

## Conductance of sodium nitrate in ethanol-water mixtures at 35° C

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**Abstract.** The conductance of sodium nitrate in ethanol-water mixtures at 35° C has been measured over a range of salt concentration and solvent composition. The data have been analysed by the method of Fuoss, Onsager and Skinner on BESM-6 computer. Ion association has been found to be negligible upto an ethanol content of about 80% in the binary solvent. The dependence of the ion-size and Walden product on the solvent composition has been examined.

**Keywords.** Conductance; Walden product; sodium nitrate; ethanol.

### 1. Introduction

Studies on electrolytic conductance in mixed solvents can provide useful information on ion-solvent and ion-ion interactions. The effect of ion association on the conductance behaviour of electrolytes has been a subject of extensive investigation. This paper deals with the conductance behaviour of sodium nitrate in ethanol-water mixtures covering a range of dielectric constant values.

### 2. Experimental

A conductivity bridge fabricated in this laboratory using the method of Jones and Josephs (1928) was used for conductance measurements with a tuned amplifier and null detector (General Radio Company, U.S.A.). A precision of 0.1 ohm in 10,000 ohms was attainable for impedance measurement with a decade resistance box. Conductance water (0.1  $\mu$  mho) was obtained by distillation of double distilled water, under nitrogen atmosphere, from an all-glass apparatus. Ethanol was purified by distillation and a series of ethanol-water mixtures was prepared. The exact composition of each binary solvent mixture was determined by density measurements with a pycnometer (Srinivasan 1963). Sodium nitrate (E Merck G.R.) was purified by repeated recrystallisation from conductivity water and dried at 150° C for 3 hr. A stock solution was prepared by dissolving a

known weight of the salt in the specified solvent mixture at  $35 \pm 0.01^\circ \text{C}$ . Solutions of very low concentrations were obtained by suitable dilution of an aliquot of known strength. A Townson and Mercer thermostat (type X 27, England), maintained at  $35 \pm 0.01^\circ \text{C}$  by means of a calibrated Beckmann thermometer, was used and solutions were equilibrated for 1 hr during dilution and prior to all measurements. A Washburn Cell (Cenco, U.S.A.) and a bottle-type cell (L & N, U.S.A.) were used for conductance measurements. The electrodes were smoothly platinised and the cell constants were determined with 0.01 N solution of potassium chloride.

### 3. Results and discussion

#### 3.1. Analysis of conductance data

The dependence of equivalent conductance  $\Lambda$  on the concentration,  $c$  of sodium nitrate in ethanol-water mixture at different compositions is given in table 1. The physical constants like the density  $d$ , viscosity  $\eta$  and dielectric constant  $D$  of the solvent mixture at each composition were obtained by interpolation of the data of Spivey and Shedlovsky (1967) and are included in table 2. It can be seen from figure 1 that a plot of  $\Lambda$  vs  $\sqrt{c}$  is a straight line in each case.

The theory of electrolytic conductance for associating systems has been examined by several workers although the simplest and the most widely used treatment is that of Fuoss *et al* (1965). When ion association is absent or negligible, the conductance data can be analysed by the more familiar expression Fuoss and Onsager (1957, 1958)

$$\Lambda = \Lambda_0 - Sc^{1/2} + Ec \log c + Jc, \quad (1)$$

which can be rearranged and rewritten as

$$\Lambda' = \Lambda_0 + Jc = \Lambda + Sc^{1/2} - Ec \log c, \quad (2)$$

where  $\Lambda'$  is a quantity which can be calculated and then used for the solution of (2) by graphical iteration method. In the present work, the initial value of  $\Lambda_0$  was obtained from Shedlovsky (1932) plot whereas  $S$  and  $E$  were calculated. It can be seen from figure 2 that the plot of  $\Lambda'$  vs  $c$  is a straight line over the entire salt concentration range and solvent composition and indicates the absence of ion association. The ion-size parameter  $a^0$  was calculated from  $J$ , the slope of the line, and is given in table 2.

