THERMODYNAMIC STUDIES OF POTASSIUM BROMIDE IN 10% GLYCEROL-WATER MIXTURE USING CONDUCTOMETRIC TECHNIQUE

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The conductance of potassium bromide at $(25\text{-}45)^{O}C$ in 10 % glycerol-water mixture in a concentration range $(10^{-5}\text{-}10^{-3})$ M has been measured. The association constant, K_A, values have been determined, where the conductometric data were treated by the Fuoss and Edelson method. The K_A values were decreased as the temperature increased where the thermal motion, probably destroys the solvent structure and hence the mobility of the ions should increase. The activation energy derived in this work is a little lower than the value obtained in aqueous media. The thermodynamic parameters $\triangle G^O$ $\triangle H^O$ and $\triangle S^O$ were also calculated. It is obvious that the entire process of the ionic association in this system is exothermic. The Walden product, $\Lambda_o \eta$, decreases with an increase in temperature at $25\text{-}45^O$. The results are explained in the light of solute-solvent interaction.

Key words: Thermodynamics, Ionic-association, Conductance.

INTRODUCTION

The association of ions in solvents of low dielectric constants [1,2] and in water-rich mixtures of high dielectric constants [3] to form ion-pairs is considered at present as an accepted fact. In solvents of higher dielectric constant, and especially in water, association is slight. The first estimate for 1 : 1 salts in water was made by Davies [4]. Most previous work [5,6,7] on the association of 1 : 1 electrolytes by conductometric methods was carried out.

This paper deals with the conductance measurements of potassium bromide, KBr, in glycerol-water mixture which is characterized by viscosity higher, and a dielectric constant which is lower, than that of water. Only few scattered studies has so far been made on such systems despite numerous investigation in aqueous and non-aqueous media [8-12].

EXPERIMENTAL

(i) *Chemicals* potassium bromide, which was used in this study, was of A.R. grade. The individual stock solution was standardize by ion-exchange procedure. Also, glycerol was A.R. grade, and deionized distilled water was used for different dilutions. All other chemicals were special-grade materials (Merck).

(ii) *Physical properties of glycerol-water mixture:*

The viscosities and dielectric constants of 10 % glycerol-water mixture at 25, 35 and 45° were available from the handbook [13], the conductivity of 10 % glycerol-water mixture were 1.035×10^{-4}, 1.215×10^{-4} and 1.38×10^{-4} $mho.Cm^{-1}$, at 25, 35 and 45°, respectively.

The physical properties of 10 % glycerol-water mixture are summarized in Table 1.

(iii) *Electric conductance.* The measurements were carried out with a conductivity meter, model LBR, at a frequency of 50 C/S, corresponding to mains frequency and at 3 KC/S ± .3 % since shaped distortion factor < than 5 %. The resistance range is 0.1 ohm to 10 megohms in 7 ranges (when converting mho into ohms up to 1000 megohms). The cell model used in these measurements is LTA 100, where the cell constant value equals 1.00. Temperature was maintained constant by circulating through the cell compartement water at fixed temperature from a water bath controlled to ± 0.05^O. The concentrations of KBr, C, measured in the solutions were in the range of 1×10^{-5} M to 1×10^{-3} M.

Data treatment and conductometry results

The conductometric data were treated by the Fuoss

Table 1. Viscosities and dielectric constants of 10 % glycerol-water mixture at $298\text{-}318^O K$

	$298\,^O K$	$308\,^O K$	$318\,^O K$
Viscosity (p)	1.153	0.911	0.736
Dielectric constant	75.500	72.500	69.500

and Edelson method [14]. In our solutions, the following ionic equilibria are considered

$$K^+ + Br^- \rightleftharpoons KBr \quad (K_A) \qquad \ldots (1)$$

and the following proposed equation [15,16]

$$\Lambda F = \Lambda_o - X K_A / \Lambda_o \qquad \ldots (2)$$

where

$$X = CY_{L+} \Lambda F (\quad F - \Lambda_o/2)$$

$$F = [(1- \delta \sqrt{c})^{-1} + (\quad \Lambda_o - \lambda_o)/2]/[1 + (\Lambda_o - \lambda_o)/ 2 \Lambda_o]$$

in which Λ and Λ_o are the equivalent and the limiting equivalent conductances, respectively, λ_o is the limiting equivalent conductance of Br^-, δ is Onsager's slope, divided by Λ_o, C is the molar concentration of the Br^-, and F is the Fuoss and Edelson function. The ion activity coefficient of KBr, Y_1, Y_{1+}, was estimated by the debye-Huckel equation :

