에탄올—물 혼합용매에서 염화카륨의 전도도에 관한 연구

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Studies on Electrical Conductivities of Potassium Chloride in Ethanol-Water Mixed Solvent

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요　　약

에탄올—물 혼합용매에서 염화카륨의 전도도를 25~40°C에서 측정하여 Limiting Equivalent Conductance와 Walden Product를 구하였다.
또한 혼합 용매의 밀도, 점도, 유전상수로부터 용매—용매 및 이온—용매 상호작용을 검토하여 물과 에탄올의 회합으로 물의 구조가 0.1 몰분율에서 가장 강화됨을 알았다.

Abstract

The equivalent conductivity of the potassium chloride was measured at various temperatures between 25 and 40°C in ethanol-water mixed solvent system. Density, viscosity, and dielectric constant data are also reported for the mixed solvent.

Limiting equivalent conductivity and Walden product as a function of solvent composition and temperature are reported. The interactions between solvent-solvent and ion-solvent are discussed.

Maxima of $\Lambda_0 \eta_0$ are found for the potassium chloride solutions in 0.1 mole fraction of ethanol. It is assumed that the maxima of $\Lambda_0 \eta_0$ correspond to an association of water and ethanol with higher degree of hydration than the association of viscosity.

Introduction

For many years, conductance behavior of potassium chloride in aqueous and mixed solvent have been studied.[1-15] Especially, the effect of the nature of the ions and of the solvent have been discussed.[14-18]

Potassium chloride is a small ion and water is a hydrogen-bonding solvent. Ethanol is also a good hydrogen bond donor and acceptor.[19] Consequently, ethanol-water mixed solvent system posseses a significant structure which varies with temperature and its concentration.

In this work, we measured the conductivity of potassium chloride in ethanol-water mixed solvent at 25, 30, 35, and 40°C, in order to investigate the effect of interactions between solvent-solvent and ion-solvent.

Experiment

Potassium chloride and ethylalcohol (E. Merck, reagent grade) were used. Potassium chloride was pulverized to a fine powder and dried under vacuum at 70°C.[7]

Water sample used in this work was prepared in pyrex stills after adding acidic potassium dichromate to distilled water. It was found that the specific conductance of water and ethanol were 7×10^{-7} and 0.2×10^{-7} ohm^{-1}·cm^{-1}, respectively at 25°C.

The conductivity bridge (Beckman Model RC 19) was used for all resistance measurements. For accuracy conductivity bridge was required external capacitors (General Radio Co. Decade condenser). All measurements were carried out at 1 kHz.

The conductance cell of 30 ml flask was constructed by means of modifying the Kraus Erlenmeyer flask type.[20] This cell consisted of two platinum electrodes, which were sealed in the pyrex glass, and was equipped with grond glass cap.

The cell was calibrated with the solution of potassiun chloride by the Fuoss method.[6]

The cell constant was found to be 0.1147 cm^{-1} in 0.02% error. The change in the cell constant from

25°C to 30, 35, and 40°C, as calculated by the method of Robinson and Stokes[23] using the geometry of the cell and coefficients of expansion, was found to be less than 0.01% of the value of cell constant at 25°C.

Potassium chloride was weighed in the pyrex weighing bottle on a Mettler H-20 T Semimicro Balance. The solutions were prepared about 1/100 mole per kilogram of stock solution. Each sample solutions was prepared from this stock solution by dilution.

All solutions were prepared by weight and corrected for the weights to the vacuum. The values of densities used in this calculation were 1.984, 7.77, and 2.30 g/ml,[22] for patassium chloride, weights, and pyrex glass, respectively.

The densities of solution and solvent were measured by 25 ml pycnometer which were calibrated with water.

The densities, d, of the dilute solutions were linearly related to the concentration in mole per kilogram of solution (m) such that $d = d_0 + \theta m$, where d_0 is density of solvent. The constant θ was obtained from density measurement in the concentrated solution. The values of θ were found for all the potassium chloride solutions in ethanol-water mixed solvent at various temperatures between 25 and 40°C as shown in table 1.