Fuoss *et al* (1965) have shown that

$$\Lambda = \Lambda_0 - Sc^{1/2} \gamma^{1/2} + E'c \gamma \ln(\sigma E'_1 c \gamma) + Lc \gamma - K_{AC} \gamma f^2 \Lambda, \quad (3)$$

and

$$\Lambda = \Lambda_0 - Sc^{1/2} + E'c \ln(\sigma E'_1 c) + Lc, \quad (4)$$

where the symbols have their original significance. It should be noted that (4) is valid only for non-associated electrolytes whereas for associated electrolytes (3) is applicable. Based on (3) and (4) a computer program was developed to



Table 2. Conductance parameters and constants for  $\text{NaNO}_3$ 

Wt. % of alcohol	D	$\eta \times 10^3$	d	$\Lambda_0$	Computer method			
					L	$L_2(b)$	$a^0(L)$	$\Lambda_0 \eta$
0.0	74.78	7.225	0.99406	145.98 ± 0.005	181 ± 1.6	89.9	2.80 ± 0.03	
10.05	69.20	10.06	0.97677	111.10 ± 0.002	136 ± 0.5	45.4	2.53 ± 0.01	
20.28	63.34	13.37	0.96081	87.49 ± 0.004	128 ± 2.6	32.5	2.67 ± 0.05	
39.43	52.46	17.04	0.92492	67.50 ± 0.002	136 ± 0.6	2.9	2.78 ± 0.01	
53.52	44.58	16.79	0.91586	64.00 ± 0.004	181 ± 1.6	— 17	3.13 ± 0.02	
60.18	40.90	16.57	0.87810	57.36 ± 0.003	149 ± 0.8	— 90.8	2.75 ± 0.01	
77.75	32.13	13.89	0.86062	57.53 ± 0.003	379 ± 1.0	— 121.4	3.87 ± 0.01	

Graphical method		Graphical method	
$\Lambda_0$	J	$a^{0*}$	$\Lambda_0 \eta$
145.98	190	2.8 ± 0.1	1.054
111.10	150	2.55 ± 0.2	1.118
87.50	150	2.7 ± 0.2	1.169
67.50	190	2.8 ± 0.1	1.150
63.98	300	3.1 ± 0.1	1.075
57.36	300	2.7 ± 0.1	0.951
57.53	800	3.9 ± 0.1	0.799

\* The limits of accuracy pertain to the maximum error involved in graphical interpolation.

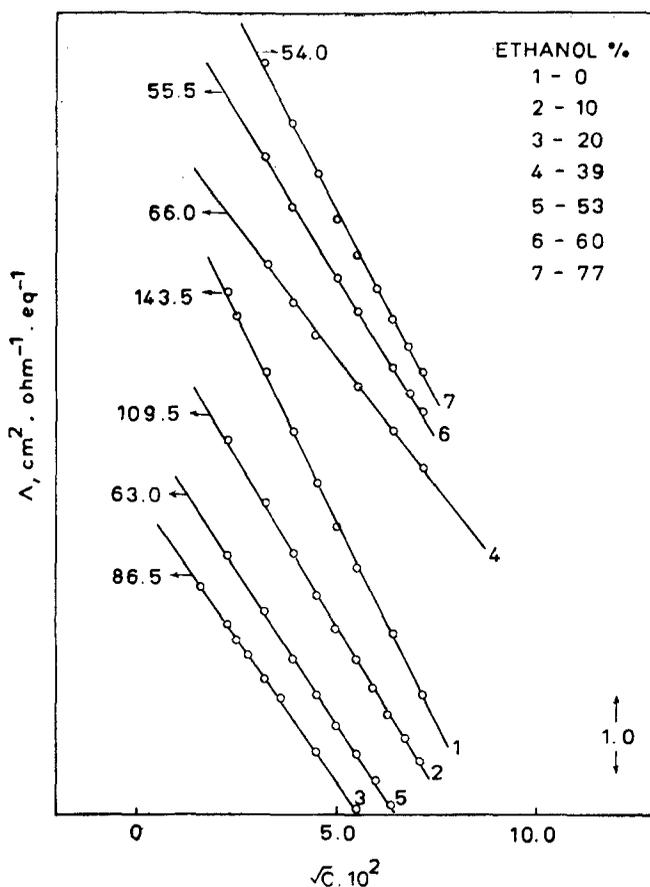


Figure 1. Plot of  $\Lambda$  vs  $\sqrt{c}$  for sodium nitrate in ethanol-water.

analyse the conductance data with BESM-6 computer. The values for  $K_A$  obtained from the three parameter equation (3) were small (either negative or less than the standard deviation) and thus indicated weak or negligible association. Spivey and Shedlovsky (1967) have also arrived at the same conclusion for other 1:1 electrolytes in ethanol-water medium. In the present study, ion association was neglected and the conductance data were analysed by the two parameter equation (4).

