

CONDUCTANCE OF TETRAALKYL AMMONIUM HALIDES IN ETHANOL-WATER MIXTURES

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Abstract—The conductance measurements are reported for tetraalkyl ammonium halides, Me_4NCl , Me_4NBr , Me_4NI , Et_4NBr , $n\text{-Pr}_4\text{NBr}$, $n\text{-Pr}_4\text{NCl}$, $n\text{-Pr}_4\text{NI}$, $n\text{-Bu}_4\text{NBr}$, in ethanol-water mixtures at 25, 30, 35 and 40°C. The conductance data were extrapolated by the Fuoss-Onsager conductance theory.

From the value of transference number of KCl, ionic cation and halides anion conductance can be readily separated. The effect of temperature and composition of solvent on the ionic mobility and conductance-viscosity product for cation and halide anion is discussed.

The results indicate that the halide anion, K^+ and Me_4N^+ ions are structure breaking ion and the structure breaking powers of these ions are maximum at 0.1 mole fraction ethanol and increase in the order $\text{Cl}^- < \text{I}^- < \text{Br}^- < \text{K}^+ < \text{Me}_4\text{N}^+$. The value of limiting ionic conductance-viscosity products relative to their values for pure water, R_{∞}^* , increase in the order $\text{Et}_4\text{N}^+ < n\text{-Pr}_4\text{N}^+ < n\text{-Bu}_4\text{N}^+$.

INTRODUCTION

Structures and properties of electrolytes have long been studied as a good topic and have been indicated that the symmetrical tetraalkyl ammonium salts are of considerable importance [1-32].

In recent, numerous studies have reported that the nature of the spherical ions, having a large variation in size in aqueous mixtures of the alcohols, has received considerable attention. The tetraalkyl ammonium ions are of great theoretical interest because they combine large size and symmetrical shape with low charge, and furthermore, some of their salts are soluble in many solvents besides water [33].

Kay and Evans et al. reported conductance for the potassium halides and tetraalkyl ammonium salts in aqueous and other solvents [8-14].

In previous work [34], we reported that potassium halides are structure breakers in ethanol-water mixtures, and the maximum in breaking power occurs at 0.1 mf. ethanol.

This paper reports the results of a systematic study of the conductivity of the series of tetraalkyl ammonium halides in ethanol-water mixtures at 25-40°C. Since we could readily separate ionic value with the aid of transference data [36], and conductance data, discussed the mobility with the change of temperature and composition of solvent.

EXPERIMENTAL

1. Materials

Reagent grade (E. Merck) tetraalkyl ammonium halides were purified by recrystallization and dried in vacuum at 70°C as described in the previous work [34, 35, 37]. The conductivity of water used in this study was obtained by distillation in a pyrex glass still after adding acidic potassium dichromate to distilled water. It was collected and stored in all pyrex glass and was equilibrated with atmospheric carbon dioxide. The specific conductivity of this water and absolute ethanol (water content; 0.2%) were always under 7×10^{-7} and $0.2 \times 10^{-7} \text{ ohm}^{-1}\text{cm}^{-1}$ respectively, at 25°C.

2. Viscosity, Density, Conductivity

All measurements were carried out as same as the previous studies [34, 36]. Computer IBM 1130, at the computing center, S.N.U. was used for carrying out all of the calculations.

RESULTS AND DISCUSSION

1. Properties of ethanol-water mixtures

The physical properties of ethanol-water mixtures used are given in Table I. Density, Viscosity and specific conductivity in the mixtures were obtained from the experiment and the dielectric constant data were calculated from the literature [36].

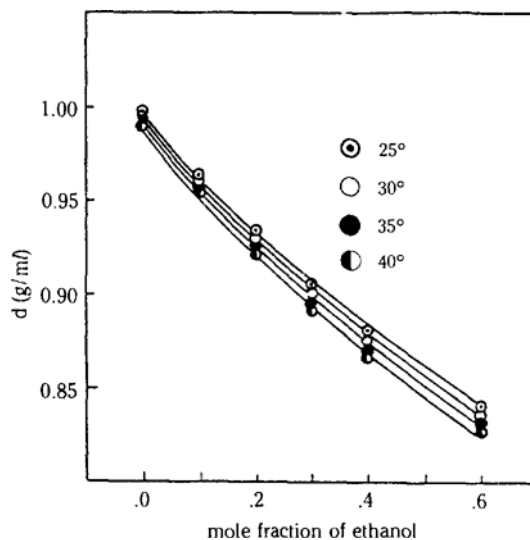
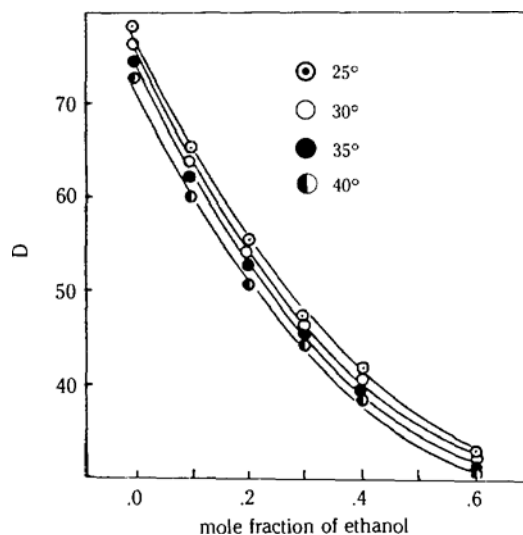
Table 1. Properties of ethanol-water mixtures.

