.N.U. was used for carrying out all of these density calculations.

The viscosities of the solutions were measured at 30 , 35 and 40°C maintained to better than $\pm 0.01^\circ\text{C}$ using an Ubbelohde-type⁽⁶⁰⁾ viscometer with a flow time of 600–1800 seconds for water. For the viscosity measurements the solutions were filtered through a fine sintered glass disk before use. Flow times were measured to 0.1 sec. Individual readings for the three measurements at a set temperature agreed with each other to within 0.1sec. Overall accuracy of the viscosity measurements was estimated to be better than 0.02%.

Results and Discussion

Relative viscosities, η_r , are related to the concentration of solute, C , by the Jones and Dole's equation⁽⁶¹⁾ (1)

$$\eta_r = 1 + A\sqrt{C} + B \cdot C \quad (1)$$

where A and B are constants characteristic of solute. The constant A can be in principle theoretically calculable,⁽⁶⁰⁾ and is considered to represent the solute-solute interaction (inter-ionic coulomb interaction for electrolyte solutes). The constant B is purely empirical and cannot be accounted for theoretically. Experimental determination of these constants involves the plot of $(\eta_r - 1) / \sqrt{C}$ versus \sqrt{C} according to the following form of the Jones and Dole's equation, (Fig. 1),

$$(\eta_r - 1) / \sqrt{C} = A + B \cdot \sqrt{C} \quad (2)$$

where A and B are given as an intercept and a

slope of the straight line, respectively.

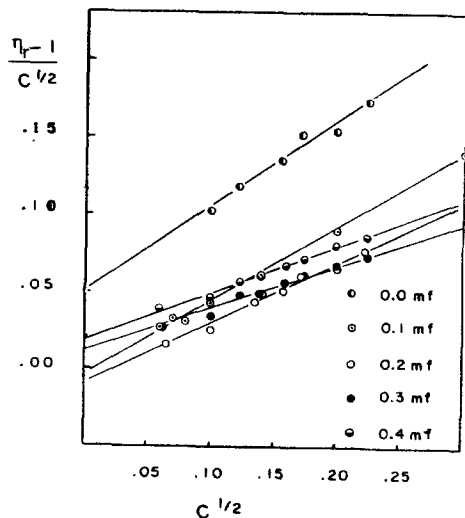


Fig. 1 Plot of $(\eta_r-1)/C^{1/2}$ vs $C^{1/2}$ for Pr_4NI in Various Ethanol-Water Mixtures at 30°C (as a typical one)

Accurate determination of viscosity A coefficient was difficult^{63,64} because the plots at extremely dilute concentration were scattered due to the experimental inaccuracies at these concentration. (see Fig. 1). Results are summarized in Table 1. A least squares fitting yield in some cases negative A -coefficients. Such results are of course without physical significance,⁶¹ since no negative values are

possible theoretically.^{42,65,66}

It is usual to equate the viscosity of a dilute electrolyte solution to that of the solvent plus the contributions from solutes in the following manner⁵⁹

$$\eta^* + \eta^E + \eta^A + \eta^D = \eta^O (A\sqrt{C} + B \cdot C) \quad (3)$$

where η^* is the positive increment in viscosity caused by coulombic interaction, i.e., contribution corresponding to A -coefficient, and η^E is the size and shape (Einstein) effect, η^A is the orientation effect of polar molecules (electrostatic effect) and η^D is the structure breaking effect, contributing additively to B -coefficients. In addition to these, large molecular ions such as R_4N^+ need a further parameter, η^S , to account for their high viscosity B -coefficient.⁵⁹ Frank^{7,67} suggested that the "ice-like" structure of the water at a distance from these ions is increased by their presence and viscosity B -coefficient of solution is increased accordingly. This viscosity increment due to the hydrophobic structure forming effect is represented by η^S .

Viscosity B -coefficients determined in this work for tetraalkylammonium iodides and for tetrapropyl and tetramethyl ammonium halides are shown in Table 2 and presented graphically in Figs. 2 and 3.