A computer program for least square fit, based on matrix inversion procedure, was used for the computation of  $\Lambda_0$  and  $L$ . A subprogram was used for calculating the ion-size parameter  $a^0$  from the equations (Fuoss *et al* 1965),

$$L_2(b) = 2E'_1 \Lambda_0 h(b) + \frac{44E'_2}{3b} - 2E' \ln b, \quad (5)$$

$$L = L_1 + L_2(b), \quad (6)$$

with

$$h(b) = (2b^2 + 2b - 1)/b^3, \quad (7)$$

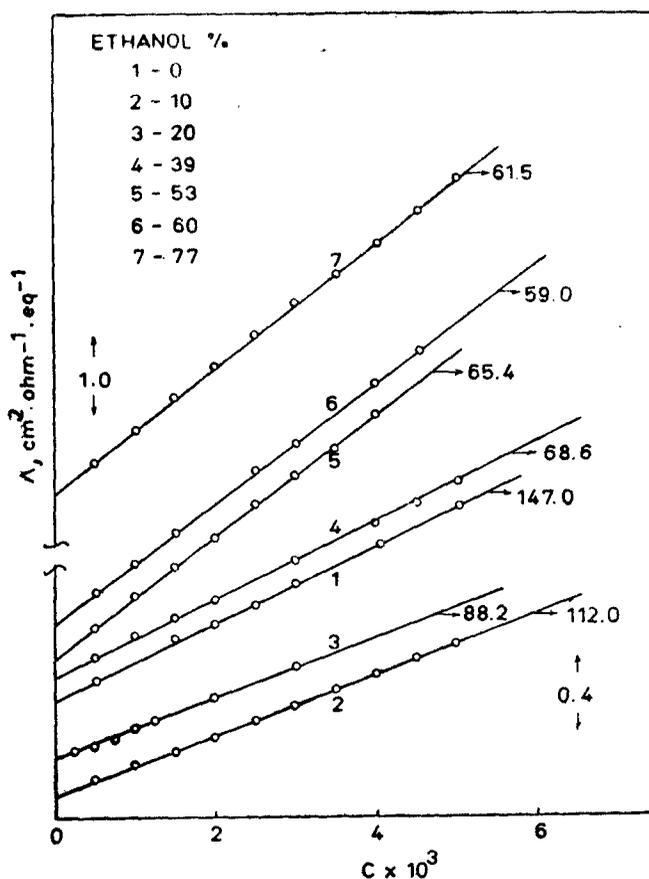


Figure 2. Plot of  $\Lambda'$  vs  $c$  for sodium nitrate in ethanol-water.

and

$$b = \frac{l^2}{adkT}, \quad (8)$$

where  $L_1$  is a constant,  $L_2(b)$  is a function of the ion size and the other symbols have their usual significance. The values of  $\Lambda_0$ ,  $L$ ,  $L_2(b)$  and  $a^0$  ( $L$ ) together with the standard deviation for  $a^0$  are included in table 2. The values for  $\Delta\Lambda$  given in table 1 correspond to the difference between the observed conductance and that calculated from (4).

Inherent limitations of the model based on rigid charged spheres, moving in a solvent continuum, preclude detailed discussion and analysis of the results. Ion pairs are usually considered as species held together by long range forces although molecular structure of the solvent and solvation effects can modify the electrical interaction. Fuoss identified  $a^0$  as the contact distance of the ion pair without explicitly taking into account the effect of solute-solvent interaction. In spite of this limitation, the value of  $a^0$  for  $\text{NaNO}_3$  in aqueous solution shows close agreement with the crystallographic value of 2.86 Å, reported by Parfitt and

Smith (1963). In general the value of the ion-size for  $\text{NaNO}_3$  in the mixed solvent increases with increase in ethanol content of the system although a minimum is noticeable at 60% ethanol.

