Effect of solvent on the conductance of L-ornithine monohydrochloride in aqueous N,N-Dimethyl formamide and aqueous dimethyl sulphoxide

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ABSTRACT

The conductances of L-ornithine monohydrochloride has been studied in water-dimethyl formamide and water-dimethyl sulphoxide mixtures of different compositions in the temperature range 300-318K. The molar conductance data collected at different concentration of the eletrolyte is analyzed using Shedlovsky and Kraus-Bray models. The limiting molar conductance is found to be dependent of the temperature and dielectric constant of the medium. The solvation number computed in each solvent suggest that the solvent solute interaction are independent of the dielectric constant of the medium.

Key words: Ion-pair association constant, ion-pair dissociation constant, solvation number, L-orinthine monohydrochloride.

INTRODUCTION

Conductance studies in single and mixed solvent systems have continued to be of great interest to chemists. The literature is replace with conductance date of many electrolytes in aqueous, organic and in binary organic solvent systems. The conductance behaviour of many ions in mixed solvent systems is reported to be influenced by a number of factors including ion solvent interactions, solvent-solvent interactions, densities and viscosities of the mixed solvent system and the extent of solvation of the ionic species.

Literature survey indicates[1-11] that the conductance data and the viscosity data of different electrolytes is useful in analyzing the ion solvent interactions and solvation behaviour of the ions, similar studies on amino acieds is lacking. As a part of the braod program on the conductance and solvation studies of different amino acid hydrochlorides in aqueous organic mixtures. The authors studied the conductance behaviour of L-ornithine monohydrochloride in aqueous dimethyl sulphoxide and aqueous N,N-dimethyl formamide at different at different temperatures. In the present communication the results of the studies are presented.

EXPERIMENTAL

Deionized water was distilled and used. Dimethyl sulphoxide (DMSO) (Merck) N,N-dimethyl formamide (DMF) (Sd-fine) were used as such, L-ornithine mono hydro chloride (Merck) sample is also used without further purification. A stock solution of this reagent was prepared by dissolving known weight of the sample in water.

A condutivity bridge (ELICO model 180) equipped with a glass conductivity cell of cell constant $0.985cm^{-1}$ was used to measure the conductance of the solution. Temperature of the reaction mixture was maintained constant using a thermostat (INSREF) with an accuracy of $\pm 0.5°C$. A stock solution of 0.05 M L-orinthine monohydrochloride was prepared in water/aqueous organic mixture of different composition (v/v) in the

range of 0 to 60% organic component. The solute was found to be insoluble above this composition. It was diluted to different concentrations using different volumes of solvent/solvent miture and the conductance values were measured in the temperature range 300-318K. The solvent mixtures used in these studies have conductance values in the range 20-40µmho. The conductance of the solvent was subtracted to get the conductance of the solute at each concentration. The molar conductance (Λ_0) values determined are analyzed using Kraus-bray equation[12] (eqn1) and Shedlovsky equation[12] (eqn 2).

Table 1: Limiting molar conductance values in mho cm² mol⁻¹ of
L-Ornithine monohyderochloride in water-DMF and water-DMSO mixture

T(K)	%DMF		20%DMF		40%DMF		60%DMF	
	1	2	1	2	1	2	1	2
300	159.94	159.92	71.91	71.92	45.63	45.20	33.62	33.61
308	101.15	101.15	84.33	83.52	56.16	51.14	40.21	41.62
313	110.92	111.61	92.52	92.52	58.91	58.92	45.12	45.13
318	140.50	140.14	94.72	94.73	66.41	66.42	46.51	46.53
T(K)	%DMF		20%DMF		40%DMF		60%DMF	
	1	2	1	2	1	2	1	2
300	159.94	159.92	66.52	66.52	44.21	44.22	43.93	46.81
308	101.15	101.15	81.31	81.31	48.62	48.62	41.93	41.91
313	110.92	111.61	84.92	84.91	53.71	53.72	43.71	43.73
318	140.50	140.14	149.50	149.51	56.72	56.71	45.53	43.90

(1) Kraus-Bray model   (2) Shedlovsky model

Table 2: K_A and K_C values of L-Ornithine monohyderochloride
in water-DMF and water-DMSO mixture

T(K)	%DMF		20%DMF		40%DMF		60%DMF	
	K_A	K_C	K_A	K_C	K_A	K_C	K_A	K_C
300	10.01	0.09	3.06	0.32	2.32	0.42	12.08	0.08
308	2.50	0.39	4.34	0.23	2.17	0.46	11.60	0.08
313	2.77	0.33	5.57	0.17	2.68	0.37	6.91	0.14
318	3.71	0.27	2.69	0.39	3.14	0.31	6.39	0.15
T(K)	%DMF		20%DMF		40%DMF		60%DMF	
	K_A	K_C	K_A	K_C	K_A	K_C	K_A	K_C
300	10.01	0.09	1.96	0.50	6.84	0.14	52.24	0.02
308	2.50	0.43	3.60	0.27	6.80	0.14	20.93	0.07
313	2.77	0.33	1.14	0.33	3.58	0.27	18.54	0.05
318	3.71	0.28	21.31	0.05	1.75	0.57	10.73	0.09

Table 3: Computed values of ΔG (kJmol⁻¹) for ion pair formation of L-Ornithine monohyderochloride in water-DMF and water-DMSO mixture