Table 1. Values of A - and B -coefficient for R_4NI in ethanol-water mixtures at 30° , 35° and 40°C

mf	$^\circ\text{C}$	A				B			
		Me_4	Et_4	Pr_4	Bu_4	Me_4	Et_4	Pr_4	Bu_4
0.0	30	0.0082	0.0084	0.0507	-0.1186	0.0407	0.2518	0.5441	1.6003
	35	0.0060	0.0015	0.0606	-0.0938	0.0729	0.2746	0.4780	1.4170
	40	0.0048	-0.0064	0.0590	-0.0764	0.0792	0.2900	0.4585	1.2963
0.1	30	-0.0308	-0.0029	-0.0036	-0.0034	0.0340	0.1852	0.4716	0.8596
	35	-0.0295	0.0009	-0.0086	-0.0434	0.0566	0.1616	0.4656	0.8639
	40	-0.0256	0.0085	0.0014	-0.0884	0.0641	0.1583	0.4124	0.8520
0.2	30	0.0015	0.0171	0.0075	-0.0160	0.0071	0.0741	0.3009	0.5459
	35	0.0086	0.0104	0.0105	-0.0163	0.0101	0.1113	0.3110	0.5449
	40	-0.0157	0.0094	0.0092	-0.0109	0.1285	0.1201	0.2909	0.5247
0.3	30	-0.0011	0.0088	0.0075	0.0064	0.1408	0.1778	0.3009	0.4433
	35	0.0302	0.0093	0.0165	0.0044	0.0861	0.1789	0.2822	0.4329
	40	0.0071	0.0053	0.0198	0.0149	0.1100	0.2135	0.2563	0.4023
0.4	30	0.0033	0.0186	0.0177	0.0057	0.2950	0.2390	0.3075	0.5105
	35	-0.0108	0.0168	0.0240	-0.0003	0.3512	0.2583	0.2819	0.4883
	40	-0.0091	0.0154	0.0190	0.0006	0.3368	0.2779	0.2968	0.4763

Table 2-A. Values of A- and B-coefficient for Me₄NX in ethanol-water mixtures at 30, 35 and 40°C

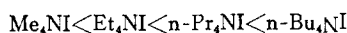
mf	°C	Cl ⁻		Br ⁻		I ⁻	
		A	B	A	B	A	B
0.0	30	0.0022	0.1169	-0.0031	0.1023	0.0082	0.0407
	35	0.0025	0.1318	-0.0033	0.1032	0.0060	0.0729
	40	-0.0023	0.1373	-0.0061	0.1171	0.0048	0.0792
0.1	30	0.0029	0.0521	-0.0055	0.0296	-0.0308	0.0340
	35	0.0080	0.0571	-0.0045	0.0390	-0.0295	0.0566
	40	0.0022	0.0769	-0.0060	0.0556	-0.0256	0.0641
Me ₄ N ⁺ 0.2	30	0.0085	0.0742	-0.0080	0.0593	0.0015	0.0071
	35	0.0065	0.0910	-0.0087	0.0817	0.0086	0.0101
	40	0.0113	0.1055	-0.0024	0.0426	-0.0157	0.1288
0.3	30	0.0127	0.1212	0.0081	0.0847	-0.0011	0.1408
	35	0.0128	0.1317	0.0100	0.0946	0.0302	0.0861
	40	0.0165	0.1404	0.0108	0.1085	0.0071	0.1100
0.4	30	0.0140	0.1843	0.0290	0.1025	-0.0033	0.2950
	35	0.0191	0.1896	0.0228	0.1333	-0.0108	0.3512
	40	0.0250	0.1864	0.0129	0.1742	-0.0091	0.3368

Table 2-B. Values of A and B-coefficient for n-Pr₄NX in ethanol-water mixtures at 30, 35 and 40°C

mf	°C	Cl ⁻		Br ⁻		I ⁻	
		A	B	A	B	A	B
0.0	30	0.0328	0.6729	0.0364	0.6813	0.0507	0.5441
	35	0.0289	0.6526	0.0344	0.6421	0.0606	0.4780
	40	0.0217	0.6288	0.0340	0.6058	0.0590	0.4585
0.1	30	-0.0045	0.5661	-0.0163	0.5228	-0.0036	0.4716
	35	-0.0044	0.5433	-0.0160	0.5051	-0.0086	0.4655
	40	-0.0081	0.5379	-0.0089	0.4369	0.0014	0.4124
n-Pr ₄ N ⁺ 0.2	30	0.0046	0.4106	-0.0066	0.4104	0.0075	0.3009
	35	-0.0000	0.4113	-0.0068	0.4058	0.0105	0.3110
	40	-0.0007	0.4019	-0.0033	0.3940	0.0092	0.2909
0.3	30	0.0069	0.3951	0.0047	0.3806	0.0075	0.3009
	35	0.0093	0.3849	0.0027	0.3781	0.0165	0.2822
	40	0.0076	0.3776	-0.0006	0.3826	0.0198	0.2563
0.4	30	0.0097	0.4479	0.0145	0.3908	0.0177	0.3075
	35	0.0136	0.4148	0.0133	0.3833	0.0240	0.2819
	40	0.0162	0.4015	0.0156	0.3685	0.0190	0.2968

B-coefficients in all cases are positive and positive value increases with the size of the cation R₄N⁺.

