

# Ethanol-물 혼합용매에서 KCl의 분몰랄부피 및 점도에 관한 연구

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## On the Partial Molal Volume and Viscosity of Potassium Chloride in Ethanol-water Mixtures

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### 요 약

염화칼륨의 ethanol-물 혼합용매에서의 분몰랄부피 및 상대점도를 30, 35 및 40°C 에서, 몰농도 0.01 <math>m</math> <math>< 0.16</math> 범위 안에서 측정하여 그 결과로 분몰랄부피 및 Jones-Dole 식으로 점도계수 B 값을 구하고 또 염화칼륨의 점성흐름에 대한 효과를 활성화에너지 및 엔트로피의 입장에서 전해질의 전해질의 전하효과와 알코올혼합으로 인한 물구조의 변화를 해석해본 결과 염화칼륨은 물의 수소결합을 약화시키는 structure breaking 효과를 가진다는 것을 알았다.

### Abstract

Apparent molal volumes and relative viscosity of potassium chloride in ethanol-water mixtures have been determined at 30, 35, and 40°C in the molal concentration range 0.01 <math>m</math> <math>< 0.16</math>. The results are discussed in terms of partial molal volumes, viscosity  $B$ -coefficients calculated from the Jones-Dole equation, and energy and entropy of activation for viscous flow. Potassium chloride was found to be a structure breaker.

### Introduction

Partial molal volumes,<sup>1,2,3)</sup> viscosity,<sup>4,5,6)</sup> and ionic conductance<sup>7,8,9,10)</sup> of aqueous potassium chloride solution have been reported.

Viscosity  $B$ -coefficients for salts are approximately additive<sup>4,11,12)</sup> though this additivity tends to break down for large ions.<sup>13)</sup> The additivity of individual ionic  $B$ -coefficient has been a subject of many recent

investigation<sup>(11,14,15,16,17,18)</sup> in view of the importance of individual ionic  $B$ -coefficient contribution in understanding ion-solvent interactions. Generally, in non-aqueous and mixed solvent systems no division into ionic  $B$  values has been attempted. The individual ionic  $B$ -coefficient seems to differ according to the salt used for its determination. If the two factors, low overall effects and equivalence of mobilities are taken into account, potassium chloride appears to be the best choice.<sup>4)</sup>

The viscosity  $B$ -coefficient attributed to the chloride ion<sup>5)</sup> is very small ( $-0.007$  at  $25^\circ$ ;  $-0.005$  at  $35^\circ\text{C}$ ) and reasonable estimates of cationic  $B$ -coefficients should therefore be obtainable by assuming the principle of additivity. In other words, the division of viscosity  $B$ -coefficient into its ionic components may be possible in the mixture solvents on the basis that

$$B(\text{K}^+) = B(\text{Cl}^-)$$

In this work we have determined viscosities in ethanol-water mixtures for KCl at 30, 35 and  $40^\circ\text{C}$ . The viscous flow is interpreted as an activated rate process.<sup>20)</sup> The activation energies and entropies for viscous flow are calculated, and the significance of the effect of this salt on these quantities discussed.

## Experiment

1. **Merk's reagent grade** potassium chloride and absolute ethanol (G. R.) was used without further purification throughout the course of experiment.

In all measurements, water was redistilled twice in a pyrex still after adding acidic potassium dichromate in distilled water, and was equilibrated with atmospheric  $\text{CO}_2$ . The conductivity was less than 1 megohm.

All solutions were made by weight (corrected to vacuum) and converted to molalities from the known densities.<sup>19)</sup> These densities were also used for calculating viscosities. For the viscosity measurements, the solutions were filtered through a fine sintered glass disk. All measurements were made at 30, 35 and 40 maintained to better than  $\pm 0.01^\circ\text{C}$ .

### 2. Measurement and calculation of densities

Densities were measured in a 25 ml. capacity pycnometer calibrated with distilled water for 0.01~0.16  $m$  solutions of salt. For each salt solution and solvent, at least three measurements at each temperature were taken and the average value is reported. Average reproducibility of density was  $\pm 0.00003$ . All weighings were measured to fifth decimal 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 the

following equation<sup>20,21)</sup> for empty pycnometer

$$W_{\text{vac}} = W_{\text{obs}} + d_{\text{air}} \left( \frac{W_{\text{obs}}}{d_{\text{pyr}}} - \frac{W_{\text{obs}}}{d_{\text{wts}}} \right) \quad (1)$$

where

$W_{\text{vac}}$  = true (vacuum) weight of the body

$W_{\text{obs}}$  = apparent weight of the body in air

= mass of the weights

$d_{\text{air}}$  = density (g/ml) of air at time of weighing

(depends upon pressure, temperature and

humidity of atmosphere)

