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The Electrical Conductivity of Some Alkali Nitrates in Propanol-Water Mixtures at 298K

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ABSTRACT

The electrical conductivity of some symmetrical (1:1) alkali nitrates in different percentages of propanol-water mixtures at 298K have been measured.

The results were analysed using Lee-Wheaton (LW) equation, that is based on a method of which involving definite sizes for the ions. The electrical conductivities of $NaNO_3$, KNO_3 and $CsNO_3$ in propanol-water mixtures, were measured. The values of conductivity parameters, (Λ_o, K_a, and R) at the best fit values of the standard deviation $\sigma_s(\Lambda)$ have been calculated.

التوصيلية الكهربائية لبعض نترات الفلزات القلوية في مزيج البروبانول-الماء عند درجة 298 كلفن

الملخص

يتضمن البحث دراسة توصيلية الكتروليتات متناظرة (1:1) في نسب مختلفة من مزيج البروبانول-الماء. وقد تم تحليل النتائج باستخدام معادلة لي-ويتون في التوصيلية التي تستند على نموذج يفترض ان الايونات تكون على شكل كروي ذي حجم محدد.

فقد تم قياس التوصيلية لاملاح $NaNO_3$, KNO_3, $CsNO_3$ في مزيج من (البروبانول-الماء) ذي مكونات مختلفة عند درجة 298 كلفن. وتم حساب معطيات التوصيلية (Λ_o, K_a, R) عند احسن قيم من $\sigma_s(\Lambda)$.

INTRODUCTION

Lee and Wheaton (Lee and Wheaton 1978,1979) describe in a series of papers the derivation of a conductance equation based on a model identical to that suggested by Fuoss [Fuoss 1975,1976] but using a new boundary condition to replace that used by Fuoss. The equation describes transport in solution containing any number of ionic species of any valancey type, and hence is suitable for use with symmetrical, asymmetrical or mixed electrolysis in solvents of different dielectric constant (D).

In the new and specifically chemical model used by Lee & Wheaton attempts were made to get close to the actual physical situation by allowing for dielectric saturation near the ions, and including the concept of ion association in the initial model.

It is well known that Lee and Wheaton have introduced their equation in 1978 which is an extended form of the Debye-Huckel equation for the calculation of molar (or equivalent) conductance of electrolyte solutions.

In this work Lee-Wheaton (LW) equation is used to test its validity to single electrolyte solution (symmetrical 1:1) in different media of different physical properties (dielectric constant, viscosity, solvent structure…etc.) of different percentages of propanol-water mixtures, and also to calculate the equivalent conductance for the ion-pair conducting species formed in the solution.

EXPERIMENTAL

Solvent purification and preparation:

n-Propanol was purified by the method described by [Ito et.al, 1988]. The properties of alcohol and water used are given in Table (1). Triple distilled water was prepared (Kubota et.al, 1988) by distilling the distilled water three times, or a deionized water was prepared by an ion exchanger instruments. n-propanol-water mixtures were prepared by weighing the required amount of the purified solvents to obtain the required mixture percentage.

Table 1: Physical properties of the solvents with their specific conductance at 25°C.

Solvent	**Density gm/cm^3**	**Dielectric Constant**	**Viscosity Kg.m^{-1}.s^{-1}x 10**	**Boiling Point °C**	**Specific Conductance Ω^{-1}.cm^{-1}**
n-propanl	0.79950	20.45	1.9480	97.20	$< 1\text{x}10^{-6}$
Water	0.99707	78.30	0.8903	100.00	$< 5\text{x}10^{-6}$

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Solute purification:

The salts were recrystallized three times from conductance water, then dried at the required temperature for the required time for each salt as: sodium nitrate (at 130°C for 3 days), potassium nitrate (70°C, 12 days), cesium nitrate (100°C, 2 days).

Instruments and apparatus:

A 427 multi-frequency LCR meter (Hewlett-Packard) was used for measuring the resistance of the solution from which the conductance (reciprocal of resistance) of the solutions were obtained. It's accuracy was within 0.05%. All the resistance measurements were made at 1 KH_z frequency. A water thermostat of type Hakke G3 with thermobath D3 was used for controlling the temperature of the conductance cell. It's sensitivity was within ± 0.1.

Nitrogen line:

Because the higher sensitivity of the solvent for carbon dioxide and atmospheric water, a nitrogen line was designed to ensure complete isolation of the system. The nitrogen gas was passed through several traps: lime water for carbon dioxide absorption, sulphuric acid for water absorption, calcium chloride for water absorption also, and an empty trap.