For iodide series, B increases in the order (Fig. 2),



while for n-tetrapropyl and tetramethyl series, B decreases with the size of anion in the order

(Fig. 3),



where R is n-propyl or methyl group. In terms of the four parameters contributing to B,

$$(\eta^E + \eta^A + \eta^S) > \eta^D$$

in all cases, since B is positive. Tetraalkylammonium cations are large and therefore the electrostriction

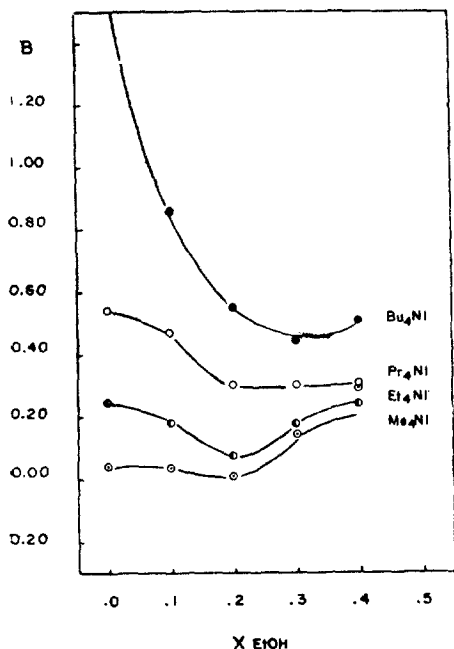


Fig. 2. Viscosity B-coefficient of tetraalkylammonium iodide as a function of solvent composition (mole fraction ethanol) at 30°C

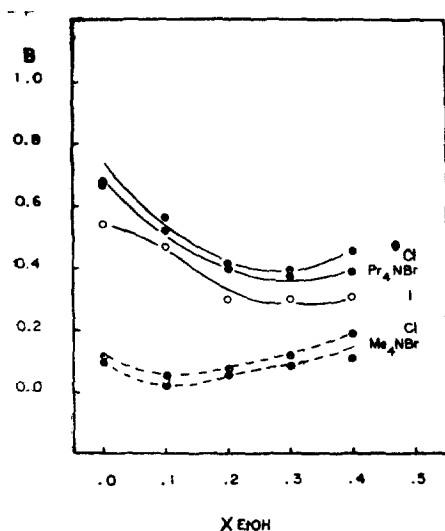


Fig. 3. Viscosity B-coefficient of Me_4NX and Pr_4NX as a function of Solvent composition (mole fraction ethanol) at 30°C

effect, η^A , should be small⁽⁵⁹⁾ as compared with the size, η^E , and hydrophobic, η^S , effects, and the B will be determined mainly by the latter two effects. Although the additivity of B coefficient, $B^+ + B^- = B$,

is well established for aqueous electrolyte system,^(52,54) no such attempt has been made for mixed solvent systems⁽⁵⁹⁾

In a previous paper,⁽⁵⁶⁾ we have reported viscosity B-coefficients of KCl in a series of ethanol-water mixtures. If we make the same assumptions as in water⁽⁵²⁾ then for the ethanol-water mixtures,

$$B_{\text{Cl}^-} = B_{\text{K}^+} \quad (4)$$

therefore it is possible to obtain $B_{\text{R}_4\text{N}^+}$ and B_{X^-} value from the following equation,

$$B_{\text{R}_4\text{N}^+} = B_{\text{R}_4\text{NCl}} - B_{\text{Cl}^-} \quad (5)$$

$$B_{\text{X}^-} = B_{\text{R}_4\text{NX}} - B_{\text{R}_4\text{N}^+} \quad (6)$$

The B values determined in this manner are summarized in Table 3, and presented graphically in Fig. 4. It is interesting to note in this figure that B_{X^-} values are all negative whereas $B_{\text{R}_4\text{N}^+}$ values are all positive. Thus for anions, structure-breaking effect predominates, i. e.,

$$\eta^D > (\eta^S + \eta^A + \eta^E)$$

while for cations this is reversed to,

$$\eta^D < (\eta^S + \eta^A + \eta^E)$$

since in this case the size and hydrophobic of R_4N^+ ions are expected to become important. Comparison of Figs. 2 and 4 shows that $B_{\text{R}_4\text{NI}}$ values are controlled by $B_{\text{R}_4\text{N}^+}$ while comparison of Figs. 3 and 4 shows that $B_{\text{Pr}_4\text{NX}}$ values are controlled by $B_{\text{Pr}_4\text{N}^+}$ but $B_{\text{Me}_4\text{NX}}$ values are controlled by B_{X^-} values. In other words, for large R group, $(\eta^S + \eta^E) > \eta^D$ and for small R group, $(\eta^S + \eta^E) < \eta^D$ since η^A is negligible in all cases.