$d_{\text{pyr}}$  = density of the body

$d_{\text{wts}}$  = density of the weights

simplified to

$$W_{\text{vac}} = W_{\text{obs}} \left[ 1 + \left( \frac{1}{d_{\text{pyr}}} - \frac{1}{d_{\text{wts}}} \right) d_{\text{air}} \right] \quad (2)$$

$$W_{\text{vac}} = W_{\text{obs}} (1 + 0.31973 d_{\text{air}}) \quad (3)$$

where the density of pyrex,  $d_{\text{pyr}}$ , is taken to be 2.23 g/ml, and that for the balance weights is taken as 7.77 g/ml.<sup>22)</sup> For the filled pycnometers the following modification was made. Using the same principle as in equation (1)

$$W_{\text{vac}} = W_{\text{obs}} \left( 1 - \left( \frac{1}{d_{\text{wts}}} - \frac{1}{d_{\text{liq}}} \right) d_{\text{air}} \right) + W_{\text{pyr}} \left( \frac{1}{d_{\text{pyr}}} - \frac{1}{d_{\text{liq}}} \right) d_{\text{air}} \quad (4)$$

In general, the liquid densities were close to unity in dilute solution, and therefore the buoyancy corrections were small. Thus the density of the liquid,  $d_{\text{liq}}$ , can be set equal to 1 in aqueous solution. But  $d_{\text{liq}}$  are variable with the salts, solvents and temperature. The following formula was used to calculate the more accurate density of solution.

Since  $V \cdot d_{\text{liq}} = W_{\text{liq}}$ ,

$$V \cdot d_{\text{liq}} = W_{\text{obs}} \left( 1 - \frac{d_{\text{air}}}{d_{\text{wts}}} + \frac{d_{\text{air}}}{d_{\text{liq}}} \right) + W_{\text{pyr}} \left( \frac{d_{\text{air}}}{d_{\text{pyr}}} - \frac{d_{\text{air}}}{d_{\text{liq}}} \right) - W_{\text{vac}} \quad (5)$$

$$V(d_{\text{liq}})^2 + \left[ W_{\text{vac}} - W_{\text{obs}} \left( 1 - \frac{d_{\text{air}}}{d_{\text{wts}}} \right) - \frac{W_{\text{air}} \cdot d_{\text{air}}}{d_{\text{pyr}}} \right] d_{\text{liq}} + (W_{\text{pyr}} \cdot d_{\text{air}} - W_{\text{obs}} \cdot d_{\text{air}}) = 0 \quad (6)$$

Equation (6) is a parabolic equation in density,

$$A \cdot d_{liq}^2 + B \cdot d_{liq} + C = 0 \quad (7)$$

where  $A = V$

$$B = W_{vac} - W_{obs} \left( 1 - \frac{d_{air}}{d_{wts}} \right) - \frac{W_{p\ddot{r}} \cdot d_{air}}{d_{p\ddot{r}}}$$

$$C = W_{p\ddot{r}} \cdot d_{air} - W_{obs} \cdot d_{air}$$

and for density of liquid solution, this, (7), is solved for  $d_{liq}$ .

The density of air used in these calculations was determined from the barometric pressure,  $p$ , room temperature  $t$ , and relative humidity  $h$ .<sup>23)</sup> Computer IBM 1130, at the computing center, S. N. U. was used for carrying out all of these density calculations.

### 3. Calibration of viscometers and viscosity calculations

The viscosities of the solutions were measured at 30.00, 35.00 and 40.00°C using an ubbelohde-type 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 used. Flow times were measured to 0.1 sec.

Individual readings for the three measurements at a set temperature agreed with each other to within 0.1 sec. Overall accuracy of the viscosity measurements was estimated to be better than 0.02 %.

The viscometer was calibrated with water 30, 35 and 40°C by means of equation

$$\eta/d = K \cdot t - L/t \quad (8)$$

where  $\eta$  is the absolute viscosity,  $d$  is the density and  $t$  the flow time of the calibrating solution. The

Table 1. Parameters for Viscosity equation

$$\eta/d = K \cdot t - L/t \text{ at } 30, 35 \text{ and } 40^\circ\text{C}$$

NO.	$K \times 10^3$	$L$	30°C (Calc.)	Error (%)
I	1.1190	-8.3831	0.7973	0.02
II	1.1211	-8.6271	0.7973	0.02
III	1.1212	-8.8764	0.7974	0.01
IV	1.1207	-8.8908	0.7973	0.02
V	1.1189	-8.4911	0.7974	0.01

characteristic viscometer constant  $K$  and  $L$  were summarized in Table (1). The absolute viscosities of water at 30, 35 and 40°C were taken as 0.7975, 0.7194 and 0.6531 centipoise,<sup>26)</sup> respectively. The densities of the solutions were taken as 0.99568, 0.99406 and 0.99224 g/ml,<sup>26)</sup> respectively.

