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CONDUCTANCE AND SOLVATION BEHAVIOUR OF L-GLUTAMICACID MONOHYDROCHLORIDE IN AQUEOUS N,N-DIMETHYL FORMAMIDE AND AQUEOUS DIMETHYL SULPHOXIDE

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ABSTRACT

The conductance of L-Glutamic acid 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 concentrations of the electrolyte 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 interactions are independent of the dielectric constant of the medium.

Keywords: *Ion-pair association constant, ion-pair dissociation constant, solvation number, L-Glutamic acid monohydrochloride.*

INTRODUCTION

Conductance behaviour of many electrolytes in mixed solvent systems is reported to be influenced by number of factors like density, viscosity, dielectric constant of the medium, Ion - solvent interactions and solvent - solvent interactions. ion solvent interactions stabilize the ion by solvating it. solvent-solvent interactions occur through hydrogen bond fomation. The conductance and viscosity measurements in pure organic solvents& aquo-organic mixutres provide valuable information regarding the ion-ion and ion - solvent interactions[1-10]. Izonfuo and obunwo[11] and Roy etal[12] studied the conductance of alkalimetals in different proportions of binary solvent mixtures. Rajmuhon etal [13-15] studided the thermodynamic parameters of different complexes. As part of the broad program of the conductance and solvation studies of differnt electrolytes in aqueous organic mixtures, we have taken up the study of conductance behaviour of different aminoacid hydrochlorides in aquo-organic solvent mixtures. The present work reports the comparative studies of conductance properties, thermodynamic behaviour of L-Glutamicacid monohydrochloride in water-N,N-dimethyl formamide (DMF) and water -dimethyl sulphoxide (DMSO) mixed solvents at different temperatures between 300-318K. The data were analyzed using shedlovsky and Kraus - Bray models.

EXPERIMENTAL

Deionized water was distilled and used. Dimethyl sulphoxide(DMSO) (Merck) N,N-dimethyl formamide (DMF) (Sd-fine) were used as such. L-Glutamicacid monohydrochloride (HIMEDIA)sample was also used without further purification. A stock solution of this reagent was prepared by dissolving known weight of the sample in water. A conductivity bridge (ELICO model -180) equipped with a glass conductivity cell of cell constant 0.945 cm^{-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 $\pm 0.5^0\mathrm{C}$. A stock solution of 0.05M L-glutamicacid monohydrochloride was prepared in water/ aqueous organic mixture of different compositions (v/v) in the ragne 0 to 100% organic component. It was diluted to different concentrations using different volumes of solvent/ solvent mixture and conductance values were measured in the temperature range 300-318k. The solvent / solvent mixtures used in these studies have conductance values in the range(20-40µ mhos). 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[16] (eqn1) and shedlovsky equation[16] (eqn 2)

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

$$\frac{1}{S\Lambda} = \frac{S f_{\pm}^2 K_A C \Lambda}{\Lambda_0^2} + \frac{1}{\Lambda_0} \text{ --------------- (2)}$$

Λ is molar conductance at concentration C,

Λ_0 is the limiting conductance, K_A is the association constant of the ion pair, K_C is the dissociation constant, $f \pm$ is the mean ionic activity, S is a factor given by

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

$$\text{Where } \quad Z = \left[\frac{\alpha \Lambda_0 + \beta}{\Lambda_0^{3/2}} \right] (C\Lambda)^{1/2} \text{ ------------------- (4)}$$

$\beta = 82.50\left(\frac{1}{\eta}\right)(\in T)^{1/2}$ $\in$ is the dielectric constant of the medium, η is the viscosity and $\alpha = 8.204 x 10^5 (\in T)^{3/2}$. S is Calculated using (Λ_0) obtained from the Onsagar model using the plot of Λ against $\sqrt{C}$. The least square analysis of the data (Λ) using the above two equations (1,2) is satisfactory with linear correlation coefficient in the range 0.93 -0.96