### 3.2. The Walden product

The dependence of the Walden product on the dielectric constant of the medium is shown in figure 3. The value of  $\Lambda_0 \eta$  attained a maximum at a particular dielectric constant corresponding to that of 20% ethanol by weight and then decreased with further increase in ethanol content. A similar trend and variation in  $\Lambda_0 \eta$  which occur during progressive addition of the organic solvent to water, have been reported for other systems and in particular for  $\text{NaCl}$ -ethanol (Spivey and Shedlovsky 1967),  $\text{NaCl}$ -propanol (Goffredi and Shedlovsky 1967),  $\text{NaNO}_3$ -methanol (Sesta 1967) and alkali perchlorates in *t*-butanol (Accascina *et al* 1970).

Various models have been proposed to account for the dependence of the Walden product on the solvent composition. The theory (Kay and Broadwater 1971), based on 'gel-effect,' attributes the initial increase in  $\Lambda_0 \eta$  to a migration process, occurring free of viscous force, through the interstices created by long range order in the solvent. Kay and Broadwater (1976) have also put forward a 'sorting mechanism' which depends on the acid-base properties of the organic solvent. It is suggested that ion-water interactions are stronger than ion-ethanol interactions presumably because of the weaker acid-base properties of alcohol. The theory envisages a preferential enrichment of water in the ionic cosphere and this causes the local viscosity near the ions to be lower than the bulk viscosity

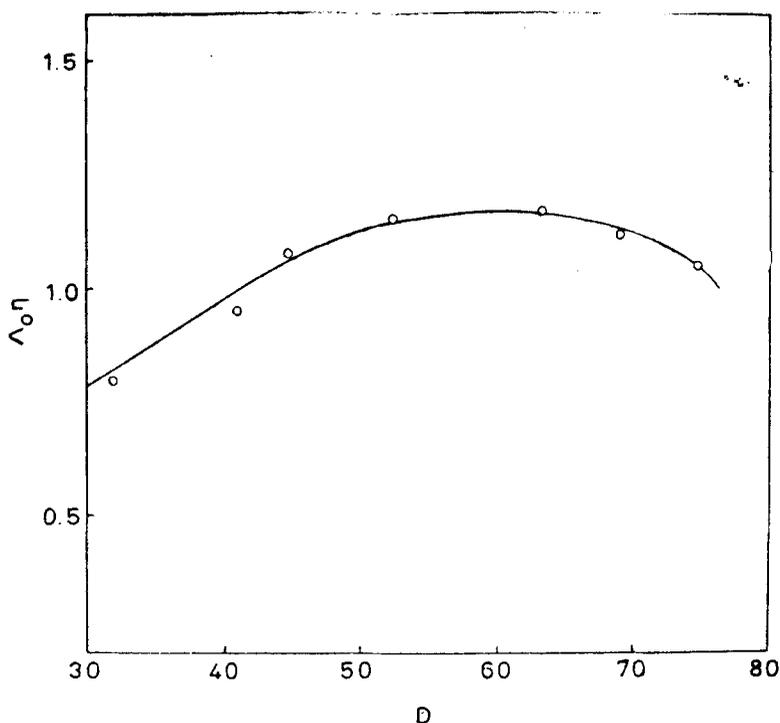


Figure 3. A plot of  $\Lambda_0 \eta$  vs  $D$  for sodium nitrate.

of the medium. As the mobility is enhanced, the Walden product appears higher for the mixed solvent. Likewise the theories (Boyd 1961; Zwanzig 1970) based on solvent-dipole relaxation effect can also be used to explain the decrease in  $\Lambda_0 \eta$  as the ethanol concentration of the mixture increases. It is generally accepted that retardation due to relaxation of the solvent dipoles around the ions in motion can decrease their mobility and the dielectric friction coefficients can be computed. However, to obtain meaningful data, it is essential to take into account the microscopic nature of the solvent in the vicinity of the ions as also the influence of the ions on the structure of the solvent.

Yet another qualitative scheme can be proposed on the assumption that the progressive addition of ethanol to water causes initially a contraction of the hydration sheath around  $\text{Na}^+$  and  $\text{NO}_3^-$  ions. This 'dehydration effect' (Broadwater and Kay 1970; Kay and Broadwater 1971) decreases the effective size of the cations and anions and as a result the ionic mobility and Walden product for  $\text{NaNO}_3$  can increase initially in the water-rich region of the mixture. Glueckauf (1964) has pointed out that as the ion-size decreases its first hydration sheath also contracts and therefore the friction between this layer and the ion increases. It appears that this enhanced drag of the hydration layer decreases the mobility and so  $\Lambda_0 \eta$  shows a maximum at a particular solvent composition. Extensive solvation of the ions with ethanol can also decrease the mobility although this process is predominant at higher ethanol concentrations and contributes to the continuous decrease of  $\Lambda_0 \eta$ . Needless to emphasise, these and other contemporary theories do not predict quantitatively either the value of the maximum or its enhanced dependence for certain electrolytes even in the same medium or in other solvents.

