----Raf. Jour. Sci., Vol.17, No. 4 Chemistry, Special Issue, pp.68-75, 2006----

The Electrical Conductivity of Potasium Halides in Methanol at Different Temperatures

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(Received 30/3/2005 , Accepted 16/1/2006)

ABSTRACT

In the present study we have measured the electrical conductivity of some potassium halides (KCl, KBr and KI) in methanol at different temperatures (298-318°K). The conductivity parameters (R, K_a and $\Lambda_\circ$) have been calculated by using Lee-Wheaton equation. The thermodynamic parameters (ΔH, ΔG and ΔS) are also calculated for these salts.

For the three electrolytes, and at any temperature, it is found that both Λ_o and K_a increase with increasing temperature following the order:
$\Lambda_{o\,KCl} < \Lambda_{o\,KBr} < \Lambda_{o\,KI}$ While $K_{aKCl} > K_{aKBr} > K_{aKI}$ The overall distance parameter (R) is inversely proportional with temperature.

التوصيلية الكهربائية لهاليدات البوتاسيوم في الميثانول عند درجات حرارية مختلفة

الملخص

يتضمن البحث دراسة توصيلية بعض هاليدات البوتاسيوم (KCl , KBr و KI) في مذيب الميثانول وعند درجات حرارية مختلفة (298-318 كلفن) وتم حساب معطيات التوصـيلية (R , K_a و Λ_o) وذلـك باستخدام معادلة لي-ويتون في التوصيلية فضلاً عن معطيات حـساب الثرموديناميكيـة ($\Delta G°$, $\Delta H°$, $\Delta S°$). ولقد وجد ولكل من الالكتروليتات الثلاثة وعند اية درجة حرارية ان قيم كـلا مـن Λ_o و K_a تزداد بازدياد درجة الحرارة حيث ان :

$\Lambda_{o\,KI} > \Lambda_{o\,KBr} > \Lambda_{o\,KCl}$ ولكن قيم ثابت التجمع الايوني تتبع التسلسل $K_{a\,KI} < K_{a\,KBr} < K_{a\,KCl}$ فضلا عن ان المسافة بين الايونات (R) تتناسب عكسيا مع درجة الحرارة.

INTRODUCTION

Wide temperature range conductivity measurements for electrolyte solution can give detailed information on ion-ion and ion-solvent interaction (Yokoyama and Kon, 1991) and also to obtain detailed thermodynamic information of ion association and examine the nature of the interaction (Yokoyama et al., 1988). Several works have been made in past on the study of the temperature effect on the electrolyte conductivity Yokoyama and Ohta (1988), studied the conductivity measurements between 0 and 50°C for aqueous KNO_3 and $KCLO_4$ solutions. They found that weak ion-ion interactions were present and that ion association constant was minimized at characteristic temperature. Also Yokoyama et al. (1988), determined ion-association constant of $Fe(phen)_3^{+2}$ with o- and m-benzendisulfonate at 0 and 50°C, which were considerably larger than the electrostatic prediction. The ion-solvent interaction of $CoSO_4$ and $NiSO_4$ in isopropanol-water mixtures at 30-45°C has been studied (Prida and Das, 1986). (Barthel et al., 1986), studied the temperature effect on the conductance of some alkali halides in propanol and the results were discussed in terms of contact and solvent separated ion pairs. NaI, KI and $NaClO_4$ solutions in DMF at 10-60°C have been also studied by Krumgalz and Barthel (1984) and the discussion of $\Lambda_\circ$ is based on solvent-solute interactions.

Conductance data were reported for alkali (Li, Na, K, Rb. and Cs) chlorides and bromides in ethylene glycol with molarity 1×10^{-4} -1×10^{-2} mol/dm^{-3} over the temperature range (5-175 ^{o}C). The advantage of using Lee-wheaton equation and the so-called (consestane) approach was demonstrated (Lebed et al., 1981). Gibbs energy of transfer and conductivity properties of NaBr and some other alkali halides solutions in mixtures of water with propanol at 298.15 K hed been measured by (Gregorwicz et al.., 1999). The conductivity parameters (Λ_o, K_a, and R) were obtained by fuoss–Justice equation. (Hammadi et al., 2000), had measured the electrical conductivity of solutions of potassium and sodium halides in glycerol at (3.37-42.24) ^{o}C Valuse of Λ_o were obtained by extrapolation using Onsager equation. The electrical conductivity of NaI in mixtures of water and butanol had been measured of 298.15 K (Gregorwicz et al.., 2000). Fuoss- Justices equation was used to obtain the conductivity parameters and the Walden product was then calculated .