Viscosities were measured with a Ubbelohde-viscometer as the previous work.[25]

The water bath was maintained at a constant temperature ±0.01°C for each experiment by a mercury-in glass thermoregulator.[26]

Table 1. Coefficient for density increment of potassium chloride in ethanol-water mixed solvent

$d = d_0 + \theta \cdot m$

m.f.: mole fraction of ethanol
d: density of solution
d_0: density of mixed solvent
m: mole per kilogram

Temp. (°C) \ m.f.	θ				
	0.0	0.1	0.2	0.3	0.4
25	0.0479	0.0455	0.0441	0.0423	0.0420
30	0.0468	0.0450	0.0432	0.0422	0.0415
35	0.0455	0.0446	0.0423	0.0420	0.0414
40	0.0447	0.0444	0.0421	0.0419	0.0413

Results and discussion

1. The properties of solvent

The properties of ethanol-water mixed solvent at various temperatures are summarized in table 2. In this table dielectric constant were used literature values. [27]

The specific conductances, k_0, are the "solvent correction" values that were subtracted from the measured specific conductances of the solutions.

Table 2. Properties of ethanol-water mixed solvent

$mf.$	Temp (°C)	d_0 (g/ml)	D	γ_0 (cp)	K_0 (ohm^{-1}·cm^{-1})
0. 0	25	0. 99707	78. 54	0. 8903	7.0×10^{-7}
	30	0. 99568	76. 75	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. 96355	65. 85	1. 8902	0. 8
	30	0. 96102	64. 27	1. 5864	0. 9
	35	0. 95823	62. 82	1. 3537	1. 0
	40	0. 95530	60. 06	1. 664	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. 08	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. 5834	0. 7
	40	0. 86738	38. 15	1. 3538	0. 8

The conductance behavior of electrolytes can not be explained without the phenomena of the solvent participation. In mixed solvent, solvent-solvent interactions play also a considerably important part as these lead to structural variations which are decisive in defining the conductance behavior of electrolyte.

In case of ethanol-water mixed solvent, ethanol is good hydrogen bond donor and acceptor. Consequently, the ethanol molecules are extensively associated among themselves, forming hydrogen bonded. Since water is a hydrogen-bonding solvent, the change of physical properties with the change of mole fraction of ethanol may clarify the structure of this mixtures to some extent.
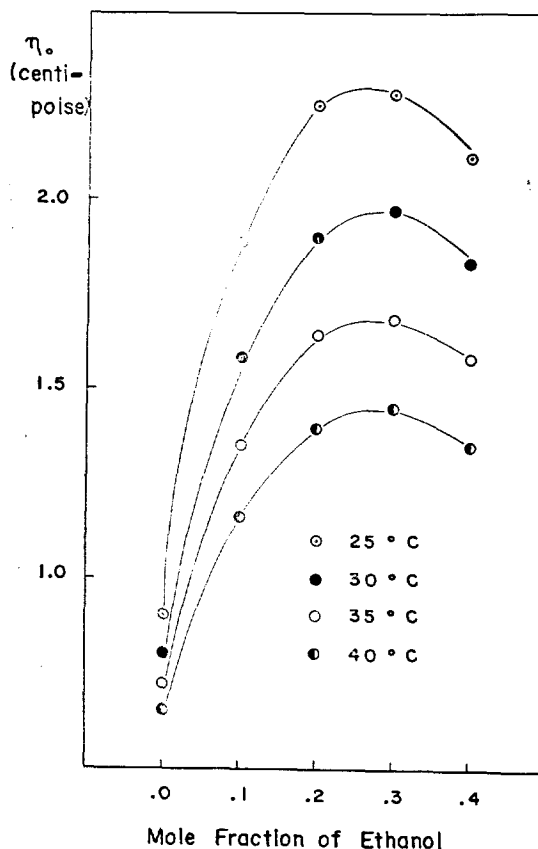

Fig. 1 Viscosities of ethanol-water mixed solvent

In figure 1, the variation in viscosity of the mixed solvent is shown graphically as a function of mole fraction of ethanol at the various temperatures indicated. As it can be seen, the maxima of the curves grow flatter with increasing temperature and seem to shift gradually in position from 0.2 to 0.3 mole fraction of ethanol. The viscosity maxima may be ascribed to the formation of loose association of water and ethanol. [19] These maxima characterizing the viscosity isotherms do not show in the corresponding plots of density (fig. 2) and dielectric constant (fig. 3) as related to ethanol concentration.