Conductivity cell and Syringe

The conductivity cell used in this work, has the same design as that used by Akrawi (Akrawi, 1981). The electrodes used were platinized platinum electrodes type WTW electrode (W.Germany). The cell constant was measured by using the method of (Lind-Zwolenik-Fuoss (LZF), 1959) for different concentrations of potassium chloride solution in conductivity water are found to be 0.005582 cm^{-1}. A plastic syringe (1ml) was used for injection of the stock solution into the conductance cell.

Conductivity measurements

All stock solutions were generally prepared by weighing using freshly prepared solvents. The required amount of the salt was placed in a weighed conical flask, then the required amount of the solvent was added and the flask with its contents were reweighed again. For conductivity measurements a known amount of the solvent was added to the clean, dried and weighed conductivity cell, and the cell reweighed again, then the cell was placed in a water bath, which was thermostated at the required temperature for about 30 minutes. To ensure that there is no weight loss, the cell was weighed again, then the resistance of the solvent was measured. Small amount of the stock solution (which was weighed before and after each addition) was injected by the plastic syringe through a rubber cap into the cell. By suitable design of four taps combined with the cell and by raising and lowering the level of the solution one can insure complete washing of the added stock solution into the cell.

Nitrogen gas was then passed for about 2-3 minutes for complete mixing the solution, then the resistance of the solution was measured. This procedure was repeated for 10-12 times for each run.

After all additions were completed the cell was dried, reweighed to find the weight change which had taken place through the run. This loss was found to be not more than 0.02%.

RESULTS AND DISCUSSION

1. Interpretation of symmetrical electrolyte conductances in n-propanol (n-PrOH)-water (H_2O) mixtures at 25°C

Studies of electrolytic conductance in the binary systems are of interest not only because of the relevance to electrolyte theory but also because of the light they can through on the structural interactions between the two components of the binary solvents system (Goffredi and Shedlovsky, 1967). Contrary to the prediction of electrolytic theory the association of electrolytes in solvents containing hydroxyl groups appears to increase with increasing proportion of alcohol and ionic size (Kay *et al.*, 1965). This has, however, been explained (Lee and Wheaton, 1979) in terms of formation of solvent-separated ion-pair (SSIP) and contact ion-pairs (CIP).

Several conductometric studies of alkali salts have been undertaken during the last few decades in mixed solvents, conductance of $LiClO_4$, $NaClO_4$ and $KClO_4$ have been measured in diethyl formamide-water mixtures (Jauhar *et al.*, 1988), NaCl and NaI in formamide-water mixtures at 25°C (Domench and Miro, 1988), alkali metal chlorides in 1,2-dimethoxyethane-water mixture (Parbbi *et al.*, 1988), alkali metal nitrate in aqueous glycerol([Dash ., 1988] were studied.

However, very little work has been done on the conductance of alkali metal nitrate in solution of n-propanol-water mixtures. Therefore we have measured the electrical conductances of $NaNO_3$, KNO_3, $CsNO_3$ in n-propanol water mixtures over a wide variety of compositions.

The organic solvent, n-propanol, is chosen in view of its unusual behavior as compared to that of other normal alcohols in having stable rotational isomerism in its trans (planer) form(Islam and Ansari, 1982).

The conductance-concentration data obtained were analysed by the LW equation (Lee and Wheaton, 1979), which were given an expression for the single ion equivalent conductance of an ion of the species, in a solution containing a total of ionic species.

According to LW equation and for the "special case" of solutions containing a single symmetrical electrolyte the equivalent conductance is given by:

$$\Lambda_{equiv.} = f\,(K_A, R, \Lambda_o)$$

Where K_A is ion association constant, R is the mean distance between the ions and Λ_o is the limiting or molar conductance. A computer program named LW1 (Dawod, 1996) is used for calculating the equivalent conductivity by using a curve fitting procedure to determine K_A, R, and Λ_o at the best fit $\sigma_s(\Lambda)$ of experimental equivalent conductance to that as measured by:

$$\sigma_s(\Lambda) = \left[\sum_{n=1}^{Np} \frac{(\Lambda_{calc.} - \Lambda_{expt.})^2}{Np} \right]^{1/2} \cdots\cdots\cdots \quad (2)$$

Where Np is the number of pairs of conductance-concentration data.

The input data to this program are: temperature (T), dielectric constant (D), viscosity (η) of solvent; K_A, Λ_o, and R in the form $R_{min.}$, $R_{max.}$ and ΔR, with the solution molarities and the corresponding equivalent conductances. The plot of the measured equivalent conductances ($\Lambda_{equiv.}$. Ω^{-1}. cm^2. $equiv.^{-1}$) against the square root of molar concentration ($C^{1/2}$. mole. l^{-1}) at different composition of n-propanol-water mixtures (10-90 w/w percent) for $NaNO_3$, KNO_3, and $CsNO_3$ electrolytes at 25°C are shown in Figures 1,2 and 3 respectively.