In the present study, electrical conductivity of KCl, KBr and KI electrolyte solutions in methanol were measured at temperatures between (5-45°C). The analysis of conductance-concentration data at each temperature was made by using LW equation for symmetrical electrolytes. From the ion association constant calculated, the entropy and enthalpy changes can be estimated which enable to understand the nature of the ion-association.

EXPERIMENTAL

Methanol was purified and dried by the method described by Perrin et al. (1966). Its properties are: [D = 32.62, η = 0.005445 poise, B.P. = 64.60°C with specific conductance = 1×10^{-6} $\Omega^{-1}cm^{-1}$]. The salts were recrystallised three times from conductivity water, then dried at the required temperature for the required time for each salt as: potassium chloride (500°C for 5 hrs), potassium bromide (120°C, 3 days) and potassium iodide as (120°C, 2 days). A 427 A multi-frequency LCR meter (Hawlett-Packard) was used for measuring the resistance (reciprocal of conductivity) of the solution with accuracy within 0.05% and at frequency 1KHz.A water thermostat of type Hakke G3 with thermobath D3 was used for controlling the temperature of the conductance cell with sensitivity ± 0.1°C.The nitrogen line and the isolation of whole system was described in details in the previous published papers (Akrawi, 1992). The electrodes of the conductivity cell used were platinized platinum of 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 and found to be 0.05582 cm^{-1}.

Conductivity measurements were done by the following: all stock solutions were prepared by weighing. A known amount of the solvent was placed in a clean, dry and weighed conductivity cell, weighing the cell again then placed in a water bath at 25°C for about 20 minutes. The resistance of the solvent was measured then a small amount of the stock solution was injected by a plastic syringe (which was weighed before and after each addition) through a rubber cap 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. After all additions were completed, the cell was reweighed again to find the weight change that was found be not more than 0.02%.

RESULT AND DISCUSSION

The plots of equivalent conductances ($\Lambda_{equiv.}$) against the square rote of the molar concentration of the electrolyte solutions of KCl, KBr and KI are shown in Figures (1-3), respectively. As it can be seen from the Figures the equivalent conductances increase with increasing temperature, for the three electrolytic solutions. The analysis of the conductance-concentration data was by using Lee-Wheaton equation (computer program LW2). According to this equation for a special case for single symmetrical electrolyte is given by:

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

The conductance parameters: limiting equivalent conductance ($\Lambda_\circ$), ion association (K_A) and the distance parameter (R) are the best-fit values of (Λ) as $\sigma_s(\Lambda)$ for the three electrolyte solutions in methanol at different temperatures with the Walden product ($\Lambda_\circ\eta$) are given in Table (1). The increase of ($\Lambda_\circ$) with increasing the temperature for the three electrolytes can be attributed to increase in the fluidity of the methanol i.e. decrease in viscosity of methanol (Robinson and Stokes, 1959), It can be seen from Table (1), that the Walden product for each salt is slightly changed at different temperatures and the order for this product for the salts at each temperature is KCl < KBr < KI. This can be attributed to the decrease in the structure breaking ability of the solvent by the anion (since the cation, being the same) with increasing the anion size (Domench and Miro, 1988). It is found from Table (1), that the values of the anion association (K_A) for the three salts are increase with increasing temperature and in the order KCl > KBr > KI. The same order has been obtained by Yokoyama and Kon (1991) and Kubota et al. (1988).

The plot of $\ln K_A$ against 1/T (Arrhenius equation $\ln K_A = -\ \Delta H° / RT + C$) is given in Figure (4), for the three salt, which are linear. Thermodynamic parameters $\Delta G°$, $\Delta H°$ are determined from the values of K_A ($\Delta G° = -\ RT\ln K_A$) and temperature (Vant Hoff), and $\Delta S°$ is calculated from these two parameters ($\Delta G° = \Delta H° - T\Delta S°$) and are given in Table (2). The values of $\Delta H°$ are positive and in agreement with the theoretical $\Delta H°$ values (Doe et al., 1990). This agreement represents how much the ion solvation is weakened by ion association. The positive value has been considered (Kubota et al., 1988), as due to the decreased orientation of solvent molecules when the ion-pair form, i.e. is explained by fact that a solvation of M^{+1} is weaken by the ion pairing of$M^{+1}X^{-1}$(contact ion-pair).