mf.	temp. (°C)	d_o (g/ml)	D	η_o (cp.)	k_o (ohm ⁻¹ .cm ⁻¹)
0.0	25	0.99707	78.54	0.8903	7.0×10^{-7}
	30	0.99568	76.54	0.7975	9.0
	35	0.99404	75.00	0.7194	11.0
	40	0.99224	73.28	0.6531	13.0
0.1	25	0.95355	65.85	1.8902	0.8
	30	0.96102	64.27	1.5864	0.9
	35	0.95823	62.87	1.3537	1.0
	40	0.95530	60.06	1.1664	1.1
0.2	25	0.93468	55.61	2.2530	0.7
	30	0.93050	54.36	1.9509	0.8
	35	0.92670	53.13	1.6461	0.9
	40	0.92277	50.80	1.4014	1.0
0.3	25	0.90517	47.72	2.2834	0.5
	30	0.90091	46.64	1.9736	0.6
	35	0.89680	45.60	1.6875	0.8
	40	0.89259	44.57	1.4525	0.9
0.4	25	0.87963	41.77	2.1125	0.4
	30	0.87604	40.82	1.8383	0.5
	35	0.87177	39.91	1.5835	0.7
	40	0.86738	38.15	1.3538	0.8
0.6	25	0.84076	33.15	1.7536	0.3
	30	0.83650	32.53	1.5301	0.4
	35	0.83207	31.80	1.3417	0.6
	40	0.82785	31.09	1.1816	0.7

The conductance behavior of electrolytes can be hardly devoid of solvent participation. The structures of liquid alcohols are much simpler than that of water. They associate much less strongly, and form polymeric H-bonded chains, rather than large cluster, which rarely contain 5 to 7 molecules for sterically hindered alcohols [38].

In ethanol-water mixtures, solvent-solvent interactions play a considerable part and properties of these mixtures cannot always be interpreted on the basis of continuous miscibility of the components in all mixtures. These mixtures possess also pronounced structures which vary with temperature and ethanol content.

The plots of Figs. 1,2,3 and 4 show, respectively, the trends of variation in the density, viscosity, dielectric constant, with ethanol content and temperature and activation energy of the equivalent conductivity, E_{A_o} ,

**Fig. 1. Density of ethanol-water mixtures.****Fig. 2. Dielectric constant of ethanol-water mixtures.**

and viscosity, E_{η_o} , is calculated from the relation $A_o = Ae^{E_{A_o}/RT}$, $\eta_o = Be^{E_{\eta_o}/RT}$ [28], in which A and B are constants independent of temperature. As can be seen in Fig. 3, the plots relating to viscosity show, within the range 0.2-0.3 mf. of ethanol, temperature dependent maxima flattened and shifted towards higher ethanol content with risen temperature. The viscosity maxima may be ascribed to the formation of loosely bound associates of water and ethanol. These maxima characterizing the viscosity isotherms are not obtained in the corresponding plots of density and dielectric constant

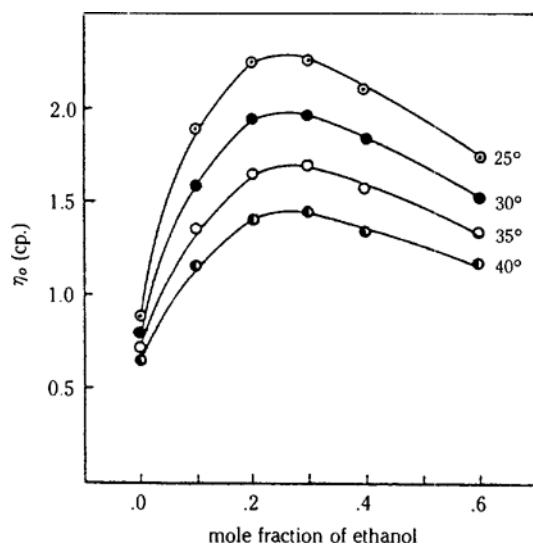


Fig. 3. Viscosity of ethanol-water mixtures.