## Results and Discussion

### 1. Concentration and temperature dependence of densities

A linear relationship<sup>27)</sup> (9) between density ( $d$ ) and concentration of potassium chloride was assumed to hold ( $\theta$  is an empirically determined constant). The results are summarized Table 2.

$$d = d_0(1 + \theta \cdot C) \quad (9)$$

Table 2. Parameters for density equation

$$d = d_0(1 + \theta \cdot C)$$

$t$ (°C)	$\theta$	RMSD
30	$3.9676 \times 10^{-2}$	$9.54 \times 10^{-6}$
35	$3.9458 \times 10^{-2}$	$1.65 \times 10^{-5}$
40	$3.9291 \times 10^{-2}$	$3.02 \times 10^{-5}$

The densities of the various solutions have been measured at five degree intervals from 30 to 40°C. The densities of the solutions were fitted to equations of the form:

$$d_{soln} = A + B \cdot t + C \cdot t^2 \quad (10)$$

Table 3. Constants for density equation

$$d = A + B \cdot t + C \cdot t^2 \text{ at } 30, 35, 40^\circ\text{C}$$

molality	$A$	$B \times 10^5$	$C \times 10^6$
0.010484	1.000388	+1.11	-5.10
0.015090	1.000945	-0.69	-4.86
0.020499	1.001330	-1.70	-4.68
0.025392	1.002151	-4.57	-4.34
0.040562	1.001220	+4.89	-5.70
0.058340	1.002844	+0.52	-5.12
0.090918	1.006048	-9.53	-3.66
0.124368	1.007571	-9.52	-3.64
0.162331	1.009582	-10.69	-3.54
mean	1.003564	-3.35	-4.52

where average  $A=1.003564$ ,  $B=-33.5 \times 10^{-6}$ ,  $C=-4.52 \times 10^{-6}$ . The results are summarized Table(3).

## 2. Concentration dependence of apparent molal volumes

The apparent molal volumes were calculated(Fig. 1) from:

$$\phi_v = \frac{1000(d_0 - d)}{m \cdot d \cdot d_0} + \frac{M}{d} \quad (11)$$

The  $\phi_v$  for infinitely dilute solution  $\phi_v^0$ , at 30°C can then be obtained by using the equation;

$$\phi_v = \phi_v^0 + S_v \sqrt{c} \quad (12)$$

Experimental limiting slope  $S_v$  and partial molal volume  $\phi_v^0$ , for ethanol-water solutions of KCl at 30°C 35, and 40°C is presented in Table 4 as a function of solvent composition.

It has been suggested<sup>31,32</sup> that the positive concentration dependence of the apparent molal volume is primarily due to the salting out effect of ionic electrostriction. The slope has maximum positive value for KCl at 0.3 mole fraction ethanol in the ethanol-water

binary solvent mixture. This observation of a maximum in the solvent composition dependence of the slope  $S_v$  suggests that at least some of the contributing factors that determine the  $S_v$  value, probably electrostriction and structural effects, have an extremum in their influence at this solvent composition.

The partial molal volumes,  $\phi_v^0$  (Table 4), given are the values obtained by least square fitting.

Table.4 Partial molal volumes and Limiting slope of potassium chloride in ethanol-water mixtures at 30°C

Solventmf. $\times$ EtOH	$\phi_v^0$	$S_v$
0.0	27.0 <sub>5</sub>	1.89
0.1	28.3 <sub>0</sub>	0.67
0.2	29.4 <sub>5</sub>	1.31
0.3	28.3 <sub>6</sub>	4.76
0.4	30.8 <sub>5</sub>	3.37

\*Literature values, 26.90,<sup>28</sup> 26.89,<sup>29</sup> 26.85<sup>30</sup> at 25°C and  $X_{\text{EtOH}}=0.0$

## 3. Ionic partial molal volumes

The additivity of individual ionic partial molal vol-

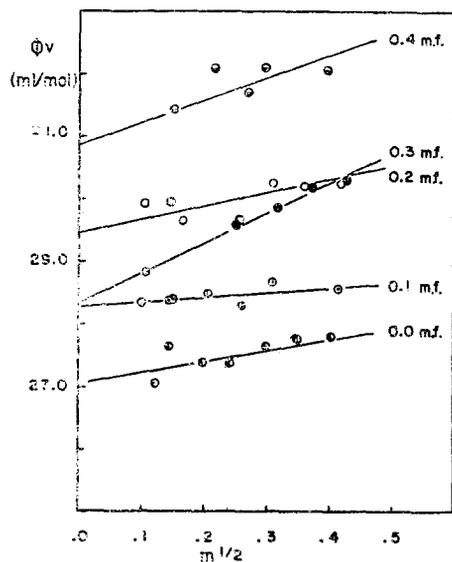


Fig. 1 The Limiting plots for KCl in various ethanol-water mixtures at 30°C (m. f. =mole fraction ethanol)