The values of ΔS^o are positive which indicates the decrease of orientation of solvent molecules at the formation of the ion-pairs or in other words that the solvation of cations decrease when M^+X^- formed.

The overall change of distance parameter (R) Table (1), is decreased with increasing in temperature (although some increases were observed at intermediate temperatures) may be due to the decreasing ion-solvent interactions at higher temperatures (Kubota et al., 1988). Also from the low values of σ_s (Λ), it could be concluded that the LW equation for 1:1 electrolytes at different temperatures is applicable.

Table 1: The conductance parameters (Λ_o, K_A and R) with the Walden product for KCl, KBr and KI in methanol at different temperatures.

Salt	Λ_o (Ω^{-1} equiv.$^{-1}$cm^2)	K_A (dm^3 mol.$^{-1}$)	R A°	σ_s (Λ)	($\Lambda_\circ \eta$) x 10^2
278°K					
KCl	78.00	14.34	6.1	0.079	0.5664
KBr	81.26	12.26	6.4	0.059	0.5900
KI	85.53	10.65	5.0	0.063	0.6210
288°K					
KCl	90.25	23.35	4.0	0.079	0.5635
KBr	96.29	18.94	6.2	0.068	0.6012
KI	97.33	14.86	4.9	0.055	0.6077
298°K					
KCl	104.97	26.01	4.2	0.061	0.5691
KBr	109.12	23.15	5.9	0.071	0.5916
KI	115.32	17.51	4.9	0.062	0.6250
308°K					
KCl	116.74	37.17	3.9	0.067	0.5539
KBr	125.14	26.95	5.2	0.051	0.5934
KI	125.91	20.39	4.7	0.065	0.5971
318°K					
KCl	134.93	45.99	4.0	0.065	0.5630
KBr	141.52	33.19	5.0	0.049	0.5907
KI	146.47	27.59	4.8	0.053	0.6114

Table 2: Thermodynamic parameters of ion association constant of KCl, KBr and KI electrolytes in methanol at different temperatures

Salt	**Temperature °K**	**$-\Delta G°$ KJ mol^{-1}.**	**$\Delta H°$ KJ mol^{-1}.**	**$\Delta S°$ JK^{-1} mol^{-1}.**
KCl	278	6.16	18.49	88.62
	288	7.07		88.70
	298	8.28		89.78
	308	9.26		90.05
	318	10.13		89.95
KBr	278	5.79	17.35	83.19
	288	7.05		84.69
	298	7.79		84.32
	308	8.44		83.69
	318	9.64		81.06
KI	278	5.47	15.57	75.64
	288	6.23		75.65
	298	7.09		75.99
	308	7.96		76.36
	318	8.77		76.50