The conductance data were analyzed by using LW equation (program LW2 in Fortran) (Akrawi, 1981), this program is used for analysis of the data of symmetrical electrolytes, The parameters K_A, Λ_o, R and the standard deviation σ_s (Λ) (equation 2) obtained are given Table (2)

Table 2: The best-fit parameters for $NaNO_3$, KNO_3, and $CsNO_3$ in n-propanol -water mixtures at 25°C.

Salts	**Λ_o (Ω^{-1}.mole^{-1}.cm^2)**	**K_A (dm^3.mole^{-1})**	**R (A°)**	**σ_s (Λ)**
10 wt% n-Pr-OH				
$NaNO_3$	92.61	3.70	4.1	0.054
KNO_3	101.75	4.39	4.5	0.033
$CsNO_3$	108.69	5.40	5.3	0.058
30 wt% n-Pr-OH				
$NaNO_3$	56.21	5.20	4.7	0.038
KNO_3	66.31	5.70	5.1	0.034
$CsNO_3$	68.09	6.10	5.3	0.037
50 wt% n-Pr-OH				
$NaNO_3$	42.57	11.95	5.2	0.052
KNO_3	46.09	8.71	5.4	0.044
$CsNO_3$	48.13	10.58	5.8	0.045
60 wt% n-Pr-OH				
$NaNO_3$	37.37	17.06	5.9	0.043
KNO_3	39.49	15.21	5.3	0.050
$CsNO_3$	40.69	17.48	5.9	0.037
70 wt% n-Pr-OH				
$NaNO_3$	30.53	25.81	6.3	0.057
KNO_3	33.91	30.11	6.4	0.029
$CsNO_3$	25.50	30.63	6.5	0.035
90 wt% n-Pr-OH				
$NaNO_3$	28.86	124.23	6.8	0.035
KNO_3	29.21	175.17	6.9	0.033
$CsNO_3$	-----	-----	-----	-----

A plot of Λ_o against the composition of the solvent mixture is shown in Figure (4), for the three salts.

In all solvent compositions, Λ_o increase in the order: $NaNO_3 < KNO_3 < CsNO_3$ in according with the decreasing solvation of cations (anion, NO_3^-, being same) and increase in ionic radii, the same behavior was found for alkali perchlorates in dimethylformamide-water mixtures (Jauhar et al., 1988). Also, it may be noted that in the case of high dielectric medium (lower n-propanol composition in the mixtures) the extent of decrease in the Λ_o

values is significant due to higher mobility as compared to that in the lower dielectric medium. This behavior is in a good agreement with that obtained by

Islam (Islam and Ansari, 1989) for tetra-alkylammonium electrolytes in isopropanol-water mixtures solvent. n-propanol-water mixture has a maximum value in viscosity at 60% n-propanol in the absence of any salt (Figure 4).

Also there is no minima in Λ_o values for the three salts at 60% propanol, it means that the viscosity effect is not the only main factor affecting the mobility of the ions. Therefore, it is better to discuss the results in terms of Walden product ($\Lambda_o\eta$), in order to analyze the structural changes of the solution when varying the solvent composition. In Figure (5), the Walden product for $NaNO_3$, KNO_3 and $CsNO_3$ electrolytes are represented as a function of the reciprocal dielectric constant (1/D). According to the walden product rule, the $\Lambda_o\eta$-product should remain constant for a given electrolyte in different solvents. However, as it can be seen from Figure (5), the $\Lambda_o\eta$-products depend on solvent composition, and it exhibits a maximum at D =57.7 (30 wt % n-propanol) which is more broad for $NaNO_3$. This departure of the Walden rule can be ascribed to the charge of ion solvation and of the solvent structure (Domench and Miro, 1988).Thus the increase in ($\Lambda_o\eta$) in n-propanol-water mixture up to the maxima in the dielectric range ($71.4>D>57.7$) may be due to more feasible ionization of the added solute in a given solvent, where the solute-solvent interaction appear to be weak (Islam and Ansari, 1989). On the other hand, the sharp decrease in the Walden product values in the range ($57.7>D>21.6$) indicates strong solvent-solute interaction as a result of which the solvent fails to decrease the mobility of the ions and increase the viscosity of the medium. The strength of such an interaction, however, increases with the increase in the proportion of n-propanol in n-propanol-water mixtures (Islam and Ansari, 1989). Also the hights of maxima decrease in the order $CsNO_3>KNO_3>NaNO_3$ in according with the structure breaking power of the cation.