As temperature rises, the properties of pure water

and ethanol mixed solvent varies with temperature and this variations indicated that the degree of short range order progressively decreases. This result decreases the viscosity of water and mixed solvent.

The density of ethanol-water mixed solvent is nearly a linear function of mole fraction of ethanol. The negative molar volumes of ethanol-water mixed solvent and rise in the temperature corresponding to the maximum density of water with addition of ethanol are an unusual feature of these mixtures. [19] Contraction in volume accompanying the admixing of water and ethanol reflects the strength of intermolecule attraction and some other complex effects. [10] Also temperature dependence of density in solvent is largely shown as concentration of alcohol is increased.
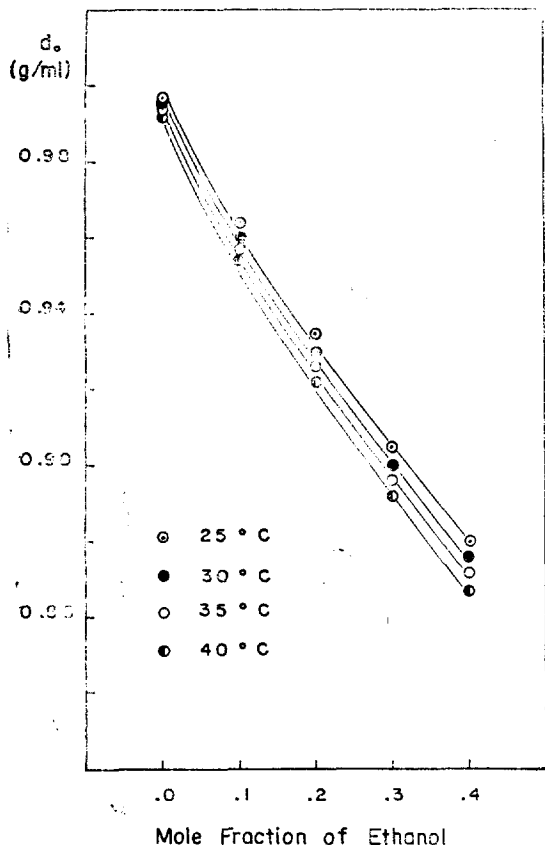

Fig. 2 Densities of ethanol-water mixed solvent

On the other hand, the dielectric constant of ethanol-water mixed solvent was deviated from linear relationship (Fig. 3).
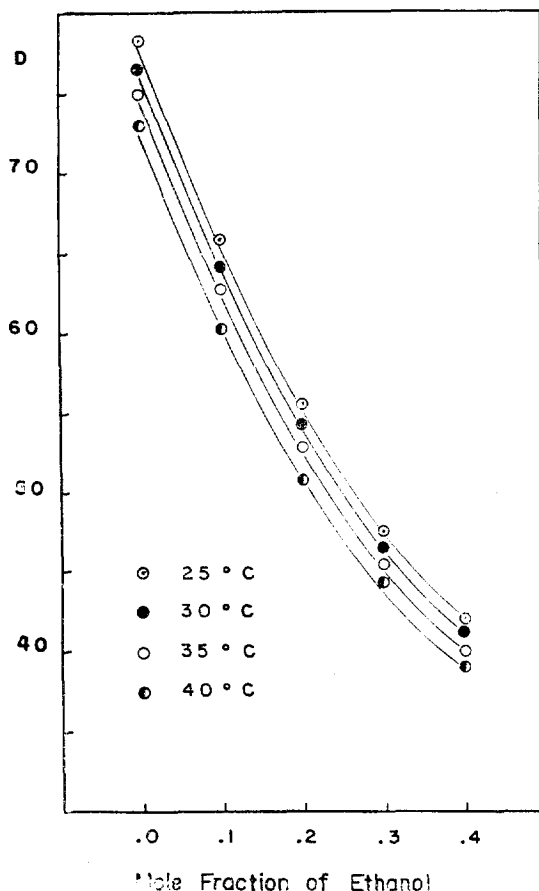
Fig. 3 Dielectric constant of ethanol-water mixed solvent

2. Concentration dependence of equivalent conductivity

The equivalent conductivities were calculated from

$$\Lambda = \frac{1000(k-k_0)}{C} \tag{1}$$

where k and k_0 are the specific conductivities of the solution and solvent, respectively, and C is the concentration in mole per liter.