Another important feature of interest from Fig. 4 is that B values show extremum behavior as the solvent composition is varied B_{X^-} values show a shallow minimum at 0.1-0.2 mole fraction while the minimum for $B_{\text{R}_4\text{N}^+}$ tends to become pronounced and shift towards larger mole fraction range as the cation size increases. Since, η^D effect, i. e., structure breaking effect predominates in B_{X^-} , this minimum at 0.1-0.2 mole fraction corresponds to the maximum breaking of structure⁽⁵⁹⁾ at this solvent composition.

This is in agreement with the fact that at about 0.1 mole fraction water structure is maximum^{14,68,69}) and therefore the structure breaking effect will be a maximum.^{14,69})

For the relatively small cation, Me_4N^+ , both structure breaking and size effect will manifest and there will be no significant change in B-coefficient. For the larger cations, however, hydrophobic effect, η^S , will be large in the water-rich region ($X < 0.2$), while size effect η^E will become large in the less structured region ($X = 0.2-0.4$) where free volume is believed to be a minimum.^{14,16,69}) These two positive increments in viscosity will give additive effect, but Fig. 4 shows that the hydrophobic effect is much stronger than the size effect.

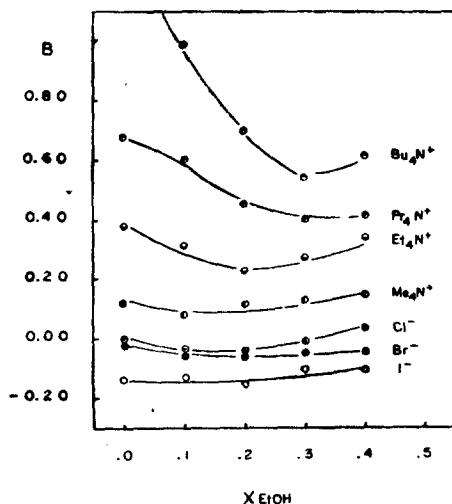


Fig. 4 Ionic Viscosity B-Coefficient of tetraalkyl Ammonium ions and Halides ions as a function of Solvent Composition (mole fraction ethanol) at 30°C

The combined effect of cation and anion shown in Figs. 2 and 3 indicate that for salts with large cation, the cation effect is predominant, while for salts with small cation, anion effect is predominant. The temperature dependence of B-coefficient is given in Fig. 5. It is clear that for Pr_4NX B value decreases with temperature whereas for Me_4NX B value increases with temperature. This is in agreement with our conclusion that Me_4NX is the structure-breaker, while Pr_4NX is the structure-former, since at

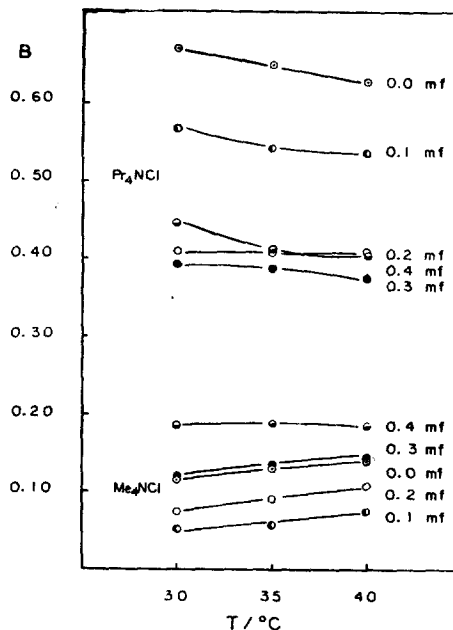


Fig. 5-a Temperature Dependence of B-coefficients for Me_4NCl and Pr_4NCl

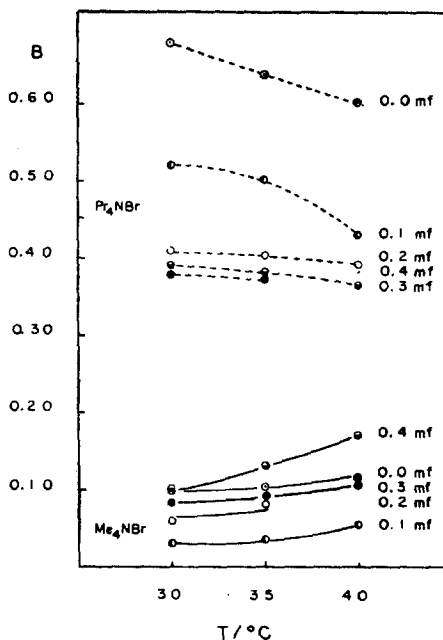


Fig. 5-b Temperature Dependence of B-coefficients for Me_4NBr and Pr_4NBr

higher temperature these will be less structural effects due to the thermal structure destruction.⁷⁰⁾