as related to ethanol content. According to Lee and Hyne [39], at about this composition (~0.3 mf.), the water structure has broken down completely and the free volume is minimum, and then, hole formation in the activation process of viscous flow will require maximum energy at this composition. The activation

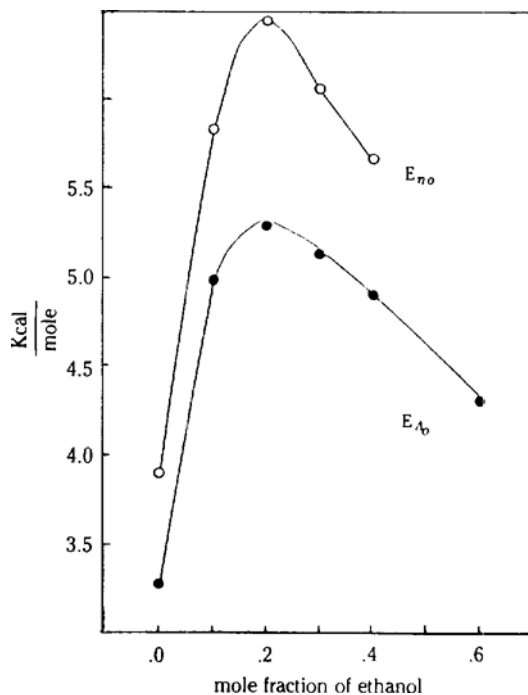


Fig. 4. Variation of activation energies of viscosity and equivalent conductivity in ethanol-water mixtures.

Table 2-a. θ values of density increments for tetraalkyl ammonium halides in ethanol-water mixtures.

Salt	mf. temp.	$\theta \times 100$				
		0.0	0.1	0.2	0.4	0.6
Me ₄ NI	25	7.41	7.90	8.60	8.68	9.35
	30	7.39	7.89	8.56	8.53	8.97
	35	7.33	7.96	8.51	8.47	9.27
	40	7.13	7.75	8.35	7.91	9.17
Me ₄ NCl	25	0.19	0.87	1.70	1.85	2.97
	30	0.18	0.88	1.65	1.85	2.73
	35	0.20	0.89	1.51	1.86	2.23
	40	0.15	0.89	1.60	1.90	2.24
n-Pr ₄ NI	25	6.20	8.20	8.60	8.80	10.84
	30	6.17	8.13	8.56	8.78	13.15
	35	6.13	8.29	8.51	8.66	10.59
	40	5.99	7.95	8.35	8.62	11.60
n-Pr ₄ NCl	25	-0.74	0.80	1.26	2.40	11.62
	30	-0.73	0.79	1.25	2.33	11.56
	35	-0.70	0.78	1.28	2.51	11.61
	40	-0.81	0.63	1.29	2.56	11.22

Table 2-b. θ values of density increments for tetraalkyl ammonium halides in ethanol-water mixtures.

Salt	mf. temp.	$\theta \times 100$				
		0.0	0.1	0.2	0.4	0.6
Me ₄ NBr	25	4.40	4.26	4.97	5.15	7.99
	30	3.93	4.24	4.94	5.05	7.78
	35	3.86	4.22	4.90	5.22	7.43
	40	3.81	4.18	4.87	5.28	6.37
Et ₄ NBr	25	4.10	4.59	4.68	5.08	7.50
	30	4.00	4.40	4.46	4.68	7.08
	35	3.90	4.39	4.30	4.34	6.85
	40	3.70	4.19	4.20	3.75	6.15
n-Pr ₄ NBr	25	3.60	4.08	4.59	5.40	5.81
	30	3.40	4.05	4.55	5.33	5.51
	35	3.20	3.96	4.47	5.41	5.47
	40	3.01	3.92	4.40	5.14	5.45
n-Bu ₄ NBr	25	3.10	4.71	4.61	5.21	5.61
	30	2.90	4.48	4.41	5.02	5.24
	35	2.70	4.43	4.28	4.41	5.07
	40	2.52	4.21	4.25	4.33	4.68

energy of the equivalent conductivity and viscosity E_{Λ_0} , E_{η_0} are shown in Fig. 4 plotted against the mole fraction of ethanol. The maximum of two peaks are occurred at 0.2 mole fraction ethanol.