T(K)	0% DMF	20% DMF	40% DMF	60% DMF
300	-5.74	-2.79	-2.10	-6.36
308	-2.34	-3.75	-1.98	-6.25
313	-2.65	-4.47	-2.57	-5.03
318	-3.40	-2.62	-3.03	-4.87
T(K)	0% DMF	20% DMF	40% DMF	60% DMF
300	-5.74	-1.68	-4.80	-9.86
308	-2.34	-3.24	-4.81	-7.78
313	-2.65	-3.41	-3.33	-7.62
318	-3.40	-8.04	-1.48	-6.27

Table 4: Energy of activation Ea (k.Jmol⁻¹) of L-Ornithine monohyderochloride in water-DMF and water-DMSO mixture

0%DMF	20%DMF	40%DMF	60%DMF
26.40	10.31	21.52	8.88
0%DMF	20%DMF	40%DMF	60%DMF
26.40	10.32	12.33	10.61

Table 5: Solvation number at (300K in water-DMF and water-DMSO mixtures

0%DMF	20%DMF	40%DMF	60%DMF
0.28	0.57	0.52	0.42
0%DMF	20%DMF	40%DMF	60%DMF
0.43	0.70	0.68	0.66

$$\frac{1}{\Lambda} = \frac{\Lambda C}{K_C \Lambda_0^2} + \frac{1}{\Lambda_0} \qquad ...(1)$$

$$\frac{1}{S\Lambda} = \frac{Sf_\pm^2 K_A C\Lambda}{\Lambda_0^2} + \frac{1}{\Lambda_0} \qquad ...(2)$$

Λ is molar conductance at concentration C, Λ_0 is the association constant of the ion pair, K_C is the dissociation constant, f±is the mean ionic activity coefficient, S is a factor given by

$$S = \left[\frac{Z}{2} + \sqrt{1 + \left(\frac{Z}{2}\right)^2}\right]^2 \qquad ...(3)$$

where

$$Z = \left[\frac{\alpha\Lambda_0 + \beta}{\Lambda_0^{3/2}}\right](C_L)^{\frac{1}{2}} \qquad ...(4)$$

and $\beta = 8250 \, [t/\eta] \, (\in T)^{1/2}$, $\in$ is the dielectric constant of the constant of the medium, η is the viscosity and $\alpha=0.8204 \times 10^6 \, (\in T)^{3/2}$ is calculated using $\Lambda 0$

obtained from the Onsager model using the plot of Λ against $\sqrt{C}$. The least square analysis of the data ($\Lambda\&C$) using the above two equations (1,2) is satisfactory with linear correlation coefficient in the range 0.93-0.96

RESULTS AND DISCUSSIONS

The limiting conductance value Λ_0 thus obtained using the two equation 1 and 2 are presented in Table 1. These values increase with increase in the temperature as expected, due to increase in the mobilities of the ions. The Λ_0 values also depend on the compositions of the binary solvent mixture. Addition of N,N-dimethyl formamide to water decrease the Λ_0 values from 160 (0% dimethyl formamide) to 34 mho cm² mol⁻¹ at 300K. Same trend in the conductance values is observed at each temperature. In aqueous dimethyl sulphoxide also, in general, similar behaviour is observed. This is attributed to the decrease in the dielectric constant of the medium when the composition of organic component is increased in the solvent mixture. From the slopes of the liner least square analysis using Kraus-Bray and Shedlovsky models, the dissociation constant Kc

and association constant K_A of the ion pair have been evaluated and presented in Table 2. The values indicate that they do not vary regularly with temperature. The same trend is observed at all compositions of solvent mixtures of dimethyl formamide and dimethyl sulphoxide. Hence it is difficult to predict whether the process is endothermic or exothermic in nature. At any given temperature the association constant K_A is observed in 40% (v/v) aquo-organic mixture in both the systems. This trend is similar at all the temperatures studied. The variation in K_A with change in the composition of the solvent indicates the influence of dielectric constant of the medium on the stability of the ion pair. Thus it can be concluded that K_A is maximum at lowest possible dielectric constant of the medium. The free energy change accompanied by the ion pair formation (ΔG) is computed using the relation, $\Delta G = RT \ln K_A$ and tabulate in Table 3. These values are all negative and vary between -1.68 and -9.68 Jmol^{-1} in both the systems, at all the temperatures. The energies of activation of the conducting process are also obtained from the Arrhenius relationship, In $\Lambda_0 = A - \frac{E_a}{RT}$ where A is a constant tabulated in Table 4. These values are highest in water than in the binary solvent mixtures.

In solution the ion pair is solvate and it is stabilized due to solvation. The solvation number (S_n) which is the number of solvent molecules in the solvent around the species is calculated from the species is calculated from the effect of dielectric constant $\in$ on Λ_0 based on the equation.

$$\log \Lambda_0 = \log \Lambda_0^1 \frac{Z_A Z_B e^2}{\in d_{AB} K_B T} \qquad ...(5)$$

$Z_A e$, $Z_B e$ are the ionic charges k_B is Boltzmann constant T is temperature and d_{AB} is the distance between the centers of the two ions. The plot of log Λ_0 against $1/\in$ is linear and from the slope of this plot, d_{AB} is computed. S_n is computed using the relation,

$$S_n \frac{D_{AB} - r_i}{r_{solvent}} \qquad ...(6)$$

where r_i is the Strokes radius of the ion calculated using the equation[13].

$$r_i \frac{0.820 \, |Z|}{\Lambda_0 \eta_0} + 0.0103 \in + r_y \qquad ...(7)$$

Where $r_y = 0.85 A°$ for dipolar unassociated solvents and $1.13 A°$ for protic and associated solvents.

The solvation number data of the ion thus determined at 27°C in all the binary solvent systems studied is shown in Table 5. These are all fractional. The suggest that the extent of interaction between the solvent and the ionic species are constant and do not depend on the composition of the aquo organic mixture.

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