In figure 4, equivalent conductivities of potassium chloride decreases with addition of ethanol and tends to negative dependence on the concentration of solution.

At constant temperature and in the same solvent composition, it has been suggested that the negative concentration dependence is decreasing ionic mobility in solution.
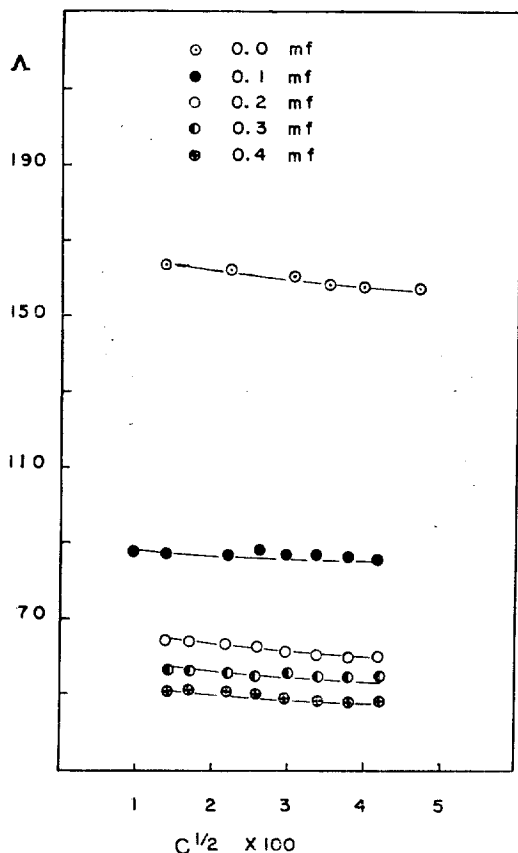
Fig. 4 Equivalent conductance for KCl as a function of concentration at 30°C

Fig. 5 Limiting equivalent conductance for KCl as a function of mole fraction of ethanol

3. Limiting equivalent conductance

The Λ for infinitely dilute solution, Λ_0, can be obtained using the Fuoss-Onsager conductance equation

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

in which S is the limiting Onsager slope. The coefficient L is a function of the ion size and is an adjustable parameter from the data as are the limiting equivalent conductance. The dimensionless variable τ is the ratio of the Bjerrum distance to the Debye Hückel ion atmosphere thickness. [29,30] The Fortran Computer Program was used for all calculation with a least square fit.
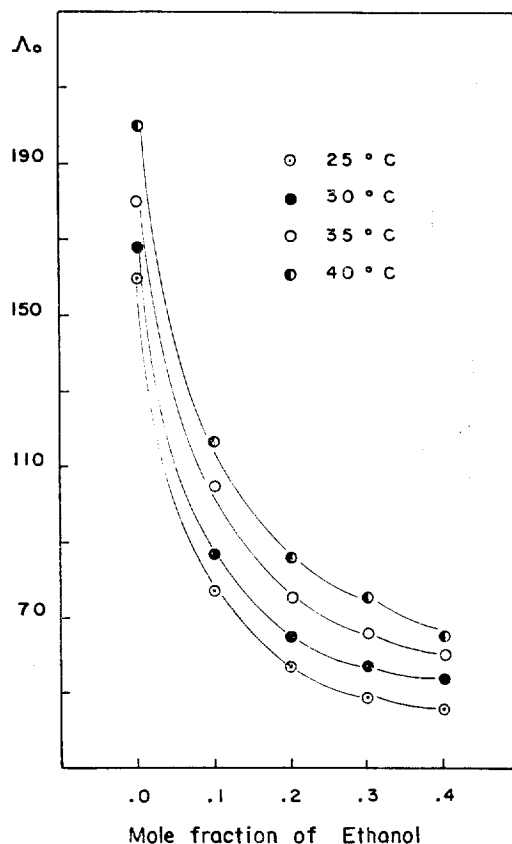
As shown in figure 5, the limiting equivalent conductivity, Λ_0, of potassium chloride in pure water rapidly decrease with the addition of ethanol and then the trends almost independent of ethanol concentration in mixed solvent.