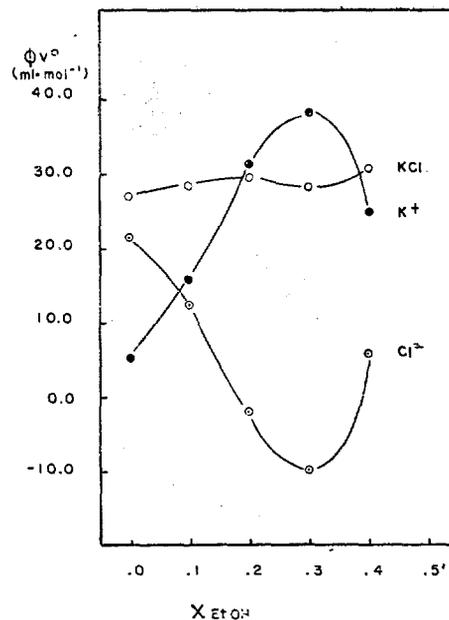


Fig. 2 Partial and Ionic molal volume of potassium chloride as a function of solvent composition at 30°C

umes has been a subject of many recent investigations in view of the importance of the individual ionic contribution in understanding ion-solvent interactions.

Figure 2 is ionic partial molal volumes of chloride ion as a function of solvent composition at 50.25°C by Lee and Hyne.<sup>33)</sup>

Figure 2 shows a deep minimum in  $V_{Cl}^{\circ}$  at 0.3 mole fraction ethanol, and  $V_{Cl}^{\circ}$  values for 0.2 and 0.3 mole fractions are negative. Since chloride ion has a high charge to surface ratio, the minimum at 0.3 mole fraction is probably due to the maximum in electrostriction effect, which agrees with the conclusion derived from the maximum value of the limiting slope at the same composition, (see Table 4).

The ionic partial molal volumes of the cations were determined by subtracting the  $V_{Cl}^{\circ}$  value from the partial molal volumes of salt  $V_{kCl}^{\circ}$ .

$$V_{k^+}^{\circ} = V_{kCl}^{\circ} - V_{Cl}^{\circ} \quad (5)$$

The individual ionic partial molal volumes of the cations obtained in this manner are plotted against solvent composition in Fig. 2. The cation show a maximum 0.3 mole fraction.

When the combined effects of cation and anion are considered, however, the partial molal volume picture changes considerably. The electrostriction effect of the chloride anion, which manifests itself as a minimum at 0.3 mole fraction ethanol (see Fig. 2.), is then in competition with the size effect of the potassium cation, which is characterized by a maximum at the same solvent composition. The balance between these two competing effects is illustrated in Fig. 2, where the partial molal volumes of the salt species are plotted against solvent composition. The maximum at 0.3 mole fraction observed for the potassium ion has

now become a minimum, indicating that the electrostriction effect of the chloride ion more than compensates for the small size effect of the potassium cation.

#### 4. Viscosity $B$ -coefficient

In 1929, Jones and Dole,<sup>34)</sup> studying viscosity for extremely dilute aqueous solutions, found that their results could be formulated in the following form

$$\eta_r = 1 + A \cdot \sqrt{C} + B \cdot C \quad (13)$$

where  $\eta_r$  is the viscosity of the salt solution relative to that of the solvent,  $C$  is the molar concentration, and  $A$  and  $B$  are constant characteristics of the electrolyte. The  $A$ -coefficient represents the contribution from the interionic electrostatic force,<sup>35)</sup> and is highly specific for the electrolyte and temperature.

The  $B$ -coefficient represents the ion-solvent interaction and measure the order or disorder introduced by the ions into the solvent structure,<sup>4,5)</sup> and is found to be fairly accurately additive properties of the constituent ions, and several independent workers.<sup>4,11,12)</sup>

The concentration dependence of viscosity for electrolyte solution has been interpreted with semiempirical Jones-Dole's equation.<sup>34)</sup>

Jones-Dole's equation (13) is transformed to

$$\eta_{sp}/\sqrt{C} = A + B\sqrt{C} \quad (14)$$

$A$ - and  $B$ -coefficients are obtained from intercept and limiting slope of plot of  $\eta_{sp}/\sqrt{C}$  vs.  $\sqrt{C}$ , respectively. Table 5, presents  $A$ - and  $B$ -coefficients obtained in this way, respectively.