The obtained values for the association constant (K_A) for all the electrolytes (Table 2) depend on the composition and hence on the dielectric constant of the solvent mixture.

The values of (K_A) increase as the dielectric constant decrease (i.e. as the n-propanol content increase) for the three salts. This increase indicates that the alkali cations in n-propanol-water mixtures are highly associated with the solvent molecules.

The plots of log K_A against D^{-1} are almost linear (Figure 6). This behavior may be understood on the basis of the fact that the resultant association behaviour depends on two opposing effects; the formation of solvent-separated ion pair (SSIP), and the formation of contact ion pair (CIP).

The overall R-values (Table 2) increase with increasing the n-propanol content (i.e. decrease in D) which indicate an increase in ionic association, and reinforces the concept of the formation solvent-separated ion pair with the decrease in D.

In view of these results, one may conclude that the (Λ_o) values of the electrolytes in the low percentage of n-propanol is higher, and the values of K_A (< 10) is small and almost the same as in pure water. A maxima were obtained at D=57.7 which did not coincide with the maxima of the viscosity against the

composition, thus the electrolyte behaviors depends on the dielectric constant and viscosity. The analysis of the conductance-concentration data by using the LW equation for these three electrolytes in different n-propanol-water compositions, gives a small values of standard deviation (< 0.1) which indicates the good applicability of this equation for interpretation of the data of symmetrical electrolytes in mixture solvents.

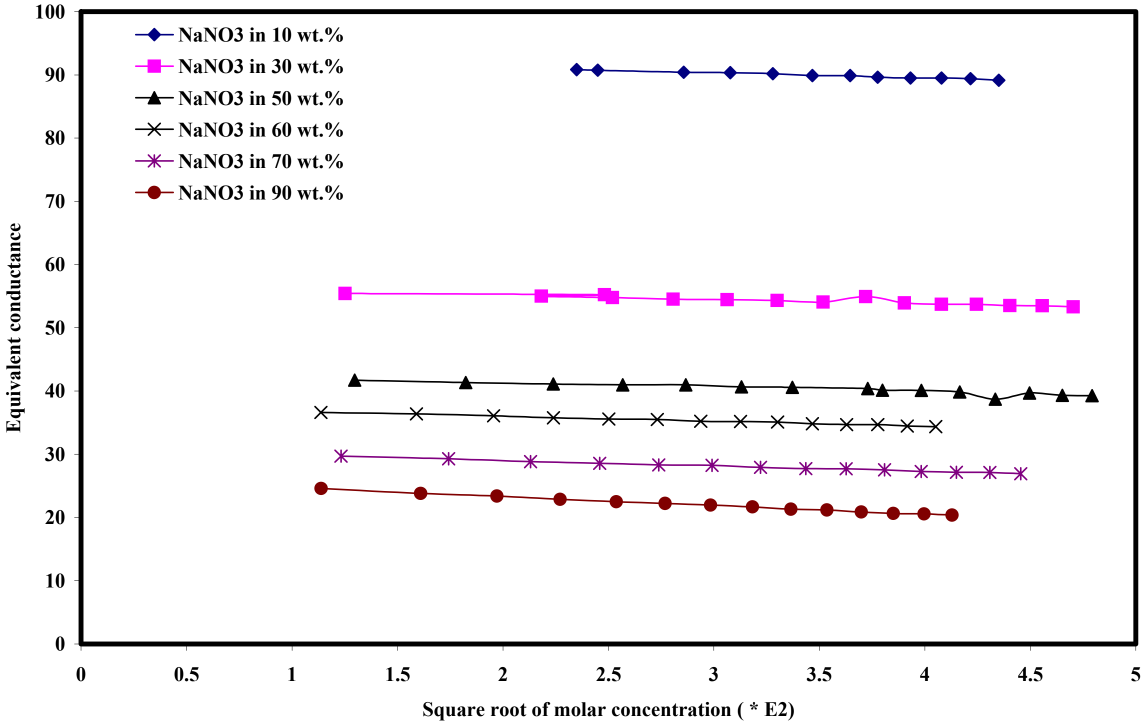

Fig. 1: The Plot of equivalent conductance against the square root of molar concentration for $NaNO_3$ in n-PrOH-H_2O mixtures.