In general, Λ_0 values are larger at higher temperature. In figure 6, the variations of Λ_0 at the various concentration of ethanol of the solvent systems are shown to have linear relationship with temperature. The value of temperature coefficients[31] of limiting equivalent conductivity can be calculated according to

$$\alpha\Lambda_0(\%)=(100/\Lambda_0)\cdot(\Delta\Lambda_0/\Delta t)_{t_1-t_2} \qquad (3)$$

The calculated values are shown in table 3.

As the temperature rise, for visible particle, the Brownian motion is observed to become more lively[2k];
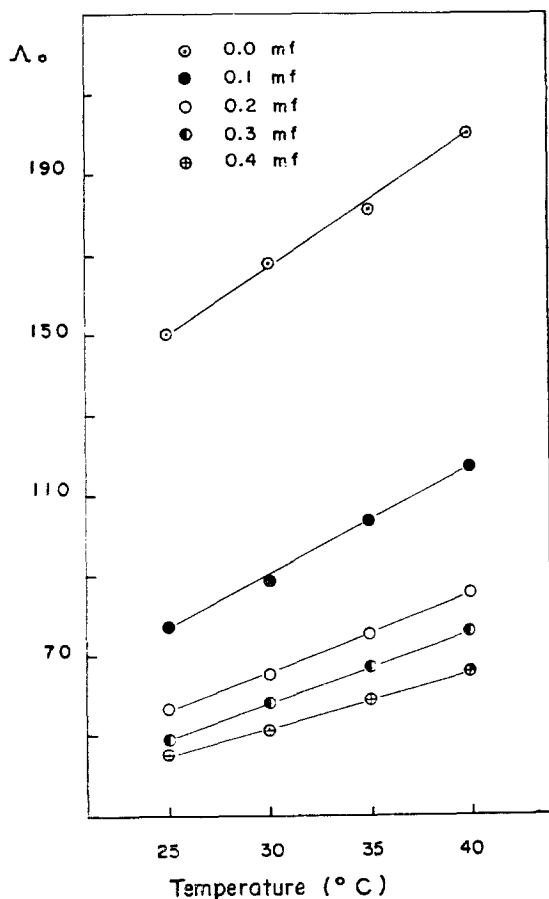
Fig. 6 Limiting equivalent conductance for KCl as a function of temperature

and in the same way it should be expected that the random motion of the solute particle becomes active. As a result, the mobility of ion should increases as the temperature rise.

Table 3. Temperature coefficients of limiting equivalent conductance and Walden products for potassium chloride in ethanol-water mixed solvent

$mf.$	$\alpha \Lambda_0 (\%)$	$\alpha \Lambda_{0\eta_0} (\%)$
0.0	1.9156	0.2350
0.1	3.1039	0.4017
0.2	3.1610	0.4116
0.3	3.2646	0.2587
0.4	2.8432	0.4010

4. Walden product

Walden found that the limiting equivalent conductivity of tetra-ethyl ammonium picrate in a wide range of solvent including water confirmed closely with the formula;

$$\Lambda_0\eta_0 = \text{constant} \qquad (4)$$

which is derived from Stokes' law and is known as Walden rule. [30]

In our results, plots of $\Lambda_0\eta_0$ vs. mole fraction of ethanol are shown in figure 7 for potassium chloride at various temperatures. As it can be seen, the deviation of $\Lambda_0\eta_0$ from contancy is such that it increases with the first addition of small amount of ethanol, and after passing through the maximum (0.1 mole fraction), it decreases by further addition of ethanol.
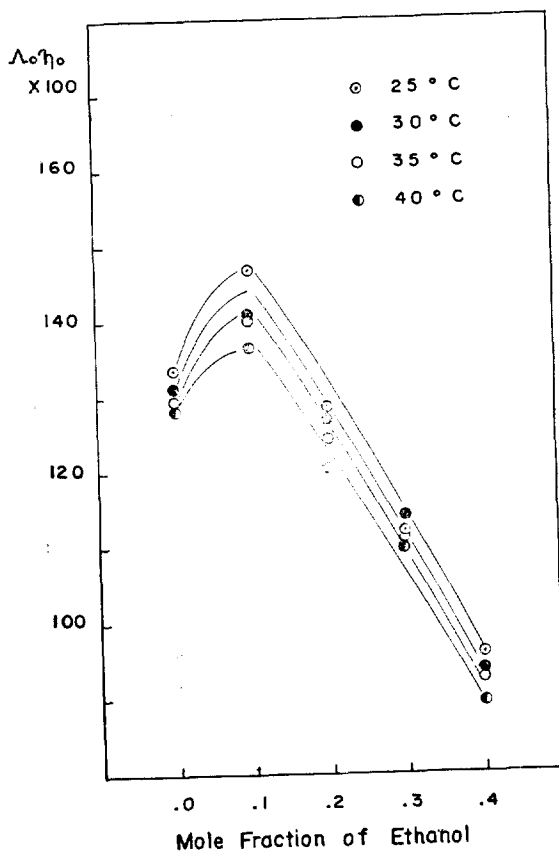