The viscosity  $A$  coefficient could not be determined unambiguously because  $\eta_{sp}/\sqrt{C}$  values at extremely

Table 5. Value of  $A$  and  $B$ -coefficients for potassium chloride in ethanol-water mixtures at 30, 35 and 40°C

Solvent (mole fraction EtOH)	A			B		
	30°	35°	40°	30°	35°	40°
0.0	0.0071	0.0061	0.0019	-0.0126	0.0060	0.0190
0.1	-0.0007	0.0025	0.0068	-0.0696	-0.0434	-0.0424
0.2	0.0177	0.0136	0.0218	-0.0849	-0.0496	-0.0470
0.3	0.0077	0.0062	0.0052	-0.0162	0.0148	0.0384
0.4	0.0092	0.0075	0.0077	0.0718	0.0984	0.1206

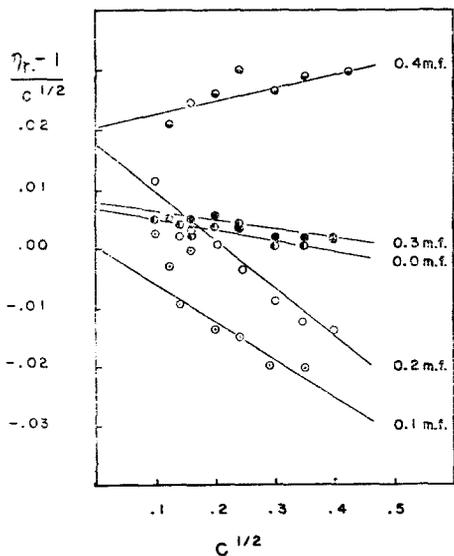


Fig. 3 Plots of  $(\eta_r - 1)/C^{1/2}$  vs.  $C^{1/2}$  for KCl in various ethanol-water mixtures at 30°C

low concentrations are scattered due to the experimental inaccuracies at these concentrations (see Fig. 3). A least squares fitting yield, in some cases negative viscosity  $A$ -coefficients. Such a result appears to be without physical significance.<sup>34)</sup>

The experimental values of  $B$ -coefficients in ethanol-water mixtures are given Fig. 4. Generally speaking,  $B$ -coefficients are smaller at lower temperatures. The temperature dependence of  $B$  values at various solvent compositions is presented in Fig. 5. Since the lower  $B$  value at lower temperature is consistent with the fact that at lower temperature there is more structure to break, i. e., the ion-solvent interaction is stronger at lower temperature when the ion tends to break the solvent structure. Clearly therefore  $K^+$  and  $Cl^-$  are the structure breakers, in the range of solvent composition studied. Fig. 4 also shows a distinct minimum in 0.1-0.2 mole fraction range. The minimum corresponds approximately to the composition ( $\sim 0.1$  mole fraction) at which the maximum structuredness of water is believed to exist.<sup>33)</sup> The minimum therefore can be interpreted as the maximum ion-solvent interaction resulting in the maximum

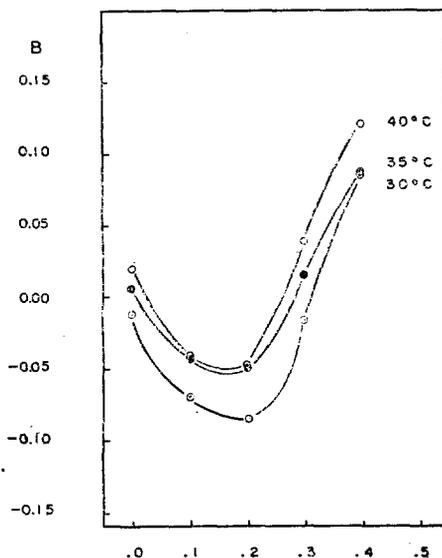


Fig. 4 Viscosity  $B$ -coefficient of potassium chloride as a function of solvent composition (mole fraction ethanol) at 30, 35 and 40°C

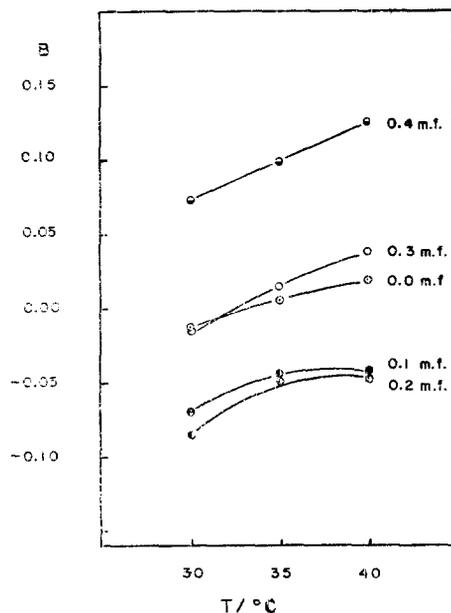


Fig. 5 Viscosity  $B$ -coefficient of potassium chloride as a function of temperature in ethanol-water mixtures

breaking of the structure, since the less the  $B$  value, the more structure is broken.