The density increments, for the tetraalkyl ammonium halides solutions used to calculate the volume concentration, were obtained from density measurements on the concentrated solutions and assumed to follow the relationship,

$$d = d_0 + \theta \cdot m \quad (1)$$

The density increments are summarized in Table 2-a,b.

2. Limiting equivalent conductance

The data were extrapolated by means of Fuoss-Onsager conductance equation [40, 41] given by

$$\Lambda = \Lambda_0 - SC^{1/2} + 2EC \log \tau + LC \quad (2)$$

and also in the few case, by

$$\Lambda_0 = \Lambda_0 - S(C\gamma)^{1/2} + 2EC\gamma \log(\tau\gamma^{1/2}) + LC\gamma - AC\gamma e(-2C\gamma^{1/2}) \cdot \Lambda \quad (3)$$

The limiting equivalent conductances for the tetraalkyl ammonium halides in ethanol-water mixtures are given in Table 3.

The limiting equivalent conductance for Me_4NBr

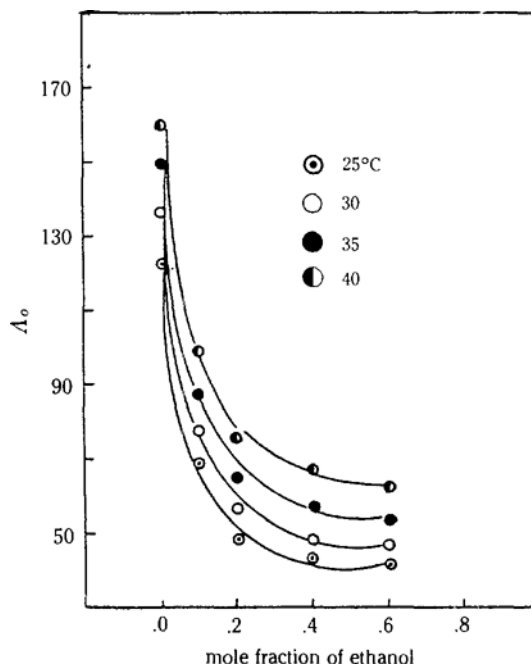


Fig. 5. Limiting equivalent conductivity of Me_4NBr in ethanol-water mixtures (typical one).

Table 3. Limiting equivalent conductance of tetraalkyl ammonium halides.

mf.	temp.	Me_4NCl	Me_4NBr	Me_4NI	Et_4NBr	$\text{n-Pr}_4\text{NCl}$	$\text{n-Pr}_4\text{NBr}$	$\text{n-Pr}_4\text{NI}$	$\text{n-Bu}_4\text{NBr}$
0.0	25	121.32	122.67	122.23	110.44	99.26	101.40	100.20	97.50
	30	131.87	136.37	139.44	123.52	109.56	111.16	107.54	108.35
	35	143.84	149.33	151.73	135.74	120.01	121.94	118.45	120.66
	40	156.45	159.82	165.14	146.61	133.05	131.89	129.76	130.33
0.1	25	63.61	69.00	58.40	58.40	61.21	55.00	51.66	51.86
	30	75.51	77.77	64.42	66.77	71.45	64.70	59.51	60.03
	35	83.57	87.71	74.82	76.81	79.64	74.17	67.52	71.32
	40	96.35	99.00	82.96	86.81	89.52	84.52	75.28	83.99
0.2	25	48.78	48.30	46.44	44.24	39.33	41.51	40.29	37.85
	30	57.20	56.73	55.24	51.36	45.67	50.80	48.63	47.11
	35	66.29	65.11	63.67	61.51	52.78	58.40	57.16	53.95
	40	74.48	74.66	72.08	68.00	62.01	66.49	64.14	61.84
0.4	25	42.42	44.09	46.76	40.93	36.15	39.59	37.84	35.54
	30	48.63	49.99	53.16	46.18	42.08	45.00	43.35	44.03
	35	54.55	57.24	61.87	53.23	48.60	52.82	50.51	47.36
	40	61.01	64.33	70.74	62.43	55.91	59.64	57.33	54.87
0.6	25	40.24	42.32	44.06	43.75	37.48	39.64	40.54	38.07
	30	46.32	47.43	54.21	47.41	41.93	46.00	50.00	42.58
	35	52.31	54.20	60.19	52.85	49.34	51.26	56.09	47.81
	40	58.48	60.13	67.58	58.78	54.70	57.39	63.54	55.10

(typical one) at various temperatures in ethanol-water mixtures are plotted in Fig. 5. The equivalent conductivity of Me_4NBr in pure water decreases with exponential by addition of ethanol.