Using the same procedure as described previously,⁵⁶⁾

Table 3. Ionic B values in various ethanol-water mixtures at 30°C

X_{EtOH}	Cl^-	Br^-	I^-	Me_4N^+	Et_4N^+	$n\text{-Pr}_4\text{N}^+$	$n\text{-Bu}_4\text{N}^+$
0.0	-0.0063	-0.0209	-0.1351	0.1232	0.3869	0.6792	1.7354
0.1	-0.0348	-0.0573	-0.1293	0.0869	0.3145	0.6009	0.9889
0.2	-0.0425	-0.0574	-0.1522	0.1167	0.2263	0.4531	0.6981
0.3	-0.0081	-0.0446	-0.1023	0.1293	0.2801	0.4032	0.5456
0.4	0.0359	-0.0459	-0.1045	0.1484	0.3435	0.4120	0.6150

Table 4-A. Energy, free energy, and entropy of activation for viscous flow at 30°C ($C=0.1$ mole/l.)

Salt	X_{EtOH}	ΔE^\ddagger	ΔG^\ddagger	ΔS^\ddagger	ΔE_\pm^\ddagger	ΔG_\pm^\ddagger	ΔS_\pm^\ddagger	$-T\Delta S_\pm^\ddagger$
		Kcal/mole		e. u.	Kcal/mole		e. u.	Kcal/mole
$n\text{-Pr}_4\text{NI}$	0.0	4.169	2.214	6.448	0.274	0.049	0.743	-0.225
	0.1	5.937	2.728	10.585	0.111	0.038	0.239	-0.072
	0.2	6.601	2.931	12.105	0.049	0.032	0.056	-0.017
	0.3	6.109	2.998	10.260	0.049	0.030	0.064	-0.019
	0.4	5.616	3.064	8.418	0.044	0.033	0.037	-0.011
$n\text{-Pr}_4\text{NBr}$	0.0	4.154	2.220	6.380	0.189	0.056	0.440	-0.133
	0.1	6.138	2.728	11.250	0.099	0.041	0.191	-0.058
	0.2	6.524	2.939	11.826	0.046	0.036	0.033	-0.010
	0.3	6.026	3.031	9.882	0.033	0.034	-0.004	+0.001
	0.4	5.634	3.067	8.467	0.040	0.034	0.018	-0.005
$n\text{-Pr}_4\text{NCI}$	0.0	4.112	2.220	6.240	0.204	0.056	0.049	-0.015
	0.1	6.177	2.730	11.370	0.065	0.045	0.067	-0.020
	0.2	6.456	2.949	11.569	0.028	0.036	-0.026	-0.008
	0.3	6.066	3.031	10.012	0.029	0.035	-0.020	-0.006
	0.4	5.617	3.068	8.408	0.637	0.037	0.002	-0.001

Table 4-B. Energy, free energy and entropy of activation for viscous flow at 30°C

$$\Delta E^\ddagger = \Delta E_0^\ddagger + B \cdot C$$

$$\Delta G^\ddagger = \Delta G_0^\ddagger + B' \cdot C$$

Salt	X_{EtOH}	ΔE_0^\ddagger	B	ΔG_0^\ddagger	B'	ΔS_0^\ddagger
		kcal/mole		kcal/mole		e. u.
$n\text{-Pr}_4\text{NI}$	0.0	3.895	2.7368	2.166	0.4860	5.705
	0.1	5.826	1.1091	2.690	0.3833	10.346
	0.2	6.552	0.4896	2.899	0.3187	12.049
	0.3	6.059	0.4932	2.968	0.3000	10.196
	0.4	5.572	0.4405	3.031	0.3268	8.381
$n\text{-Pr}_4\text{NBr}$	0.0	3.965	1.8890	2.164	0.5546	5.940
	0.1	6.039	0.9859	2.687	0.4068	11.059
	0.2	6.478	0.4572	2.903	0.3592	11.793
	0.3	5.994	0.3263	2.997	0.3374	9.886
	0.4	5.595	0.3949	3.033	0.3400	8.449
$n\text{-Pr}_4\text{NCI}$	0.0	3.908	2.0400	2.164	0.5574	5.750
	0.1	6.112	0.6521	2.685	0.4484	11.303
	0.2	6.428	0.2833	2.912	0.3615	11.595
	0.3	6.038	0.2853	2.996	0.3464	10.032
	0.4	5.580	0.3706	3.031	0.3647	8.406

Table 5-A. Energy, Free energy and entropy of activation for viscous flow at 30°C (C=0.1 mole/l.)