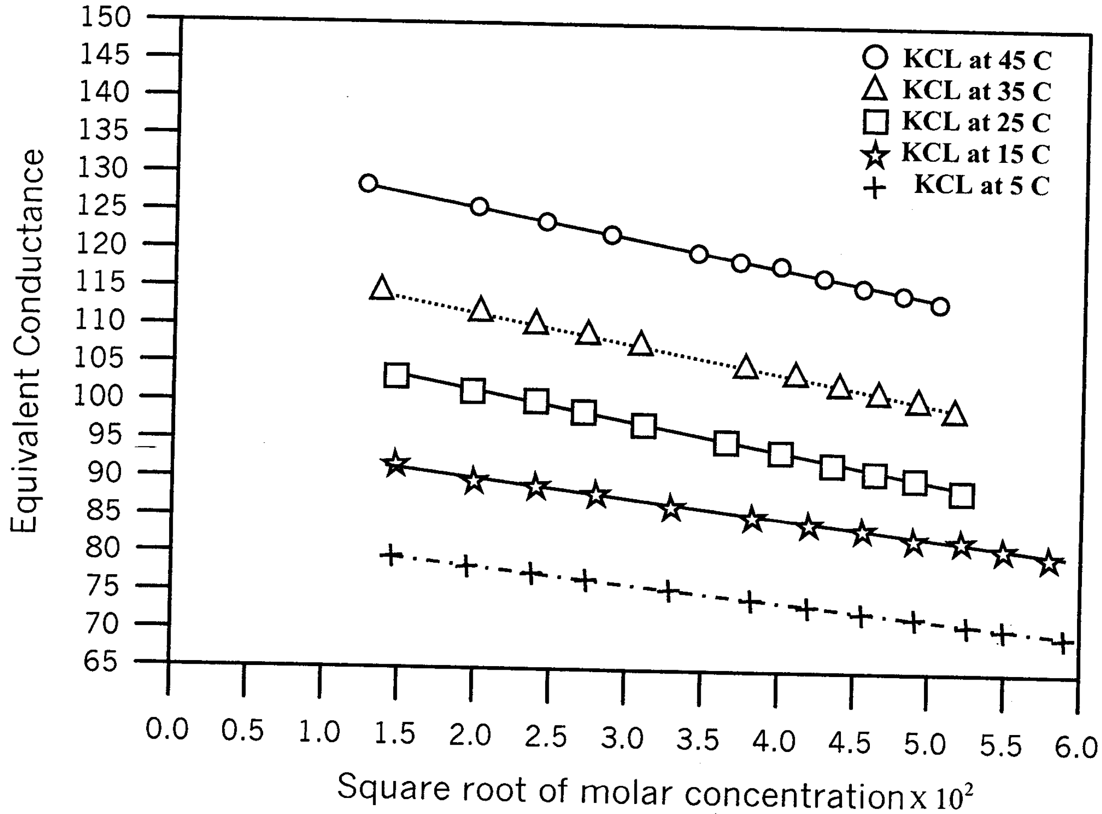

Fig:1: e **1** the plot of equivalent conductance against the square root of molar concentration for KCL at different temperatures

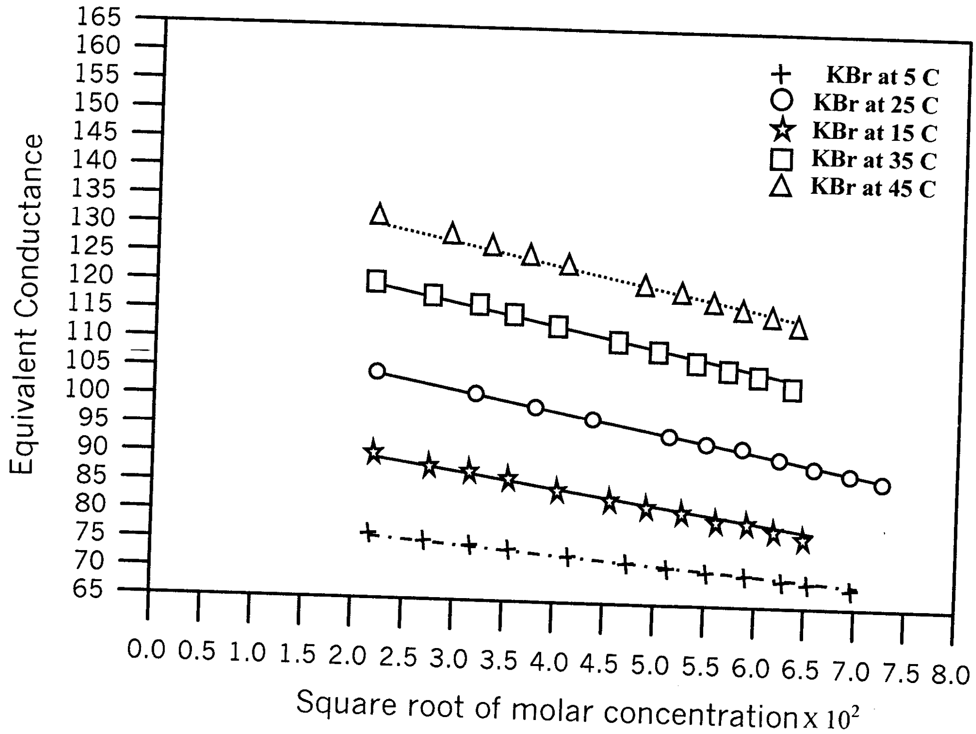

Fig:2: **2** the plot of equivalent conductance against the molar concentration for KBr in methanol at different temperatures