RESULTS AND DISCUSSION

The limiting conductance values Λ_0 thus obtained using the above two models 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 composition of the binary solvent mixture. Addition of N,N -dimethyl formamide to water decreases the Λ_0 values from 175.23 (0% DMSO) to 21.19 mhocm^{2}mol^{-1} in (80% DMSO) and then increase in 100% DMSO at 300K. Similar trend in the conductance values are observed at each temperature. In aqueous DMF also 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 linear least square analysis using Kraus - Bray and shedlovsky models, the dissociation constant K_C and association constant K_A of the ion pair have been evaluated and presented in Table -2. These values indicate that they do not vary regularly with temperature. The same trend is observed at all compositions of solvent mixtures of aqueous DMSO and aqueous DMF. Hence it is difficult to predict whether the process is endothermic or exothermic in nature. At any given temperature the association constant K_A values change randomly, with the composition of solvent mixture. However, maximum K_A is observed in 100% solvents 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 solvent - solvent interaction of the medium on the stability of the ion pair. Thus it can be concluded that K_A is maximum when there are no solvent-solvent interaction of the medium i.e. when a single solvent is present. The free energy change accompanied by the ion pair formation (ΔG) is computed using the relation $\Delta G = -RT \ln K_A$ and tabulated in Table -3. These values are all negative and vary between -0.97 and -13.76 k.J. mol^{-1} in both the systems, at all the temperatures studied. The energy of activation of the conducting process is also obtained from the Arrhenius relationship, $\ln \Lambda_0 = A - \frac{Ea}{RT}$ where A is a constant , in each solvent mixture and tabulated in Table -4. These values appear to be highly dependent on solvent composition. In each system the activation energy is maximum at 20% aquo-organic mixture.

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

$$\log \Lambda_0 = \log \Lambda_0^1 - \frac{Z_A Z_B e^2}{\in d_{AB} k_B T} \text{ -------------------- (5)}$$

$Z_A e$, $Z_B e$ are the ionic charges, k_B is Boltzmann constant, T is the temperature and d_{AB} is the distance between the centre of the two ions. The plot of $\log \Lambda_0$ against $1/\in$ is linear and from the slope of this plot, d_{AB} is computed. Sn is computed using the relation,

$$S_n = \frac{d_{AB} - r_i}{r_{solvent}} \text{ ---------------- (6)}$$

Where r_i is the Stokes radius of the ion calculated using the equation[16]

$$r_i = \frac{0.820|z|}{\Lambda_0 \eta_0} + 0.0103 \in + r_y \text{ ----------------- (7)}$$

Where r_y=0.85A^0 for dipolar unassociated solvents and 1.13A^0 for protic and associated solvents.

The solvation number data of the ion thus determined at 27^{0}C in all the binary solvent systems studied is shown in Table -5. These are all fractional. This suggests 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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TABLE – 1:VALUES OF OBTAINED FROM KRAUS-BRAY AND SHEDLOVSKY EQUATIONS FOR L-GLUTAMICACID MONOHYDRO CHLORIDE IN VARIOUS COMPOSITIONS (V/V) OF WATER-ORGANIC SOLVENT MIXTURES AT DIFFERENT TEMPERATURES.

	300K	**308K**	**313 K**	**318K**
0% DMF				
1.	175.23	248.83	268.31	268.96
2.	175.23	248.83	268.31	268.96
20% DMF				
1.	113.88	136.03	152.84	175.65
2.	113.88	136.03	152.84	175.65
40% DMF				
1.	78.83	96.39	103.26	121.41
2.	88.06	96.39	103.26	121.41
60% DMF				
1.	47.01	50.80	56.24	56.88
2.	47.01	50.80	56.24	56.88
80% DMF				
1.	35.28	37.71	50.62	55.31
2.	35.28	37.71	50.62	55.31
100% DMF				
1.	41.86	48.94	50.98	53.39
2.	41.86	48.94	50.98	53.39
0% DMSO				
1.	175.23	248.83	268.31	268.96
2.	175.23	248.83	268.31	268.96
20% DMSO				
1.	108.14	201.96	224.28	240.90
2.	108.14	201.96	224.28	240.90
40% DMSO				
1.	70.11	74.12	101.38	111.37

2.	70.11	74.12	101.38	111.37
		60% DMSO		
1.	3074	38.51	43.24	46.70
2.	30.74	38.51	43.24	46.70
		80% DMSO		
1.	21.19	36.13	26.29	28.77
2.	21.19	36.13	26.29	28.77
		100% DMSO		
1.	34.20	41.53	43.17	45.43
2.	34.20	41.53	43.17	51.12
	1- Kraus Bray Model	2-Shedlovsky Model		

TABLE – 2: VALUES OF K_C AND K_A OBTAINED FROM KRAUS-BRAY AND SHEDLOVSKY EQUATIONS FOR L-GLUTAMIC ACID MONOHYDROCHLORIDE IN VARIOUS COMPOSITIONS (V/V) OF WATER- ORGANIC SOLVENT MIXTURES AT DIFFERENT TEMPERATURES.