The effect of temperature on the limiting equivalent conductivity for this salts is shown in Fig. 6. The effect of temperature has positive coefficients as would be expected at various solvent composition.

Also the effect of the reciprocal of crystallographic size of these large cation on the limiting conductivity for salts is shown in the Fig. 7. The effect of reciprocal size also has positive coefficient. In this Fig., the rate decreases with addition of ethanol.

3. Limiting ionic conductivity

Limiting ionic conductivity in electrolytes by Kohlraush's law is,

$$\Lambda_o = \Lambda_o^+ + \Lambda_o^- \quad (4)$$

Limiting cation conductance were computed from Kohlraush's transference data[36] for KCl. Since the transference data were measured at different temperatures and solvent compositions. We were recomputed by using the literature value [42]. Therefore it is possible to obtain $\Lambda_o^+(\text{R}_4\text{N}^+)$ and $\Lambda_o^-(\text{X}^-)$ value from the following equation.

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

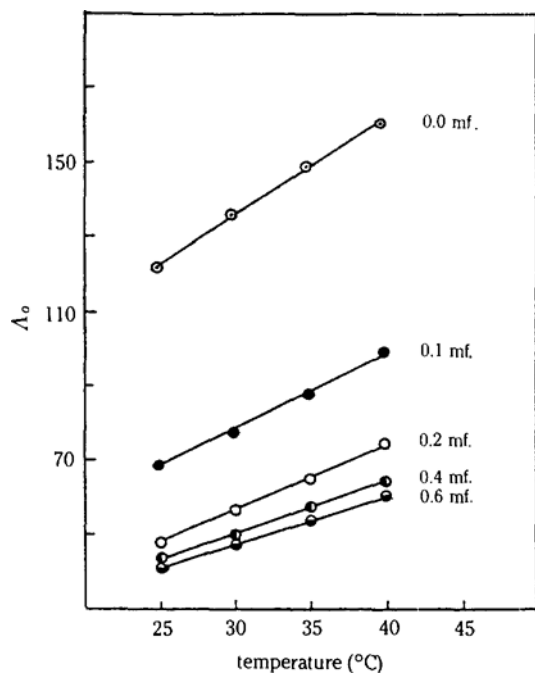


Fig. 6. Limiting equivalent conductance of Me_4NBr in ethanol-water mixtures as a function of temperature.

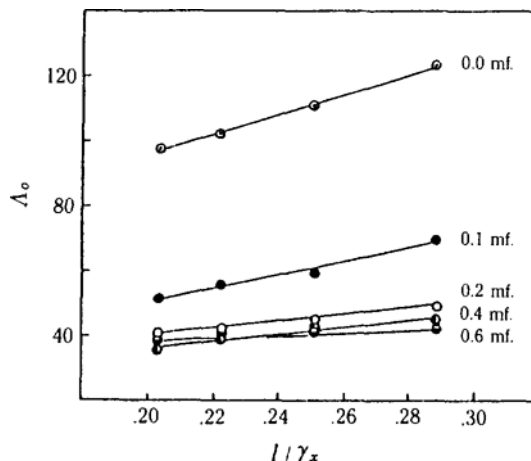


Fig. 7. Limiting equivalent conductance of R_4NBr in ethanol-water mixtures as a function of reciprocal crystallographic size.

$$\Lambda_o^-(\text{Br}^-) = \Lambda_o(\text{R}_4\text{NBr}) - \Lambda_o^+(\text{R}_4\text{N}^+) \quad (6)$$

$$\Lambda_o^+(\text{R}_4\text{N}^+) = \Lambda_o(\text{R}_4\text{NBr}) - \Lambda_o^-(\text{Br}^-) \quad (7)$$

The limiting ionic conductance values determined by this manner are summarized in Table 4-a,b and presented in Fig. 8. Within 0.01 Λ unit, our data are in