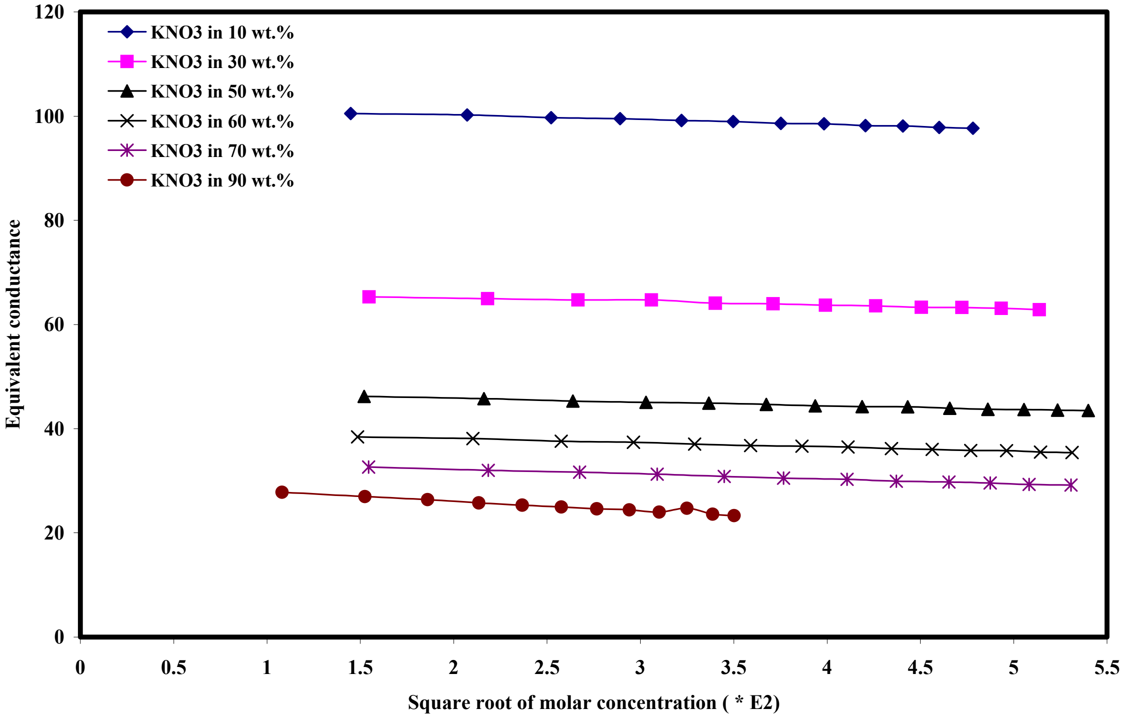

Fig. 2: The Plot of equivalent conductance against the square root of molar concentration for KNO_3 in n-PrOH-H_2O mixtures.