$$\text{Log } Y \pm = -0.509 \quad \sqrt{C} \qquad \ldots (3)$$

The value of λ_o is 78.17 Ω^{-1} Cm^2 mol^{-1} in water at 25°. However, we have no available data about the λ's for 10 % glycerol-water mixture, so we have calculated them on the basis of the value of 78.17. To begin with, the value of $\Lambda_{o)}$ at a given temperature is calculated with an arbitrary estimate of λ_o according to equation (2), which is solved for the two unknown parameters K_A and Λ_o by an iterative procedure. In this way we have determined the Λ_o of KBr at proper temperature. Then, the second estimate of λ_o is calculated by multiplying the ratio of the value $\Lambda_{o\ o}$ at the temperature to that at 25° by 78.17. The above procedure is then iterated until λ_o attains a constant value. In this work two iterations are needed to have a λ_o constant. It is not then necessary that λ_o be determined very accurately, partly because the K_A,S that we can evalute, involves relatively large errors and partly because λ_o does control the value of K_A and Λ_o strongly. Fig. 1 shows the plots according to equation (2) for KBr system at 25, 32 and 45°. The results from such plots are summarized in Table 2. The value of λ_o are also given in Table 2.

It is clearly desirable to obtain the standard enthalpy changes, ΔH^O, by studying the association constant overall

range of temperature, by means of VAnt Hoff's isochore.

$$\frac{d \log K}{d T} = \frac{\Delta H^O}{RT^2}$$

By plotting log K against 1/T, ΔH^O can be calculated from slope of straight line which equals $-H^O/R$. Standard free energy change, ΔG^O, can be calculated by $\Delta G^O = -RT \ln K$. Also, standard entropy change, ΔS^O, can be evaluated.

The representative plots of log K_A against T^{-1} are shown in Fig. 2. The values of ΔH^O, ΔS^O, and ΔGo are summarized in Table 3.

Since the conductance of an ion depends on its rate of movement, it seems reasonable to treat conductance in a manner analogous to that employed for other processes taking place at a definite rate which increases with temperature. On this basis, it would be possible to write

$$\Lambda_o = A e^- E/RT$$

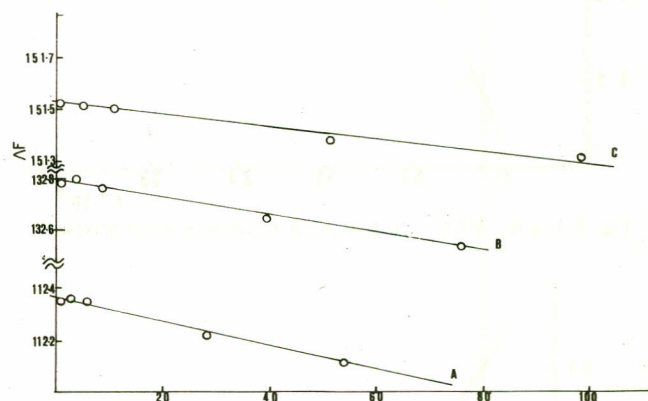where E is the activation energy of the process which determines the rate of movement of the ions, by plotting

Fig. 1. F VS X for KBr in 10 % Glycerol-water mixture (A) at 25^OC (B) at 35^OC and (C) at 45^OC.

Table 2. Limiting Equivalent Conductances (Ω^{-1} Cm^2 mol^{-1}) of KBr and Br^- in 10 % Glycerol-water mixture at (298 -318)^{O}K and association constants K_A

T. (^{O}K)	Λ_o mho.cm^2	λ_o	K_A (M^{-1})
298	112.37	78.22	5.19
308	132.80	92.37	4.64
318	151.54	105.46	3.31

of $\ln \Lambda_o$ against $1/T$, the value of E could be estimated from the slope of the straight line as shown in Figure 3.

DISCUSSION

As shown in Table 2, the Λ_o values increase as the temperature increases, and the values are in a reasonable range expected from some literature sources [10]. However, it seems that the values of Λ_o for potassium bromide
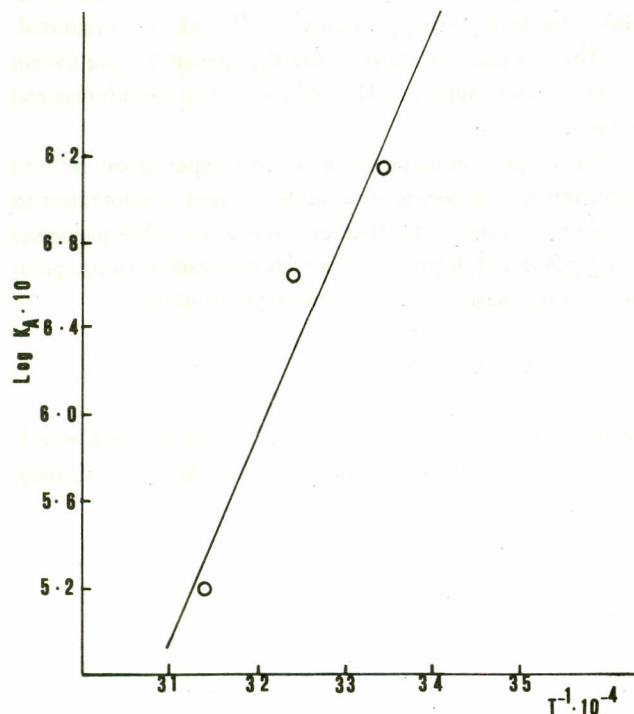
in this medium are lower than those in pure water for the same salt. However, there is a common characteristic in Walden products, $\Lambda_o \eta$: the $\Lambda_o \eta$ values decrease with an increase in temperature from 25-45° as shown in Table 4.

