

# CONDUCTANCE AND SOLVATION BEHAVIOUR OF L-LYSINE MONOHYDROCHLORIDE IN AQUEOUS N,N-DIMETHYL FORMAMIDE AND AQUEOUS DIMETHYL SULPHOXIDE.

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## ABSTRACT

*The conductance of L-Lysine 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 on 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-Lysine monohydrochloride.*

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## INTRODUCTION

Studies on electrolyte conductance of an electrolyte and the effect of ion – solvation on it in aqueous and partially aqueous media have received considerable attention in recent years as they are important both from fundamental and technological points of view<sup>1-5</sup>. The use of non aqueous and partially aqueous solvents has been widely accepted, in place of water due to their wide applicability<sup>6-8</sup> in various fields. It has become a practice to use solvent mixtures, water being one among the solvent mixtures<sup>9-11</sup>. The solvent mixtures not only give an idea about ion- solvent and solvent – solvent – interactions but also the preferential solvation of ion.

Literature survey indicates<sup>12-22</sup> 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 aminoacids are limited. As a part of the broad program on the conductance and solvation studies of different amino acid hydrochlorides in aqueous organic mixtures, the authors studied the conductance behaviour of L-Lysine monohydrochloride in aqueous DMSO and aqueous DMF at different temperatures. In the present communication the results of these studies are presented.

## EXPERIMENTAL

Deionized water was distilled and used. Dimethyl sulphoxide (Merck), N,N-dimethyl formamide (Sd-fine) were used as such. L-Lysine monohydrochloride (LOBA CHEMIE) was used without further purification. A conductivity bridge (ELICO model -180) equipped with a glass conductivity cell of cell constant  $0.9445 \text{ cm}^{-1}$  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  $\pm 0.5^\circ\text{C}$ . A stock solution of 0.1M L-Lysine monohydrochloride

was prepared in water/ aqueous organic mixture of different compositions (v/v) in the range 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 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 (16.0 to 90.0  $\square$  mho). The conductance of the solvent each composition and at each temperature was subtracted to get the conductance of the solute at each concentration. The molar conductance ( $\Lambda$ ) values determined are at different concentrations analyzed using Kraus-Bray equation<sup>23</sup> (eqn1) and shedlovsky equation<sup>23</sup> (eqn 2)

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

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

$\Lambda_0$  is the limiting conductance,  $K_A$  is the association constant and,  $K_C$  is the dissociation constant of the ion pair,  $f_{\pm}$  is the mean ionic activity, coefficient S is a factor given by

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

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

$$\beta = 82.50 \left( \frac{1}{\eta} \right) (\epsilon T)^{1/2} \quad \epsilon \text{ is the dielectric constant of the medium, } \eta \text{ is the viscosity and}$$

$\alpha = 8.204 \times 10^5 (\epsilon T)^{3/2}$ . S is calculated using ( $\Lambda_0$ ) obtained from the Onsager model using the plot of  $\Lambda$  against  $\sqrt{C}$ . The least square analysis of the data ( $\Lambda$ ) using the above two equations (1,2) is satisfactory with linear correlation coefficient in the range 0.93 -0.96

## RESULTS AND DISCUSSION

The molar conductance ( $\Lambda$ ) was determined from the solvent corrected<sup>23</sup> specific conductance for L-Lysine monohydrochloride in water, DMF, DMSO and various compositions (v/v) of water – DMF as well as water – DMSO at 300,308,313 and 318K. The values were analysed by Kraus – Bray and shedlovsky models of conductivity to evaluate molar conductance at infinite dilution  $\Lambda_0$ . Thus obtained values are shown in Table-1.

As expected  $\Lambda_0$  value increased with increase in temperature in all the cases due to increase in thermal energy and mobility of ions. Limiting molar conductance of L-lysine monohydrochloride in water decreased from 74.87 to 23.88  $\text{mho cm}^2\text{mol}^{-1}$  on adding DMF to water at 300K. Same trend in the conductance values is observed at each temperature. In aqueous DMSO also, in general similar behavior is observed. On adding the co-solvent (DMF/ DMSO) to water, the dielectric constant decreases solvent –solvent interaction increases. Due to this conductance decreases.

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 the temperature. The same trend is observed at all compositions of solvent mixtures of aqueous DMF and aqueous DMSO. Hence it is difficult to predict whether the process is endothermic or exothermic in nature. At any given temperature the association  $K_A$  values change randomly with the composition of solvent mixture also.

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. The free energy change accompanied by the ion pair formation ( $\Delta G$ ) is computed using the relation  $\Delta G = -RT \ln K_A$  and tabulated in Table-3. These values are all negative and vary between -3.75 and -11.45 kJ. mol<sup>-1</sup> in both the systems, at all the temperatures studied. The differential free energies of ion pair formation calculated taking water as reference solvent addition are computed and presented in Table-3. Except in 60% aqueous DMSO. There are all negative systems that the ion-pair is more stabilized due to addition of co-solvent to water. The energies of activation of the conducting process obtained from the Arrhenius relationship,  $\ln \Lambda_0 = A - \frac{E_a}{RT}$  where A is a constant, are tabulated in Table -4. These values appear to be highly dependent on solvent composition. The activation energy is maximum in 40% (v/v) DMF system, whereas in case of DMSO-water system it is maximum in 20% (v/v).

In solution, the ion pair is solvated 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 effect of dielectric constant  $\epsilon$  on  $\Lambda_0$  based on the equation

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

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

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

Where  $r_i$  is the Stokes radius of the ion calculated using the equation<sup>24</sup>

$$r_i = \frac{0.820|z|}{\Lambda_0 \eta_0} + 0.0103 \epsilon + r_y \quad (7)$$

Where  $r_y = 0.85 \text{ \AA}$  for dipolar unassociated solvents and  $1.13 \text{ \AA}$  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. Solvation number at all composition in both solvents is nearly constant, however in DMF the solvation number is slightly higher than in DMSO. This suggests that ion solvent interactions are slightly more in DMF compared to DMSO.