The  $B$ -Coefficient of KCl has a value not far from zero. Therefore the viscosity of the solvent is affected very little either by the presence of the positive ion or by the presence of the negative ion. 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 manner<sup>25)</sup>

$$\eta^* + \eta^E + \eta^A + \eta^D = \eta^0 (A\sqrt{C} + B \cdot C) \quad (15)$$

where  $\eta^*$  is the positive increment in viscosity caused by coulombic interaction,  $\eta^E$  is the viscosity increment arising from the size and shape (Einstein effect),  $\eta^A$  is the increment due to the alignment or orientation of polar molecules by the ionic field, (electrostriction effect) and  $\eta^D$  is the viscosity of structure leading to greater fluidity (structure breaking effect).

Therefore, at a given concentration the  $B$ -coefficient can be interpreted in terms of a competition between these specialized viscosity effects.  $K^+$  and  $Cl^-$ , as would be expected, have a close balance of viscous forces in their vicinity, i. e.,  $\eta^E + \eta^A \cong \eta^D$  so that  $B$  is close to zero<sup>25)</sup>.

### 5. Energy of activation for viscous flow

Based on absolute reaction rate theory, Nightingale<sup>35)</sup> has proposed an equation which permits the calculation of the energy of activation for viscous flow of an aqueous solution of a strong electrolyte in terms of the energy of activation for viscous flow of pure water (ethanol-water mixtures) and  $B$ -coefficient (of the salts) and its temperature derivative. Specifically

$$\Delta E^\ddagger_{(soln.)} = \frac{R \cdot \partial \cdot \ln \eta^0}{\partial(1/T)} + \frac{R}{1+B \cdot C} \cdot \frac{\partial(1+B \cdot C)}{\partial(1/T)} \quad (16)$$

where  $\Delta E^\ddagger_{(soln.)}$  = energy of activation for viscous flow of the solution,  $(R \cdot \partial \cdot \ln \eta^0) / \partial(1/T) = \Delta E^\ddagger_{(soln.)}$  = energy of activation for viscous flow of pure solvent,  $R$  = gas constant,  $B$  = the Jones-Dole  $B$ -coefficient,  $C$  = concentration and the other symbols have their usual meaning.

Using the  $B$ -coefficient obtained in the present

study, the difference between  $\Delta E^\ddagger_{(H_2O)}$  and  $\Delta E^\ddagger_{(soln.)}$  is calculated to be  $-24$  cal/mole, i. e., the energy of activation for viscous flow of the solution is less than that for pure solvent in agreement with the general notion that KCl acts as a structure breaker. Since the difference is small,  $\Delta E^\ddagger_{(soln.)}$  is approximately equal to  $\Delta E^\ddagger_{(soln.)}$ . Therefore, it can be concluded that viscous flow is largely controlled by the solvent structure.

### 6. Viscosities and energy of activation of solvents

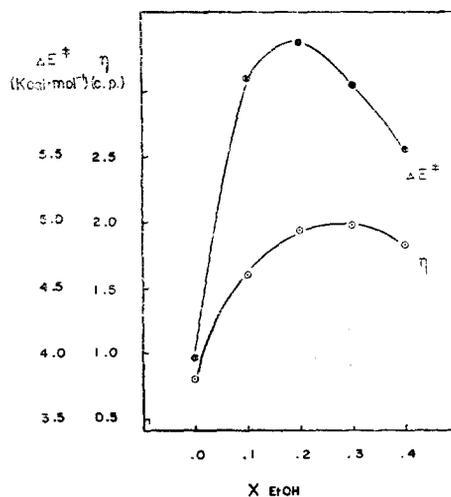


Fig. 6 The Activation energy and viscosity ethanol-water mixtures at 30°C

Solvent viscosities and energy of activation plotted against mole fraction ethanol (Fig. 6) show extremum behavior near 0.2-0.3 mf ethanol at 30-40°C. According to Lee and Hyne,<sup>33)</sup> at about this composition ( $\sim 0.3$  mf), the structure has broken down completely and free volume is a minimum. If this is so, hole formation in the activation process of viscous flow will require maximum energy at this composition. Thus our result is in fair agreement with their explanation. Fig. 7 shows the variation of  $\Delta E^\ddagger_{(soln.)}$  as a function of KCl concentration. It can be seen that  $\Delta E^\ddagger_{(soln.)}$  decreases linearly with KCl concentration in all solvent composition. This is again in agreement with the previous conclusion that KCl is a structure

breaker in all solvent composition studied.