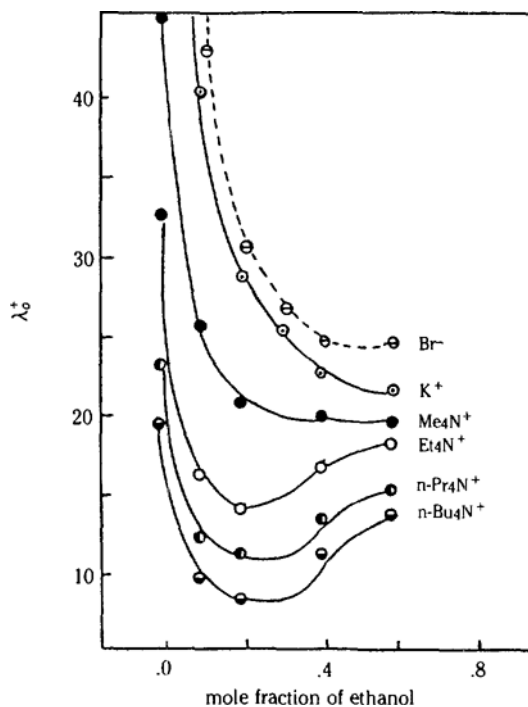


Fig. 8. Limiting cationic conductivity in ethanol-water mixtures at 25°C.

Table 4-a. Limiting ionic conductivity in ethanol-water mixtures at 25°C.

mf.	K ⁺	Cl ⁻	Br ⁻	I ⁻	Me ₄ N ⁺	Et ₄ N ⁺	n-Pr ₄ N ⁺	n-Bu ₄ N ⁺	ref.
0.0	73.52	76.35	78.20	76.90	45.00	32.70	23.50	19.20	12
	73.55	76.39	78.22	76.98	44.42	32.22	23.22	19.31	13
	73.59	76.38	78.26	77.08	44.37	—	—	19.31	
0.0	73.54	76.38	78.22	76.99	44.38	32.22	23.09	19.28	
0.1	40.23	38.86	42.43	39.87	25.66	15.97	12.18	9.43	
0.2	28.66	28.35	30.38	29.40	20.43	13.86	11.00	8.50	
0.3	25.17	25.32	26.33	27.31	—	—	—	—	
0.4	22.42	22.88	24.49	24.65	19.75	16.44	13.23	11.05	
0.6	21.51	22.51	24.67	25.57	18.49	18.16	14.97	13.40	
1.0	23.55	21.67	23.88	27.00	29.65	29.27	22.98	19.67	8

Table 4-b. Limiting ionic conductivity in aqueous solution at various temperatures.

temp. °C	K ⁺	Cl ⁻	Br ⁻	I ⁻	Me ₄ N ⁺	Et ₄ N ⁺	n-Pr ₄ N ⁺	n-Bu ₄ N ⁺	ref.
10	53.08	54.33	56.15	55.39	30.93	21.90	15.33	12.56	12
25	73.54	76.38	78.22	76.99	44.83	32.22	23.09	19.28	45
30	80.57	83.93	87.47	83.83	48.90	36.05	25.63	20.88	
35	88.09	92.10	95.85	92.19	53.44	39.89	27.92	24.81	
40	96.01	100.70	102.74	101.09	59.27	43.87	32.35	27.59	
45	103.61	108.96	110.69	108.76	65.01	47.95	35.78	30.40	

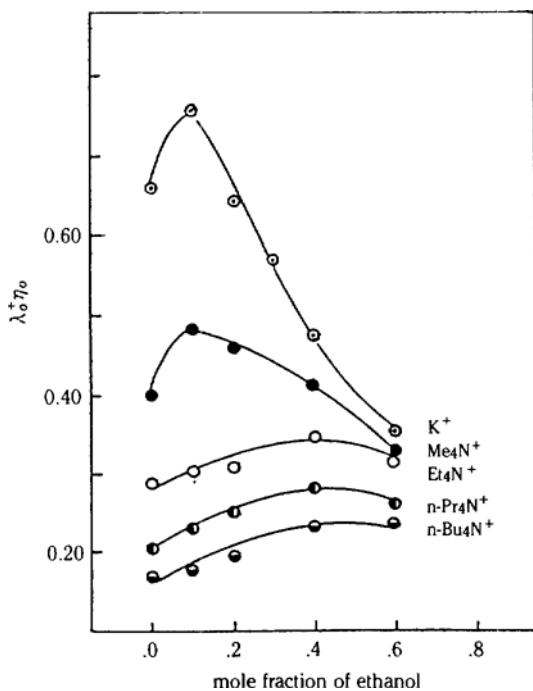
good agreement with the generally accepted values.

The most important point in Fig. 8 is the fact that the minimum in the ionic equivalent conductivity occurs at 0.2 mole fraction ethanol with exception of K⁺ and Me₄N⁺ ion.