Salt	X_{EtOH}	ΔE^*	ΔG^*	ΔS^*	ΔE_{\pm}^*	ΔG_{\pm}^*	ΔS_{\pm}^*	$-T\Delta S_{\pm}^*$
		kcal/mole		e. u.	kcal/mole		e. u.	kcal/mole
Me_4NI	0.0	3.892	2.172	5.674	-0.033	0.009	-0.141	0.043
	0.1	6.212	2.682	11.646	-0.018	0.006	-0.079	0.024
	0.2	6.373	2.919	11.393	-0.010	0.005	-0.049	0.015
	0.3	5.933	3.011	9.638	-0.037	0.009	-0.155	0.047
	0.4	5.567	3.044	8.324	-0.050	0.013	-0.207	0.063
Me_4NBr	0.0	3.951	2.167	5.885	-0.028	0.005	-0.109	0.033
	0.1	6.003	2.692	10.923	-0.029	0.002	-0.104	0.032
	0.2	6.458	2.907	11.723	-0.036	0.003	-0.120	0.036
	0.3	5.920	3.007	9.609	-0.054	0.009	-0.208	0.063
	0.4	5.517	3.063	8.094	-0.072	0.013	-0.281	0.085
Me_4NCl	0.0	3.923	2.174	5.771	-0.037	0.013	-0.164	0.050
	0.1	5.989	2.689	10.885	-0.036	0.007	-0.194	0.043
	0.2	6.527	2.909	11.935	-0.052	0.007	-0.142	0.059
	0.3	5.939	3.013	9.653	-0.070	0.010	-0.262	0.079
	0.4	5.583	3.046	8.368	-0.086	0.014	-0.330	0.100

Table 5-B. Energy, free energy and entropy of activation for viscous flow at 30°C

$$\Delta E^* = \Delta E_0^* + B \cdot C$$

$$\Delta G^* = \Delta G_0^* + B' \cdot C$$

Salt	X_{EtOH}	ΔE_0^*	B	ΔG_0^*	B'	ΔS_0^*
		kcal/mole		kcal/mole		e. u.
$MeNCl$	0.0	3.961	-0.3725	2.161	0.1252	5.935
	0.1	6.024	-0.3569	2.681	0.0727	11.027
	0.2	6.579	-0.5181	2.902	0.0693	12.129
	0.3	6.009	-0.6961	3.003	0.0986	9.915
	0.4	5.669	-0.8603	3.032	0.1405	8.698
Me_4NBr	0.0	3.980	-0.2818	2.163	0.0482	5.994
	0.1	6.032	-0.2917	2.689	0.0217	11.027
	0.2	6.494	-0.3621	2.904	0.0329	11.843
	0.3	5.974	-0.5407	2.997	0.0908	9.817
	0.4	5.589	-0.7195	3.050	0.1303	8.375
Me_4NI	0.0	3.925	-0.3341	2.163	0.0923	5.815
	0.1	6.230	-0.1793	2.675	0.0617	11.725
	0.2	6.383	-0.0968	2.914	0.0533	11.442
	0.3	5.971	-0.3739	3.002	0.0929	9.793
	0.4	5.618	-0.5037	3.031	0.1264	8.531

we have calculated the activation energy ΔE^* , and activation free energy, ΔG^* , of viscous flow for Pr_4NX and Me_4NX as summarized in Tables 4 and 5. Fig. 6 shows the variation of $\Delta E_{(soln)}^*$ and ΔG^* as a function of Pr_4NBr and Me_4NBr concentration. It can be seen that $\Delta E_{(soln)}^*$ of Me_4NBr decreases and that of Pr_4NBr increases linearly with these salts concentration in all solvent composition. This is

again in agreement with the previous conclusion that Me_4NBr is a structure breaker and Pr_4NBr is a structure maker in all solvent composition studied.

Figs. 7 and 8 show graphical presentation of the data. These figures show that curves for ΔE^* and ΔG^* have similar trend for $n-Pr_4NX$, while they have opposite trend for Me_4NX . Therefore the flow is controlled by activation energy in the case of $n-Pr_4NX$, whereas

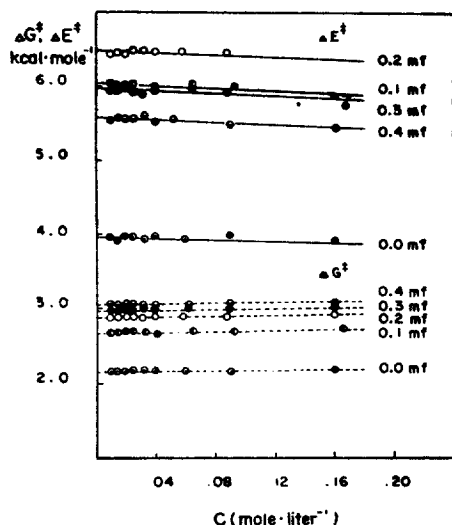


Fig. 6-a Energies and free energies of Activation for Viscous Flow as a Function of Concentration for Me_4NBr in Ethanol-Water Mixtures at 30°C