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TABLE-1

Limiting molar conductance values in  $\text{mho cm}^2 \text{ mol}^{-1}$  of L-Lysine mono hydro chloride in water-DMF & Water- DMSO mixtures.

T(K)	0% DMF		20% DMF		40% DMF		60% DMF	
	1	2	1	2	1	2	1	2
300	74.87	76.21	56.00	56.20	36.19	36.23	23.88	23.76
308	76.56	79.39	61.53	65.74	40.84	40.84	26.02	26.02

313	96.67	97.52	67.37	67.37	46.99	46.92	32.38	32.38
318	108.52	107.29	71.78	68.27	64.15	64.13	33.06	33.06
<b>T(K)</b>	<b>0% DMSO</b>		<b>20% DMSO</b>		<b>40% DMSO</b>		<b>60% DMSO</b>	
	<b>1</b>	<b>2</b>	<b>1</b>	<b>2</b>	<b>1</b>	<b>2</b>	<b>1</b>	<b>2</b>
300	74.87	76.21	59.55	54.94	38.21	37.43	20.79	21.23
308	76.56	79.39	61.1	55.06	41.55	41.55	24.43	24.53
313	96.67	97.5	63.73	61.31	51.86	51.26	26.87	26.58
318	108.52	107.29	145.31	152.39	58.81	57.21	29.87	29.87
	(1) Kraus - Bray Model				(2) Shedlovsky Model			

**TABLE-2**

**K<sub>A</sub> and K<sub>C</sub> values of L-Lysine mono hydro chloride in water-DMF & Water- DMSO mixtures.**

<b>T(K)</b>	<b>0% DMF</b>		<b>20% DMF</b>		<b>40% DMF</b>		<b>60% DMF</b>	
	<b>K<sub>A</sub></b>	<b>K<sub>C</sub></b>	<b>K<sub>A</sub></b>	<b>K<sub>C</sub></b>	<b>K<sub>A</sub></b>	<b>K<sub>C</sub></b>	<b>K<sub>A</sub></b>	<b>K<sub>C</sub></b>
300	4.95	0.22	14.24	0.07	13.63	0.08	15.85	0.07
308	6.70	0.15	16.47	0.06	11.33	0.09	10.94	0.1
313	6.98	0.15	12.13	0.08	12.59	0.08	16.19	0.06
318	7.11	0.14	8.78	0.11	26.86	0.04	11.03	0.09

T(K)	0% DMSO		20% DMSO		40% DMSO		60% DMSO	
	K <sub>A</sub>	K <sub>C</sub>	K <sub>A</sub>	K <sub>C</sub>	K <sub>A</sub>	K <sub>C</sub>	K <sub>A</sub>	K <sub>C</sub>
300	4.95	0.22	16.54	0.06	91.26	0.01	7.00	0.14
308	6.70	0.15	13.31	0.08	87.63	0.01	5.27	0.19
313	6.98	0.15	7.25	0.14	52.82	0.02	4.20	0.23
318	7.11	0.14	57.42	0.02	32.50	0.03	5.45	0.18

TABLE-3

Computed values of  $\Delta G$  (k.J.mol<sup>-1</sup>) for ion pair formation of L-Lysine monohydrochloride in water - DMF and water - DMSO mixtures

T(K)	0% DMF	20% DMF	$\square\Delta G$	40% DMF	$\square\Delta G$	60% DMF	$\square\Delta G$
300	-3.99	-6.63	-2.64	-6.51	-2.52	-6.89	-2.90
308	-4.87	-7.17	-2.30	-6.21	-1.34	-6.12	-1.25
313	-5.06	-6.50	-1.44	-6.59	-1.53	-7.24	-2.18
318	-5.18	-5.73	-0.55	-8.70	-3.52	-6.34	-1.16
T(K)	0% DMSO	20% DMSO	$\square\Delta G$	40% DMSO	$\square\Delta G$	60% DMSO	$\square\Delta G$
300	-3.99	-6.99	-3.00	-11.26	-7.27	-4.85	-0.86
308	-4.87	-6.63	-1.76	-11.45	-6.58	-4.25	<b>+0.62</b>
313	-5.06	-5.15	-0.09	-10.32	-5.26	-3.75	<b>+1.31</b>
318	-5.18	-10.71	-5.53	-9.20	-4.02	-4.45	<b>+0.73</b>

**TABLE-4**

**Energy of activation values  $E_a$ ( $\text{k.J.mol}^{-1}$ ) of L-Lysine monohydrochloride in water - DMF and water - DMSO mixtures**

<b>0% DMF</b>	<b>20% DMF</b>	<b>40% DMF</b>	<b>60% DMF</b>
14.98	8.82	23.69	15.99
<b>0% DMSO</b>	<b>20% DMSO</b>	<b>40% DMSO</b>	<b>60% DMSO</b>
14.98	20.1	18.6	14.76

**TABLE-5**

**Solvation number of L-Lysine monohydrochloride in water - DMF and water - DMSO mixtures at 300K.**

<b>0% DMF</b>	<b>20% DMF</b>	<b>40% DMF</b>	<b>60% DMF</b>
1.38	1.49	1.44	1.35
<b>0% DMSO</b>	<b>20% DMSO</b>	<b>40% DMSO</b>	<b>60% DMSO</b>
0.25	0.40	0.41	0.40

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