4. Limiting ionic Walden product

The limiting Walden products for tetraalkyl ammonium cations at 25°C are shown in Fig. 9. As it can be seen, the products of K⁺ and Me₄N⁺ ion have higher values than other cations at 0.1 mf. ethanol-water mixtures. This means that the maxima occur in the composition region in which ethanol-water mixtures are known to be more structural than pure water. On the other hand, the products for the Et₄N⁺, n-Pr₄N⁺, n-Bu₄N⁺ ion have lower values at this composition than ethanol rich content. This is pointed out that clathrate-like structures form about the hydrocarbon portions of these ions as the length of the side chain increases. Such enforcement of water structure would tend to increase the local viscosity as well as increase the size of the moving entity.

The effect of temperature on the Walden product in aqueous solution for K⁺, halide anion and these cations is seen in Fig. 10, where the data of Kay[13] at 10° and 45°C are included in our data at 25, 30, 35 and 40°C. K⁺, alkali halide anions and Me₄N⁺ ion

**Fig. 9. Limiting cation Walden products in ethanol-water mixtures at 25°C.**

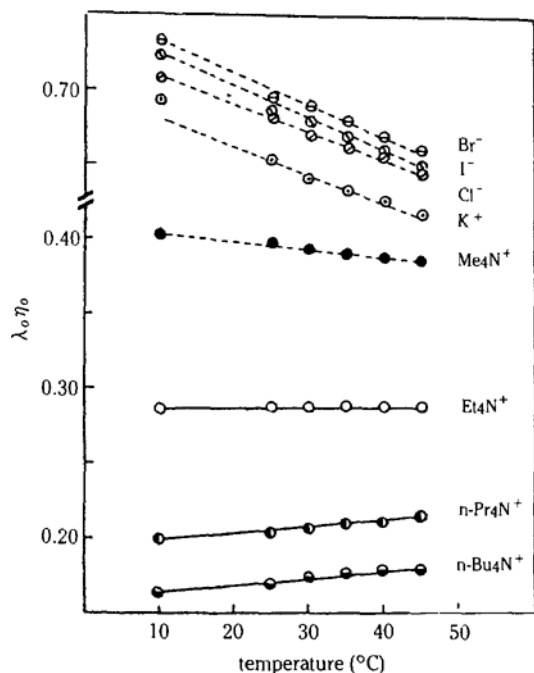


Fig. 10. Limiting ionic Walden products in aqueous solutions as a function of temperature.

have a negative temperature coefficient, typical of structure breaking ions, as the temperature increases, less structure is to break at high temperature and the above ions are less effective in reducing the local viscosity. Particularly, as pointed out in the previous work [35], in the same solvent composition, the mobility of the Br^- ion relative to that for the I^- ion has higher value. This effect could result from that Br^- ion is somewhat larger and has smaller charge density to surface ratio. Therefore this ion should be pointed out that the greater mobility than I^- ion is due to the stabilization by electrostrictive hydration. By the recent dielectric constant data, Pottel and Lossen [43], Walden product should decrease with temperature but the decrease rate should be greater for the smaller ion.

Et_4N^+ ion shows no temperature dependence, owing to a cancellation of the effects of structure breaking and structure making. Kay et al. indicated this ion to be a slight structure maker whereas Evans indicated a slightly structure breaking tendency. That means, Et_4N^+ ion is a borderline case.

Both Pr_4N^+ and Bu_4N^+ ion have positive temperature coefficients as would be expected.

5. Limiting ionic conductance-viscosity products relative to their value for pure water

$\Lambda_o\eta_o$ products for all cations and anions in pure water have been normalized to unity by defining R_w^x by

$$R_w^x = \frac{(\Lambda_o\eta_o)_x}{(\Lambda_o\eta_o)_{\text{H}_2\text{O}}} \quad (8)$$

where x is the mole fraction of ethanol in the mixture involved.

The ratios of limiting ionic conductance-viscosity are shown in Table 5 and plotted in Fig. 11 in ethanol-water mixtures at 25°C. The ratios show systematic and significant deviations from unity. The breaking effect due to the electric field of ions is one of the probable factors which cause $\Lambda_o\eta_o$ to deviate from constancy [44]. For Et_4N^+ , $\text{n-Pr}_4\text{N}^+$, $\text{n-Bu}_4\text{N}^+$ ion, R_w^x is slightly above than unity all over the solvent composition owing to greater enforcement of water structure about the hydrogen chains of these ions as compared to the effect in pure water. The other hand, in K^+ , Me_4N^+ ion, the maxima in the value of R_w^x occur at 0.1 mf ethanol-water mixtures and from this point, the value of these ions rapidly decrease with further addition of ethanol.

Also the most important point-out in Fig. 11 is the fact that the heights of the maxima are not in the expected order.