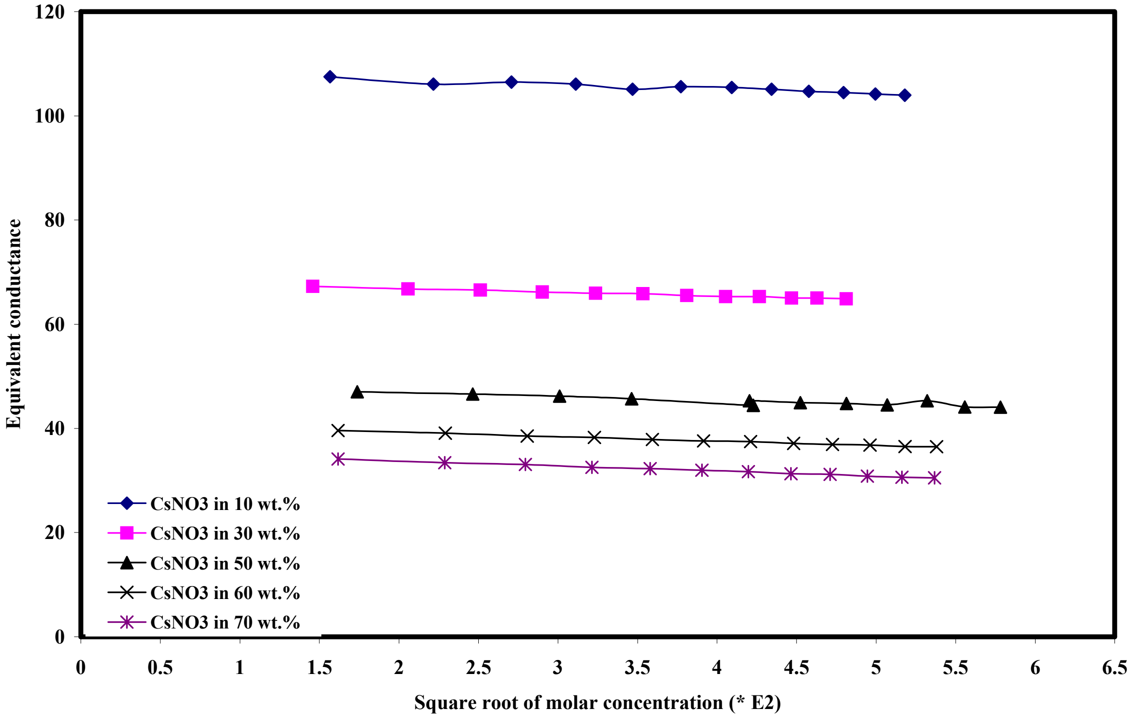

Fig.. 3: The Plot of equivalent conductance against the square root of molar concentration for $CsNO_3$ in n-PrOH-H_2O mixtures.

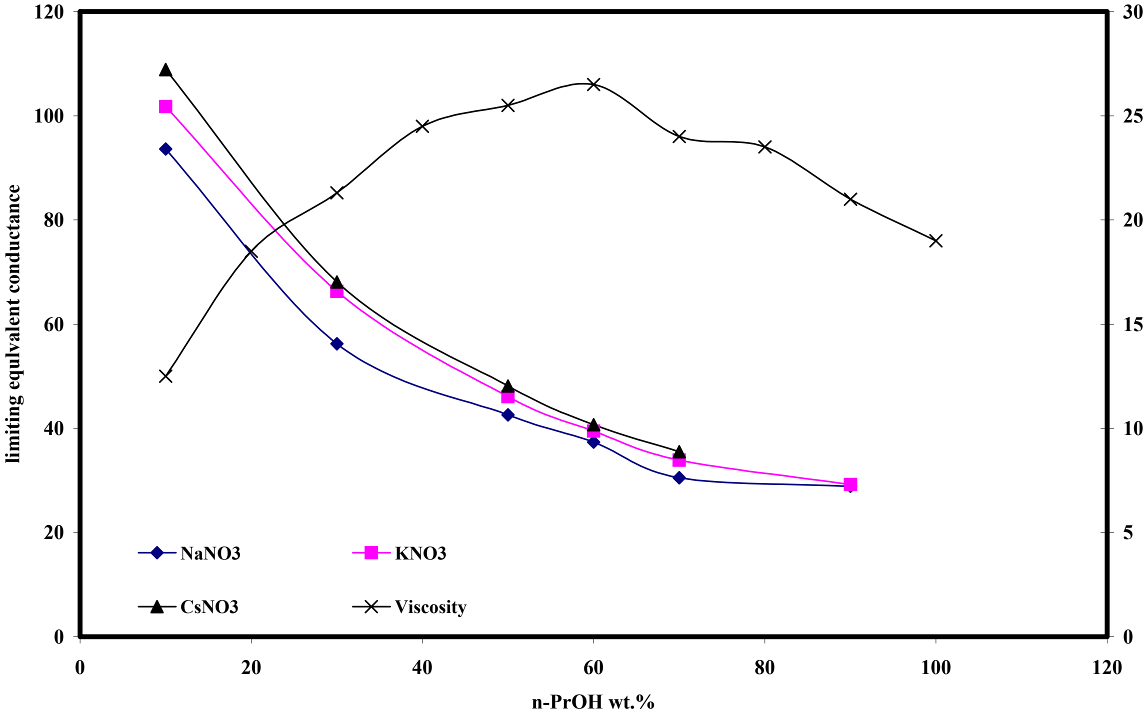

Fig. 4: The Plot of limiting conductance and viscosity against the wt.% in n-PrOH-H_2O mixtures at 25°C.