It is clear that the complex dependence of the Walden product on solvent composition is in effect a manifestation of the ion-solvent and solvent-solvent interactions on the mobility of the ions. The Eyring model (Glasstone *et al* 1941) can provide a possible explanation for this dependence on the ion-type, composition and structure of the solvent, as the Walden product is given by

$$\Lambda_0 \eta = \frac{F^2}{V} \left[ \lambda_c^2 \exp\left(\frac{\epsilon_c}{kT}\right) + \lambda_a^2 \exp\left(\frac{\epsilon_a}{kT}\right) \right] \exp\left(\frac{-\epsilon_s}{kT}\right) \quad (9)$$

where  $\epsilon_c$  and  $\epsilon_a$  are the activation energies needed by the cations and anions to jump from one equilibrium site to another at distances  $\lambda_c$  and  $\lambda_a$  respectively. The activation energy for the motion of the solvent is denoted by  $\epsilon_s$ , whereas  $V$  is the molar volume of the solvent. It has been pointed out by D'Aprano *et al* (1976) that the values of  $\epsilon$  and  $\lambda$  depend on the size and shape of the ions and solvent molecules. In addition, factors like medium composition, molecular structure of the solvent and ion-solvent interactions can exert a decisive influence.

Kay *et al* (1968) have identified two domains in ethanol-water system which correspond to a water-rich region (upto about 10 mole % ethanol) and an alcohol-rich region. Further Franks (1967) points out that in the water-rich region there is enhancement of long range order or structure, possibly through hydrogen bonding. On the contrary in the alcohol-rich region, there is progressive destruction of the water structure. In agreement with this, the slope of the viscosity vs composition curve for ethanol-water system shows (Kay and Broadwater 1976) a maximum at 10 mole % and a minimum at 40 mole % ethanol. According to

Eyring model, ionic transport in any structured solvent involves local destruction of structure of the medium. In (9), the values of  $\epsilon$  and  $\lambda$  will change and increase progressively for the water-rich region of the system upto about 10 mole % ethanol. As a result the Walden product is higher for the mixed solvent and shows a maximum at approximately 9 mole% of ethanol for  $\text{NaNO}_3$  and near 10 mole% alcohol for many alkali halides (Kay and Broadwater 1976). The activation energy and distance parameters are smaller for unstructured solvents and this might explain the progressive decrease in  $\Lambda_0 \eta$  for  $\text{NaNO}_3$  at higher ethanol concentrations. The enhancement in the values of the maxima observed by Kay and Broadwater (1971, 1976) for some 1 : 1 electrolytes in this medium can also be tied up with the relative ability of the anions and cations to act as structure breakers. In general, the structure-breaking effect is greater when the charge-to-surface ratio of the ion is smaller (Kay and Evans 1966). On this basis monovalent ions like  $\text{Na}^+$  and  $\text{NO}_3^-$ , with large charge-to-surface ratios, are less effective as structure breakers. Consequently they do not significantly decrease the activation energy and distance parameters by influencing the solvent structure in the Eyring model. In addition, as compared to an efficient structure breaker such as  $\text{CsI}$ , one should expect for  $\text{NaNO}_3$  in ethanol-water system a more pronounced maximum in the Walden product. The height of  $\Lambda_0 \eta$  maximum should therefore be in the reverse order of the structure-breaking ability of the ions. The observed trend and dependence of  $\Lambda_0 \eta$  (Kay and Broadwater 1976; Broadwater and Kay 1970) for various alkali halides in alcohol-water medium also support this view. The theory (Kay and Evans 1966; Kay and Broadwater 1971) that the structure-breaking ions decrease the local viscosity of the medium and thereby enhance the mobility and Walden product is not tenable and has also been discarded recently by Kay and Broadwater (1976).

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