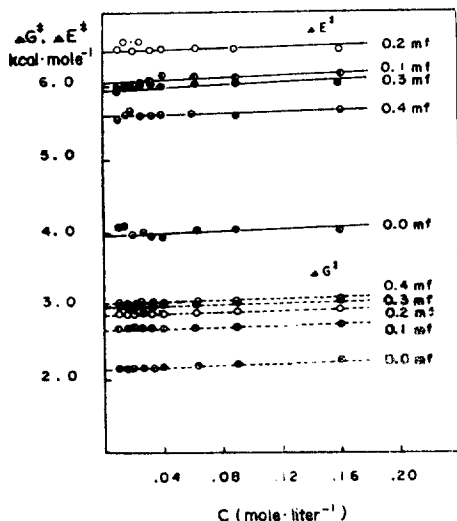


Fig. 6-b Energies and Free Energies of Activation for Viscous Flow as a Function of Concentration for Pr_4NBr in Ethanol-Water Mixtures at 30°C

it is controlled by entropy of activation in the case of Me_4NX . This becomes clearer if we plot the three parameters, i.e., ΔG^\ddagger , ΔE^\ddagger , and ΔS^\ddagger in the same figure as can be seen in Fig. 9. Fig. 9 shows the close similarity of ΔE^\ddagger and ΔG^\ddagger for $n\text{-Pr}_4\text{NBr}$. Thus

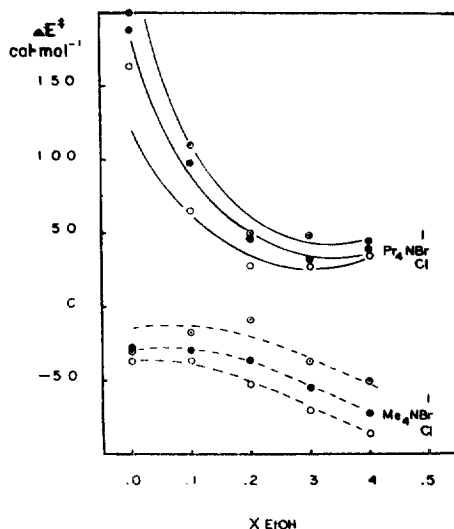


Fig. 7 Variation of ΔE^\ddagger for Me_4NX and Pr_4NX With X_{EtOH} at 30°C ($C=0.1\text{mole/l.}$)

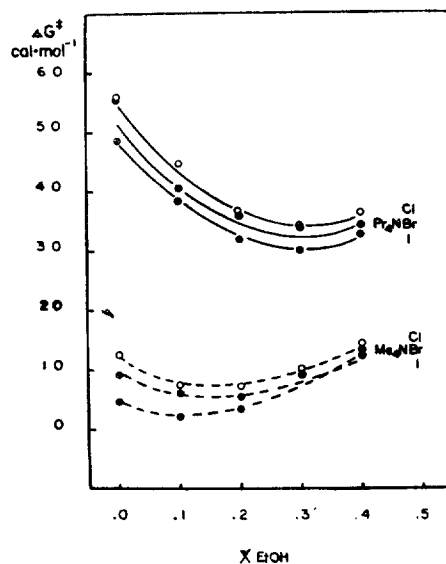


Fig. 8 Variation of ΔG^\ddagger for Me_4NX and Pr_4NX with X_{EtOH} at 30°C ($C=0.1\text{mole/l.}$)

energy factors in viscous flow of $n\text{-Pr}_4\text{NBr}$ determine flow velocity of the salt solution. This is consistent with the fact that this salt is bulky (large η^E) and has relatively large hydrophobic effect (large η^S).