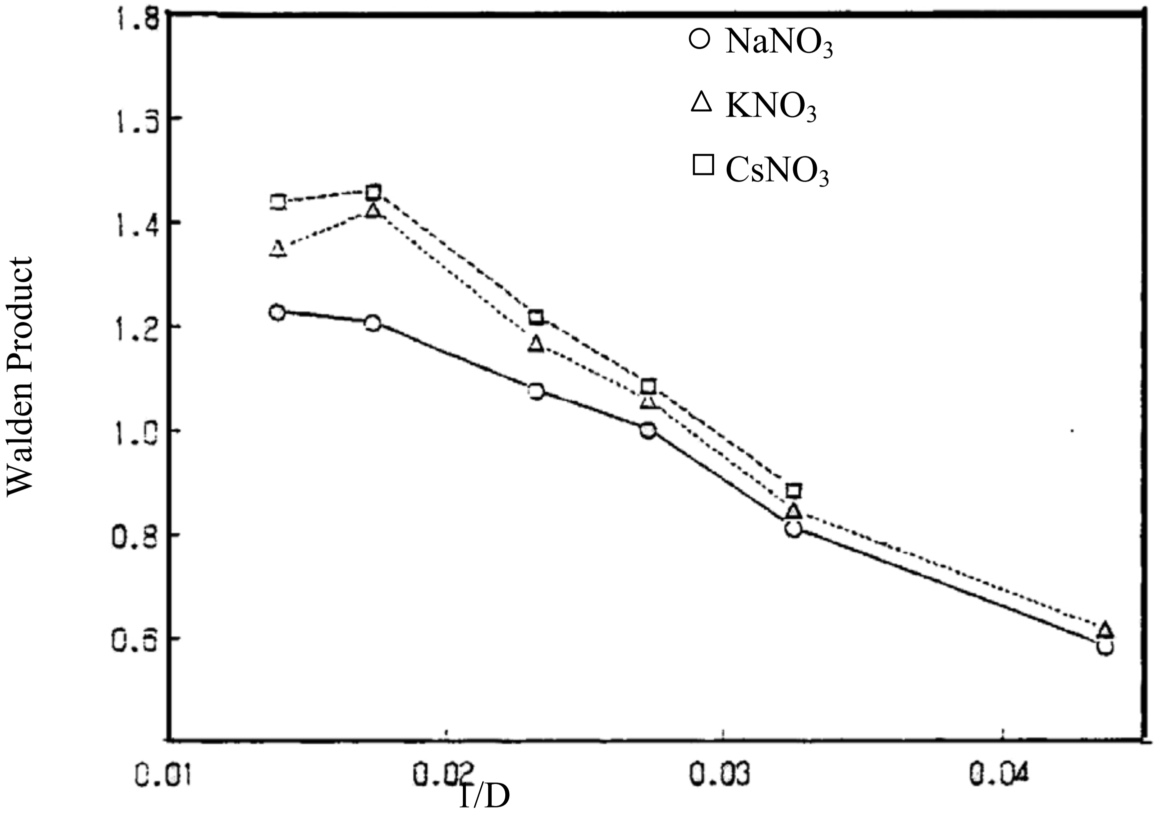

Fig. 5: The plot of the Walden product against 1/D for the $NaNO_3$, KNO_3 and $CsNO_3$ in n-PrOH-H_2O mixture at 25°C.