Fig. 7 Limiting Walden product for KCl as a function of mole fraction of ethanol
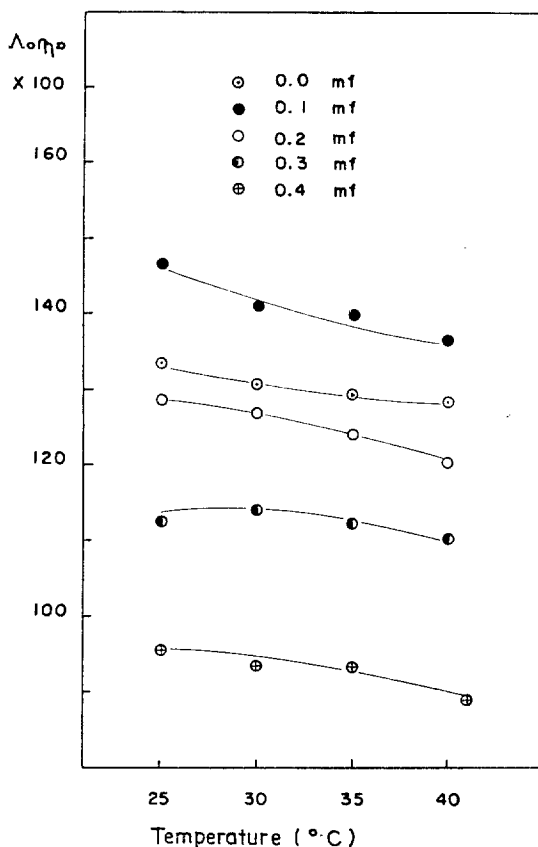
Fig. 8 Limiting Walden product for KCl as a function
       of temcerature

The "breaking effect" due to the electric field of
ions[28] is one of the probable factors which causes
$\Lambda_0\eta_0$ to deviate from constancy. As a result of this
effect the viscosity in the vicinity of the ions becomes
lower than in the bulk of solution.[34]

In the same alcohol composition, $\Lambda_0\eta_0$ exhibited
higher values at lower temperature than higher tem-
perature. (fig. 8). The temperature coefficient of limi-
ting Walden product for potassium chloride can be
calculated according to

$$\alpha\Lambda_0\eta_0(\%) = (100/\Lambda_0\eta_0) \cdot (\Delta(\Lambda_0\eta_0)/\Delta t)_{t_1-t_2} \qquad (5)$$

is reported in table 3.

As the temperature rises, the ionic mobility increa-
ses by a smaller extent than the relevant decreases
in the macroscopic viscosity.

At constant temperature, the maxima of $\Lambda_0\eta_0$ exhi-
bited at 0. 1 mole fraction of ethanol whereas those

of voscositis are shown within the range of 0. 2—0. 3
mole fraction (see fig. 1). It is assumed that the ma-
xima of $\Lambda_0\eta_0$ correspond to an association of alcohol
and water with higher degree of hydration than the
association of viscosity. This is emphasized by the
fact that several physical properties such as partial
molal volume and viscosity[25] agreed with the values
in mixed solvents of 0. 1 or 0. 3 mole fraction of etha-
nol. That is, The maximum of $\Lambda_0\eta_0$ correspond app-
roximately to the solvent composition at which the
maximum structuredness in water is believed to exi-
st.[34]

Nomenclature

Λ, Λ_0; Equivalent conductivity, limiting equivalent
      conductivity

η, η_0; Viscosity of solution, 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

M; Molecular weight

$mf.$; Mole fraction of ethanol

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 Hükel ion
   atmosphere thickness

T; Absolute temperature

t; Temperature, °C

Acknowledgement

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