According to the absolute rate theory,<sup>37)</sup> the free energy of activation for viscous flow is given by<sup>26)</sup>

$$\Delta G^\ddagger = R \cdot T \cdot \ln \frac{\eta \bar{V}}{hN} \chi_{\text{EtOH}} \quad (17)$$

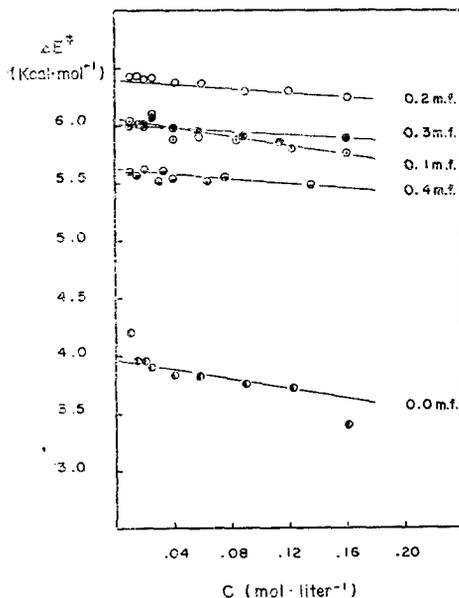


Fig. 7 Activation energies for viscous flow as a function of concentration for KCl in ethanol-water mixtures

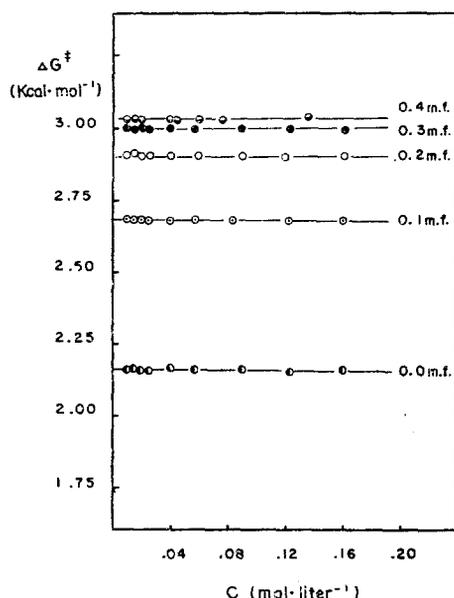


Fig. 8 Free energy of activation for viscous flow as a function of concentration for KCl in ethanol-water mixtures

where  $h$  is the Plank constant,  $N$  is Avogadro's number,  $R$  is the gas constant, and  $\bar{V}$  is the volume of 1 mole of solution particle. The values of  $\Delta G^\ddagger$  have been calculated for KCl as a function of concentration and plotted in Fig. 8.

This figure shows that  $\Delta G^\ddagger$  does not vary much with the concentration whereas Fig. 8 shows the decrease of  $\Delta E^\ddagger$  with the concentration. Assuming that activation enthalpy does not differ appreciably from the activation energy, the entropy of activation  $\Delta S^\ddagger_{(\text{soln})}$  may also be calculated as

$$\Delta S^\ddagger = (\Delta E^\ddagger - \Delta G^\ddagger) / T \quad (18)$$

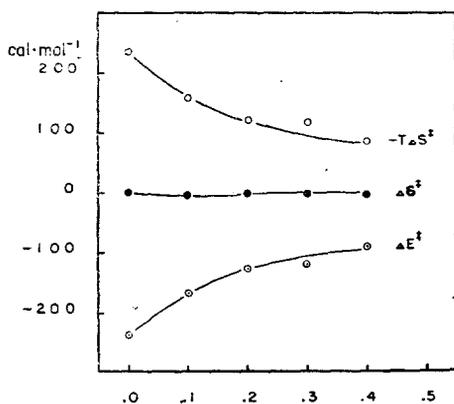
The fact that  $\Delta G^\ddagger$  does not vary with the concentration shows  $\Delta E^\ddagger$  and  $\Delta S^\ddagger$  are compensated effectively when  $C$  is varied. This indicates that as the more structure is broken with increasing  $C$ , the less energy is needed for viscous flow but entropy is increased since structure breaking increases disorder in the solvent. Although the difference in activation energies of the solution and solvent is small, the variation of this difference ( $\Delta E^\ddagger_{(\text{soln.})} - \Delta E^\ddagger_{(\text{solv.})} = \Delta E^\ddagger_i$ )<sup>38)</sup> as a function of solvent composition will give some qualitative information as to the effect of ion on the activation energy of viscous flow.

The difference,  $\Delta E^\ddagger_i$ , may be interpreted as the increase or decrease of the activation energy for viscous flow for the pure solvent due to persence of the ions. The  $\Delta E^\ddagger_i$  and the similary calculated,  $\Delta G^\ddagger_i$  and  $\Delta S^\ddagger_i$ , are summarized in Table (6) and presented graphically in Fig. 9.