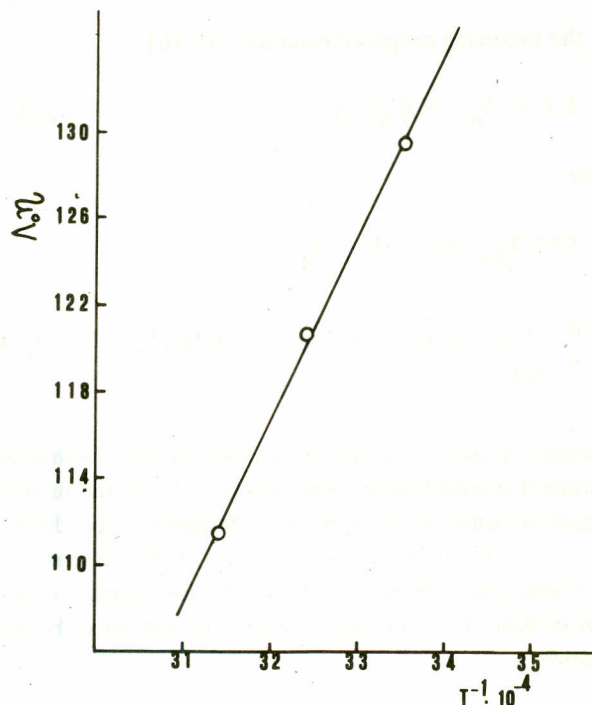Fig. 2. Log K_A VS T^{-1} for KBr in 10 % Glycerol-water mixture.

Fig. 3. Ln Λ_o VS T^{-1} for KBr in 10 % Glycerol-water mixture.

Fig. 4. $\Lambda_o \eta$ VS $1/T$ for KBr in 10 % Glycerol-water mixture at (25-45)°C.

Table 3. Thermodynamic parameters of KBr in 10% G/H_2O at $(298 - 318)°K$

T °K	K LM^{-1}	ΔH^o K.Cal/mol	ΔG^o K.Cal/mol	ΔS^o K.Cal/mol°.K
298	5.19	− 1.8905	− 0.9765	− 0.003067
308	4.64	− 1.8905	− 0.9406	− 0.003084
318	3.31	− 1.905	− 0.7574	− 0.003563

Table 4. Walden's products for KBr in 10 % G/H_2O Mix at 25°C, 35°C and 45°C

T °K	η Poise	Λ_o mho.Cm^2	$\Lambda_o \eta$ mho.Cm^2 Poise	T^{-1} . 10^4 °K^{-1}
298	1.1530	112.37	129.56	33.55
308	0.9110	132.80	120.98	32.46
318	0.7360	151.54	111.53	31.44

The extent of decrease in $\Lambda_o \eta$ is very small. The decrease in $\Lambda_o \eta$ with temperature, which are often found in the data for water solutions [17], can probably be interpreted as a thermal expansion of the solvent sheath (which envelopes an ion and moves with it by ion-solvent interactions), that is, the expansion of a solvent ion, because of the activation of solvent molecules forming the sheath.

In such a medium, glycerol-water mixture, the intramolecular hydrogen bonding must be retarding the mobility of the ions and hence resulting in a decrease of the equivalent conductance from that in pure water. Such hydrogen bonding is expected to be greater in glycerol-water mixture as compared with other alcohol-water mixtures, such a medium probably facilitates ion-association [18]. This is confirmed by the comparatively large values of the association constant (K_A) as indicated in Table 2. With increasing temperature of the glycerol solvent structure and hence the mobility of the ions should increase. This may account for the fact that the values of K_A decreased as the temperature increased.

The activation energy, E, derived in this work, at 2.79 K Cal/mol is less than the values obtained in aqueous media (3.8 K Cal/mol). It is well accepted that the activation energy for electrolytic conductance is almost identical with that for the viscous flow of the solvent. The constancy of E means that the positive temperature coefficient of ion conductance is roughly equal to the negative temperature coefficient of viscosity [19].

It is well accepted that the extent of ion association in KBr solutions depends on the nature of the ion-solvent interaction which take place in the solution rather than being dependent on the dielectric constant of the medium [20,21].

It also appears that the entire process of the ionic association in this system is exothermic : according to the results of thermodynamic functions in Table 3, we find that the values of ΔH^O and ΔS^O of the ion-pair formation have negative values.

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