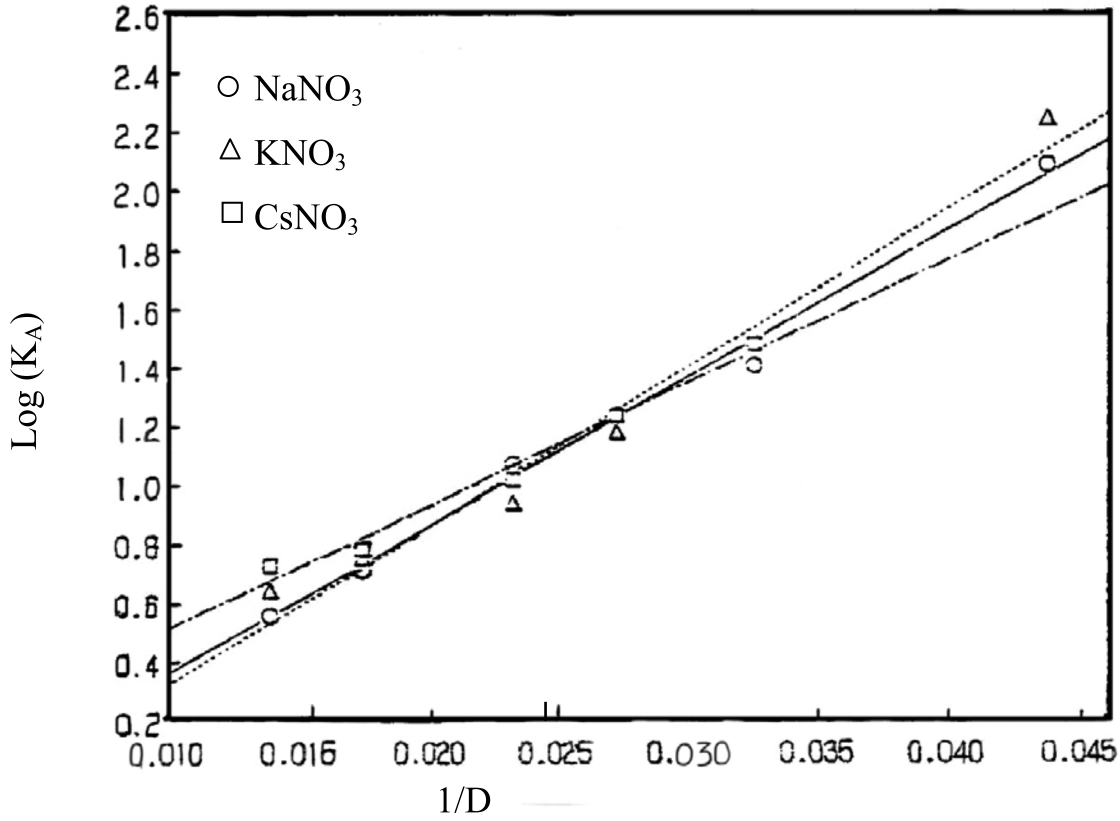

Fig. 6: The plot of log (K_A) against the reciprocal of dielectric constant for $NaNO_3$, KNO_3 and $CsNO_3$ in n-PrOH-H_2O mixture at 25°C.

REFERENCES

Akrawi, B. A., 1981, The Analysis of Conductance Data for Single and Mixed Electrolyte Solutions. Ph. D. Thesis, Univ. of Surrey, Guildford, England.

Dash, U. N., Das, B. B., Biswal U. T. and Panda, T., 1988, Standard Thermodynamics of Transfer.III. Silver and Silver Salt Electrodes in Water + mono – and + dihydric Alcohol Mixtures, J. Electrochem. Soc. India, 37, pp.285- 294.

Dawod, A. M., 1996, An Application of the Lee-Wheaton Conductance Equation to Single and Mixed Electrolytes in Different Media, Ph.D. Thesis, Mosul University, Mosul, Iraq.

Domench, J. and Miro, J., 1988, Electrical Conductance of Sodium Bromide in formamide-Water Mixtures, Monatsh Chem., 119, pp.277- 290.

Fuoss, R. M., 1975, Conductance-Concentration Function for Associated Symmetrical Electrodes, J. Phys. Chem., 79, pp.525- 534.

Fuoss, R. M., 1976, Conductance-Concentration Function for Associated Symmetrical Electrodes. Supplementary Comments, J. Phys. Chem., 80,pp. 2091- 2105.

Goffredi, M. and Sedlovsky T., 1967, Studies of Electrolytic Conductance in Alcohol-Water Mixtures.III. Sodium Chloride in 1-Propanol-Water Mixtures at 15,25, and 35^{o}C, J. Phys. Chem. 71, pp.2176- 2191.

Islam, M. R. and Ansari, A. S., 1989, Conductivity of Some Tetra alkyl ammonium Halides in n-Propanol-Water Mixture, Indian J. Chem., 28A,pp. 477- 493.

Islam, M. R. and Ansari, A. S., 1989, Conductivity of Some Tetraalkyl ammonium Halides in Isopropyl-Water Mixture, Indian J. Chem., 28A, pp.486- 499.

Jauhar, S. P., Gurays, P. S. and Narula, S. P., 1988, Physicochemical Studies in Mixed Solvents, Viscosity, Measurements of Some 1:1 Electrolyte solutions in diethyl-sulfoxide Mixtures at 25^{o}C, Indian J. Chem., 27,pp.629- 642.

Kay, R. L., Zawoyski C. and Evans, D. F., 1965, Conductance of the Symmetrical Tetra-alkylammonium Halides and Picrates in Methanol, J. Phys. Chem., 69,pp. 4208-4221.

Lee, W. H. and Wheaton, R. H., 1978, Conductance of Symmetrical, Unsymmetrical Electrodes, J. Chem. Soc. Faraday II, 74, pp.743- 765.

Lee, W. H. and Wheaton, R. H., 1978, Hydrodynamic Terms and Complete Conductance Equation, J. Chem. Soc. Faraday II, 74, pp.1456- 1482.

Lee, W. H. and Wheaton, R. H., 1979, Examination of New Model and Analysis of Data for Mixed Electrolytes, J. Chem. Soc. Faraday II, 74,pp. 1128-1145.

Lind, J. E., Zwolenik J. J. and Fuoss R. M., 1959, Electrolytic Conduc- tance of Salts of Several Cyanocarbon Acids, J. Amer. Chem. Soc., 81, pp.1557- 1560.

Parbbi, P. V. and Ramanamutti, N., 1988, Conductivities of Alkali Metal Chloride in 1,2-Dimethoxyethane-Water Mixture, Bull. Chem. Soc., 61,pp.2595-2609.