	300K	**308K**	**313 K**	**318K**
		0% DMF		
K_C	0.03	0.04	0.14	0.17
K_A	32.72	26.46	6.85	5.94
		20% DMF		
K_C	0.16	0.13	0.11	0.08
K_A	6.24	7.35	9.20	13.00
		40% DMF		
K_C	0.08	0.13	0.13	0.08
K_A	11.89	7.70	7.31	12.92
		60% DMF		
K_C	0.10	0.16	0.15	0.70
K_A	10.20	6.09	6.53	1.44
		80% DMF		
K_C	0.15	0.11	0.05	0.04
K_A	6.77	9.09	18.75	25.03
		100% DMF		
K_C	0.008	0.0055	0.0052	0.0053
K_A	132.54	181.83	189.25	185.75
		0% DMSO		
K_C	0.03	0.04	0.14	0.17
K_A	32.72	26.46	6.85	5.94
		20% DMSO		

K_C	0.05	0.047	0.046	0.04
K_A	20.12	21.06	21.72	24.15
		40% DMSO		
K_C	0.24	0.37	0.11	0.09
K_A	4.15	5.92	9.17	11.22
		60% DMSO		
K_C	0.34	0.18	0.19	0.20
K_A	2.92	5.41	5.34	5.01
		80% DMSO		
K_C	0.12	0.022	0.15	0.20
K_A	8.79	45.53	6.75	4.95
		100% DMSO		
K_C	0.023	0.013	0.017	0.02
K_A	42.69	74.45	57.88	72.26

TABLE – 3:COMPUTED VALUES OF FOR ION PAIR FORMATION OF L-GLUTAMIC ACID MONOHYDROCHLORIDE IN VARIOUS COMPOSITIONS (V/V) OF WATER - ORGANIC SOLVENT MIXTURES AT DIFFERENT TEMPERATURES.

300K	308K	313 K	318K
	0% DMF		
-8.69	-8.36	-4.97	-4.68
	20% DMF		
-4.56	-5.10	-5.77	-6.82
	40% DMF		
-6.17	-5.22	-5.77	-6.75
	60% DMF		
-5.86	-4.62	-4.88	-0.97
	80% DMF		
-4.76	-5.70	-7.61	-8.51
	100% DMF		
-12.17	-13.32	-13.60	-13.76
	0% DMSO		
-8.69	-8.36	-4.97	-4.68
	20% DMSO		
-7.56	-7.79	-7.96	-8.39
	40% DMSO		
-3.55	-2.47	-5.75	-6.38

		60% DMSO	
-2.67	-4.32	-4.31	-4.25
		80% DMSO	
-5.42	-9.71	-4.91	-4.91
		100% DMSO	
-9.36	-11.01	-10.54	-11.24

TABLE – 4: **ENERGY OF ACTIVATION Ea(k.J. mol^{-1}) of L-GLUTAMIC ACID MONOHYDROCHLORIDE IN WATER- ORGANIC SOLVENT MIXTURES.**

0% DMF	20% DMF	40% DMF	60% DMF	80%DMF	100% DMF
19.43	18.88	9.46	16.28	21.27	10.67
0 % DMSO	20% DMSO	40% DMSO	60% DMSO	80%DMSO	100% DMSO
19.43	14.11	5.33	18.70	51.19	12.41

TABLE – 5: **SOLVATION NUMBER AT (300K) IN WATER - ORGANIC SOLVENT MIXTURES**

0% DMF	20% DMF	40% DMF	60% DMF	80%DMF	100% DMF
0.85	0.98	0.96	0.95	0.88	0.80
0% DMSO	20% DMSO	40% DMSO	60% DMSO	80%DMSO	100% DMSO
0.24	0.40	0.43	0.40	0.37	0.21

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