On the other hand Fig. 9 shows the similarity between ΔG^\ddagger and $-T\Delta S^\ddagger$ for Me_4NBr . This indicates

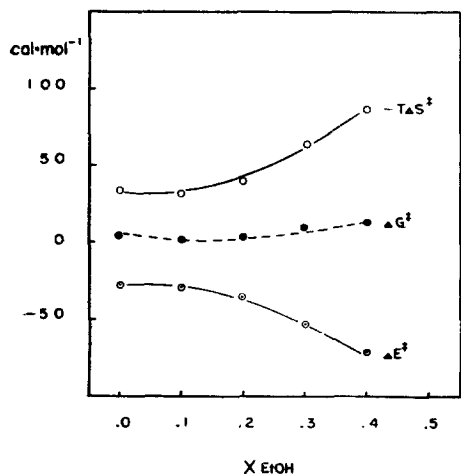


Fig. 9-a Variation of ΔG^\ddagger , ΔE^\ddagger and $T\Delta S^\ddagger$ of Me_4NBr with X_{EtOH} at 30°C ($c=0.1\text{mole/l.}$)

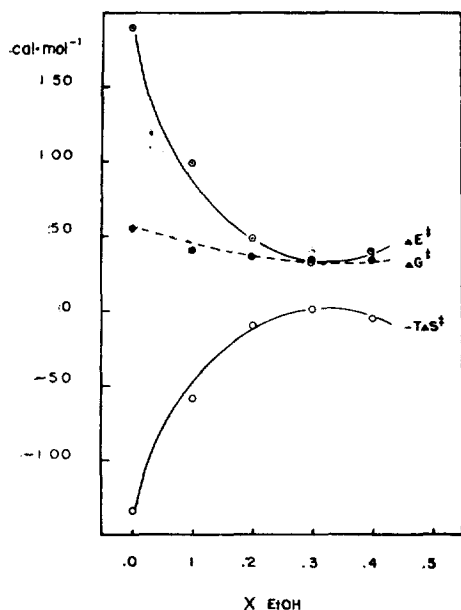


Fig. 9-b Variation of ΔG^\ddagger , ΔE^\ddagger and $T\Delta S^\ddagger$ of Pr_4NBr with X_{EtOH} at 30°C ($c=0.1\text{mole/l.}$)

that for the solution containing salts with small size the viscous flow is controlled by the entropy factor. We have concluded above that Me_4NX is a structure-breaker, and therefore structure-breaking is accompanied with large entropy effect in the activation process for viscous flow. This is reasonable since large degree

of rearrangement is expected in the activation process for the broken down structure.

The overall change in ΔG^\ddagger as solvent composition is varied are however small for both compounds. This was also found to be true for KCl solution.⁵⁶⁾ We can thus conclude that for viscous flow ΔE^\ddagger ($\approx \Delta H^\ddagger$)⁵¹ and ΔS^\ddagger are nearly compensating. Since the activation in viscous flow of a solution involves solute solvent interaction, the compensation of ΔE^\ddagger and ΔS^\ddagger is in accord with the principle of linear external enthalpy-entropy relation.

Nomenclature

A Viscosity A-coefficient

B Viscosity B-coefficient

C Concentration (mole/l)

η , η_0 , η_r , η_{sp} Viscosity of solution, solvent, relative and specific, respectively

η^* , η^E , η^A , η^S Viscosity increment caused by coulombic interaction, Einstein effect, electrostriction effect and hydrophobic structure forming effect, respectively

η^D Viscosity leading to structure breaking effect

ΔE^\ddagger , ΔG^\ddagger , ΔE_i^\ddagger , ΔG_i^\ddagger , ΔS_i^\ddagger

Energy, free energy and entropy of activation for viscous flow about solution and solvent, respectively

ΔE_i^\ddagger , ΔG_i^\ddagger , ΔS_i^\ddagger Energy, free energy and entropy of activation for the i ions, respectively

X_{EtOH} mole fraction of ethanol

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요 약

Tetraalkylammonium halide 의 ethanol-물 혼합용매에서의 상대점도를 30, 35 및 40°C 에서 측정하여 Jones-Dole 식으로 점도계수 B 값을 구하고, 또 B 값의 가성성으로부터 ionic B 값을 계산하여 tetraalkylammonium 및 halide 이온의 점성흐름에 대한 효과를 검토하여 점성흐름에 대한 활성화에너지 및 엔트로피의 일장에서 전해질의 전하효과와 알코올 혼합으로 인한 물 구조의 변화를 해석해 보았다.

Halide 이온은 모두 negative B 값을 가지며 0.1~0.2 몰분율 ethanol에서 물 구조 파괴효과가 최고이고, 그 효과는 $I^- > Br^- > Cl^-$ 순서로 감소하는데 비해 tetraalkylammonium 이온의 B 값은 $Me_4N^+ < Et_4N^+ < n-Pr_4N^+ < n-Bu_4N^+$ 순서로 증가하며 모두 positive 값을 갖는다. Me_4NX 는 온도가 상승함에 따라 B 값이 증가하고, Pr_4NX 는 이와 반대이다. 점성흐름 입장에서 고찰하면 Me_4NX 는 활성화 엔트로피 효과가 지배적이고, Pr_4NX 는 활성화 에너지가 지배적이다.