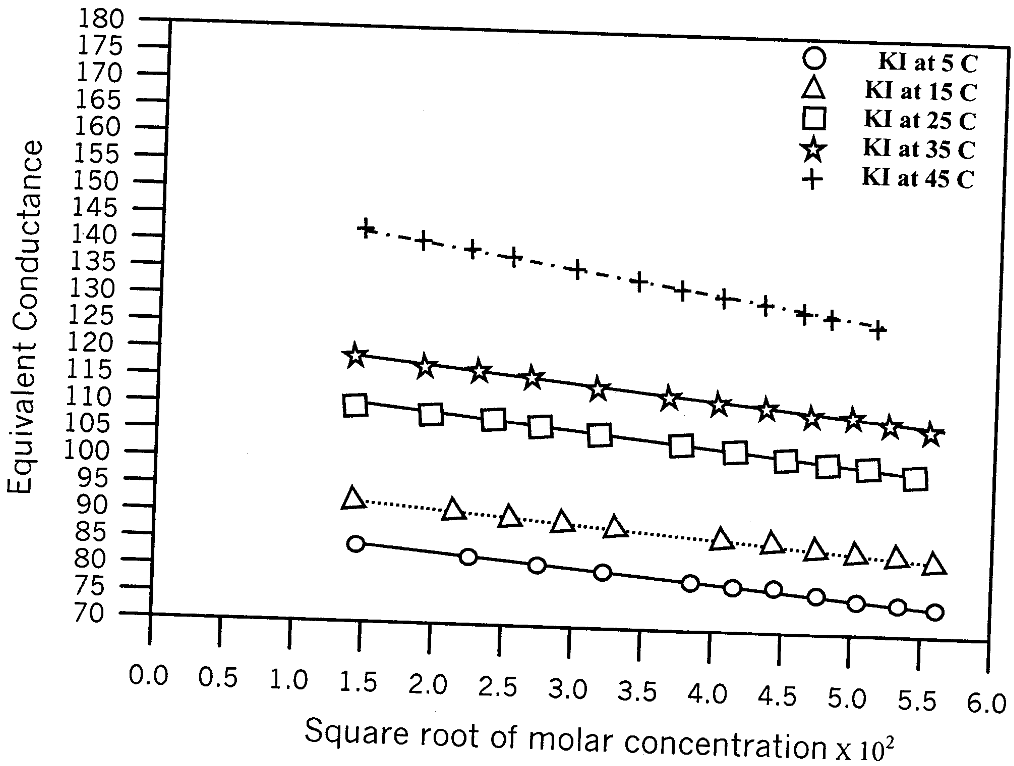

Fig:3: ıre 3 the plot of equivalent conductance against the square root of molar concentration for KCL at different temperatures

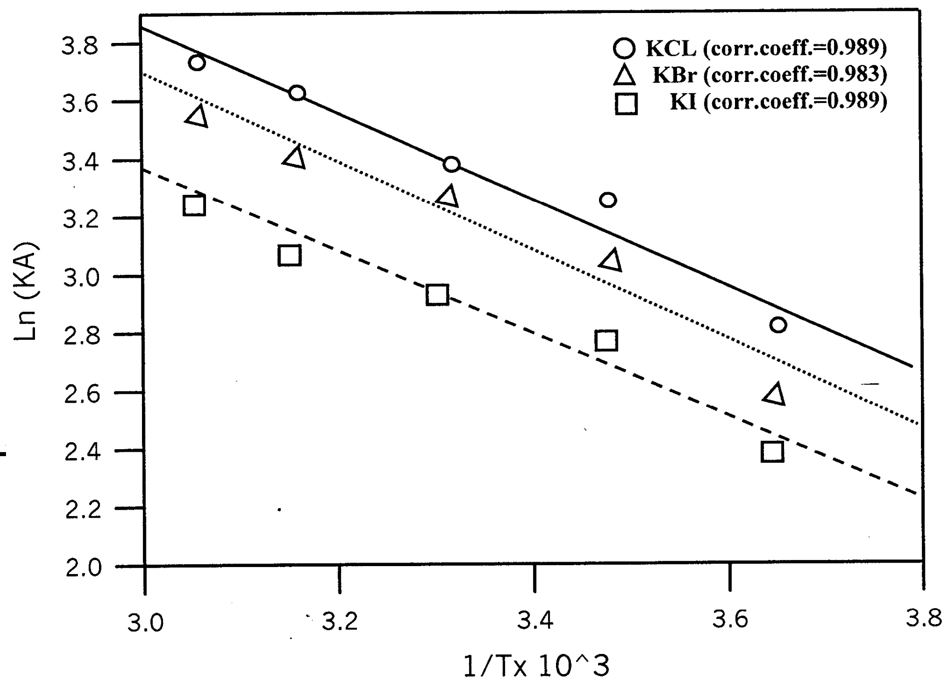

Fig:4: ıre 4 The plot of Ln(K_A) against the KCL, KBr and KI electrolytes in methanol.

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