This figure shows clear and interesting features of ionic influence on viscous flow of the solvent.  $\Delta E^\ddagger_i$  is shown to increase with the ethanol content while  $-T\Delta S^\ddagger_i$  decreases (since  $\Delta S^\ddagger_i$  itself increases) with ethanol content. In other words, the addition of KCl makes the solvent increasingly difficult for hole formation since structure breaking causes decrease in free volume in solvent, but it brings in the increase of disorder, i. e., increase in entropy (decrease in  $-T\Delta S^\ddagger_i$ ). This effects are compensated each other and gives very little change in  $\Delta G^\ddagger_i$ . A slight minimum in  $\Delta G^\ddagger_i$ , however, can be seen at 0.1 mole fraction. Since  $\Delta G^\ddagger_i$  is the change in free energy of viscous flow due

Table 6. Energy and Entropies of Activation of KCl for Viscous Flow in Ethanol-Water Mixtures at 30°C and C=0.1M

KCl mf.	$\Delta E_0^\ddagger$ , Kcal	$\Delta E^\ddagger$ , Kcal	$\Delta G_0^\ddagger$ , Kcal	$\Delta G^\ddagger$ , Kcal	$\Delta S_0^\ddagger$ , e. u.	$\Delta S^\ddagger$ , e. u.	$\Delta E^\ddagger - \Delta E_0^\ddagger$ , kcal	$\Delta G^\ddagger - \Delta G_0^\ddagger$ , kcal	$\Delta S^\ddagger - \Delta S_0^\ddagger$ , e. u.
0.0	3.988	3.964	2.164	2.1632	6.017	5.942	-0.238	-0.0008	-0.781
0.1	6.003	5.836	2.688	2.6835	10.935	10.408	-0.167	-0.0044	-0.535
0.2	6.453	6.327	2.908	2.9041	11.693	11.291	-0.126	-0.0039	-0.402
0.3	6.043	5.923	2.997	2.9954	10.047	9.657	-0.120	0.0016	0.390
0.4	5.600	5.511	3.031	3.0285	8.474	8.189	-0.089	-0.0025	-0.285

Fig. 9 Variation of  $\Delta G^\ddagger$ ,  $\Delta E^\ddagger$  and  $T\Delta S^\ddagger$  of KCl with  $X_{EtOH}$  at 30°C (C=0.1mole/l)

to the presence of ions, it is the rate theory equivalent of the  $B$  coefficient, and therefore the relative variation of the two should agree. The approximate agreement of the position of minimum suggests that the argument is indeed not unfounded.

### Nomenclature

$A$ ; viscosity  $A$ -coefficient

$B$ ; viscosity  $B$ -coefficient

$C$ ; concentration (mole/l.)

$d$  ( $=d_{liq}$ ),  $d_{air}$ ,  $d_{pr}$ ,  $d_{wt}$ ,  $d_o$

density of solution, air, body, weights and solvent respectively

$h$ ; plank constant

$M$ ; molecular weight

$mf$ ; mole fraction

$m$ ; molality

$N$ ; Avogadro's number

$R$ ; gas constant

$S_V$ ; experimental limiting slope

$T$ ; absolute temperature

$t, t_o$ ; flow time of solution and solvent respectively

$V$ ; volume of liquid

$\bar{V}$ ; volume of one mole of solution particle

$\phi_V$ ; apparent molal volume of salt

$\phi_V^\ddagger$  ( $=\bar{V}_i^\ddagger$ ); partial molal volume of salt

$W_{obs}$ ,  $W_{pr}$ ,  $W_{vac}$ ; weight of observed, pycnometer and compensated in vacuum respectively

$\eta$ ,  $\eta_o$ ,  $\eta_r$ ,  $\eta_{sp}$ ; viscosity of solution, solvent, relative and specific, respectively

$\eta^*$ ,  $\eta^E$ ,  $\eta^A$  viscosity increment caused by coulombic interaction, Einstein effect, electrostriction effect, respectively

$\eta^D$ ; viscosity leading to structure breaking effect

$\Delta E^\ddagger$ ,  $\Delta G^\ddagger$ ,  $\Delta S^\ddagger$ ,  $\Delta E_0^\ddagger$ ,  $\Delta G_0^\ddagger$ ,  $\Delta S_0^\ddagger$ ; energy, free energy, and entropy of activation for viscous flow about solution and solvent, respectively

$\Delta E_i^\ddagger$ ,  $\Delta G_i^\ddagger$ ,  $\Delta S_i^\ddagger$ ; energy, free energy and entropy of activation for the  $i$  ions, respectively

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