If the height is concerned with structure breaking power, the order should be $\text{I}^- > \text{Br}^- > \text{Cl}^-$ and $\text{n-Bu}_4\text{N}^+ > \text{n-Pr}_4\text{N}^+ > \text{Et}_4\text{N}^+ > \text{Me}_4\text{N}^+$. But, it can be seen that the order of anions is $\text{Cl}^- < \text{I}^- < \text{Br}^-$ in 0.1-0.2 mf. and is $\text{Cl}^- < \text{Br}^- < \text{I}^-$ in 0.3-1.0 mf. ethanol-water mix-

Table 5. Limiting ionic conductance-viscosity products for cations and anions in ethanol-water mixtures at 25°C relative to their values for pure water.

mf.	K^+	Cl^-	Br^-	I^-	Me_4N^+	Et_4N^+	$\text{n-Pr}_4\text{N}^+$	$\text{n-Bu}_4\text{N}^+$
0.1	1.1614	1.0801	1.1516	1.0995	1.2137	1.0523	1.1196	1.0379
0.2	0.9863	0.9393	0.9829	0.9664	1.1519	1.0885	1.2053	1.1153
0.3	0.8778	0.8503	0.8633	0.9098	—	—	—	—
0.4	0.7234	0.7107	0.7430	0.7597	1.0440	1.2105	1.3594	1.3593
0.6	0.5761	0.5804	0.6212	0.6542	0.8113	1.1101	1.2768	1.3687
1.0	0.3899	0.3454	0.3718	0.4270	0.8043	1.1021	1.2116	1.2417

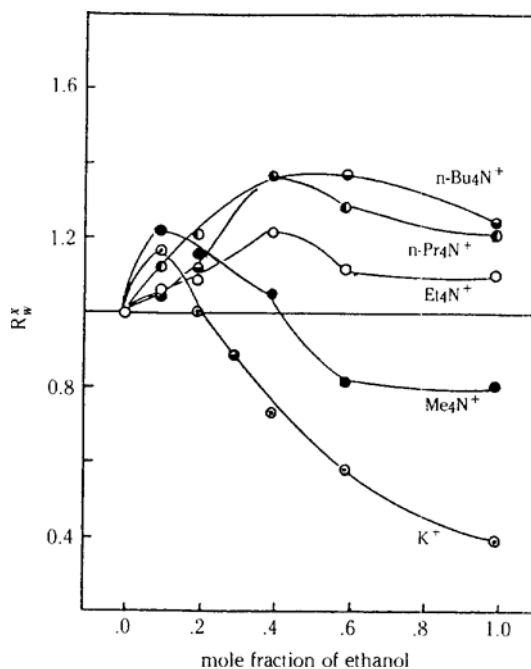


Fig. 11. Limiting cationic Walden products in ethanol-water mixtures divided by that in H_2O at 25°C.

tures, and the order of cations is $n-Bu_4N^+ < Et_4N^+ < n-Pr_4N^+ < K^+ < Me_4N^+$ in 0.1 mf. and $K^+ < Me_4N^+ < Et_4N^+ < n-Pr_4N^+ < n-Bu_4N^+$ in 0.3-1.0 mf.. In 0.1 mole fraction of ethanol-water mixtures, ion-solvent interactions, particularly in structure breaking ions are predominant, while in 0.2-0.4 mole fraction, solvent interactions are predominant.

CONCLUSION

Me_4N^+ , K^+ and halide ions are structure breaking ion and the structure breaking powers of these ions are minimum at 0.1 mole fraction ethanol and increase in the order $Cl^- < I^- < Br^- < K^+ < Me_4N^+$.

The value of limiting ionic conductance-viscosity products relative to their values for pure water, R_w^x , increase in the water $Et_4N^+ < n-Pr_4N^+ < n-Bu_4N^+$.

NOMENCLATURE

Λ, Λ_0	: Equivalent conductance, limiting equivalent conductance
η, η_0	: Viscosity of solution and solvent
k, k_0	: Specific conductance of solution, solvent
d, d_0	: Density of solution, solvent
D	: Dielectric constant
C	: Mole per liter

m	: Mole per kilogram
mf	: mole fraction
S	: Onsager limiting slope
L	: Function of ion size
E	: Function of Λ_0 and property of solvent
τ	: Ratio of Bjerrum distance to the Debye-Hückel ion atmosphere thickness
e	: Empirically determined constant
γ	: Degree of dissociation
A	: Association constant
α	: Temperature coefficient
T	: Absolute temperature
t	: Temperature, °C
R_w^x	: Limiting Walden products in mixed solvent divided by that in H_2O
E_{A_0}, E_{η_0}	: Activation energy of the equivalent conductivity & viscosity

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