



Association Constant and Free Energy Change Properties of Sodium Stearate in Aqueous CH₃OH and Aqueous DMSO Composition

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ABSTRACT

Various facets, similar to density, viscosity, medium dielectric constant, ion-solvent interactions, and calculations of solvent-solvent and ion-conductance and ion solvent related to different electrolytes in solvents. In curing it, ion-solvent relations pacify that ion. Throughout the study of ion solvent associations and overcoming activities of ions, conductance data and association constant figures of distant electrolytes have been used. Property of conductance and ion solvation of Sodium stearate measured in aqueous methanol and aqueous DMSO of diverse composition in the temperature range of 298K to 318K. Limiting molar conductance, Association constant of ion pair, KA figure out using Shedlovsky limiting law. $\Delta\theta$ increase with percentage of water in the solvent mixture. KA value and free energy change are maximum in 80% aqueous-methanol mixture suggesting that ion-solvent interactions are maximum at this composition of solvent blend and ion conductance properties as a purpose of specific ion-solvent connections including structural effect.

Keywords: Molar Conductance, Association constant, free energy change, Aqueous-MeOH, Aqueous DMSO, Sodium stearate.

1. INTRODUCTION

Solvent corrected conductance of this salt is used to calculate molar conductance data. Applying Krauss-Bray and Shedlovsky equations, the limit molar conductance (Λ°) values are obtained. Conductance values (Λ°) obtained using above said two models are in good agreement. Ion conductance and Ion solvation properties of different electrolytes in unlike solvent systems are reported to influence all the way through a range of factors like density, viscosity, dielectric constant. Conductance data and viscosity in turn of different electrolytes are handy to study ion solvent relations and solvation behavior of ions. Conductance data is recorded in binary solvent systems of different compositions in the range of 0-100 % (V/V). The KA values for every electrolyte is greater than 1 ($KA > 1$), indicates the fraction of ions that exist as ion pairs are higher than the free ions. These ion pairs don't carry any charge, so they do not contribute towards conductance. Thermodynamic parameter, free energy change gives useful focus into the

nature of ion –solvent interactions. The interaction of positive and negative ions with water molecules conclude that the hydration energy depends on the sign of ionic charge and heat of hydration of anion is higher than that of cation of the same size. This implies stronger interaction between anion and water molecules than cation.

Nevertheless, passage is full with such information. Related information on Sodium stearate is not there. In the recent study, observations on Association constant and free energy change properties of Sodium stearate within aqueous mixture of methanol and dimethyl sulphoxide at different temperatures among 298,308, 313 and 318 K study is described [1-10].

2. MATERIAL AND METHODS

Accuracy of the conductivity bridge was found to be 0.02 μ S. A stock solution of 0.01M Sodium stearate was prepared in water/aqueous organic solvent mixture of different composition (v/v) in varies of 0 to 100% organic component. Solution

was diluted to a variety of concentrations with different volume of solvent/ solvent mixture and conductance values are calculated in temperature range of 298-318 K. Solvent / Solvent in mixture used in these study, encircle conductance values in range 10-20 μ S. Conductance of solvent is taking away to get conductance of solute at every concentration. Shedlovsky limiting law (eqn1) of medium, ion-solvent relations and solvent-solvent associations analyzes molar conductance values are computed from experimental conductance.

Fuoss - Shedlovsky Method

In this method the values of association constant (K_A) were calculated by using the sets of the following equations from (1) to (8)

$$\frac{1}{\Lambda_{1,2}} = \frac{1}{\Lambda_{\infty}} + \left(\frac{K_A}{\Lambda_{\infty}^2} \right) (C \Lambda_{1,2}^2 S_{1,2}) \quad (1)$$

$$S_{1,2} = \left(\frac{z}{2} + \left(1 + \left(\frac{z}{2} \right)^2 \right)^{1/2} \right)^2 \quad (2)$$

$$Z = S \cdot (\Lambda_{\infty})^{3/2} \cdot (C\Lambda)^{1/2} \quad (3)$$

$$S = a \cdot \Lambda_{\infty} + b \quad (4)$$

$$a = 8.2 \times 10^5 (\epsilon T)^{1/2} \quad (5)$$

$$b = \frac{0.825}{\eta_0 (\epsilon T)^{1/2}} \quad (6)$$

$$\log y_1 = \frac{-A(\alpha C)^{1/2}}{[1 + B \gamma (\alpha C)^{1/2}]} \quad (7)$$

$$\alpha = \frac{\Lambda_{\infty}^2}{A_0} \quad (8)$$

The entropies of association ($T\Delta S_A$) of Sodium stearate were calculated by the use of Gibbs-Helmholtz equation:

$$\Delta G_A = \Delta H_A - T\Delta S_A \quad (9)$$

3. RESULTS AND DISCUSSION

Molar conductance (Λ°) determined from solvent correct specific conductance used meant for Sodium stearate Concentration 0.01M at 0.02 μ S conductance in aq-MeOH and aq-DMSO in different composition (v/v) of water at 298, 308, 313 and 318K. Shedlovsky law of conductivity to calculate molar conductance at infinite strength values determined and are represented in Table 1.

Table 1. Molar conductance ($S \text{ cm}^2 \text{ mol}^{-1}$), Association constant (K_A) values of Sodium stearate in Aq-MeOH and Aq-DMSO Mixtures.

% Organic Component	Aq MeOH		Temperature	Aq DMSO	
	Λ°_K	K_A		Λ°_K	K_A
0	89.60	4.50	298 K	88.60	4.50
20	66.25	5.10		60.60	4.80
40	59.00	5.25		54.20	11.30
60	53.62	9.30		35.15	14.20
80	56.80	10.80		33.40	24.15
100	68.50	2.70		31.20	18.25
0	107.29	4.19	308 K	107.29	4.19
20	81.45	5.25		79.60	5.90
40	72.50	6.03		60.25	10.58
60	65.72	8.38		54.10	17.64
80	65.05	9.82		39.80	28.46
100	73.86	10.67		36.20	20.18
0	118.27	4.45	313 K	118.27	4.45
20	95.15	6.12		85.76	6.05
40	81.67	5.68		66.16	9.90
60	73.49	11.05		50.10	17.23
80	75.50	8.96		42.74	28.92
100	79.42	10.17		40.82	20.03
0	130.65	4.73		130.65	4.73
20	104.52	6.82		95.60	6.22

40	88.42	5.98	318 K	76.50	10.95
60	83.26	10.58		60.58	19.60
80	84.21	9.98		47.64	26.80
100	82.30	11.52		40.25	22.30

Association constant (KA) of Sodium salt of Lauryl Sulphate increased with increase in the percentage of organic component in aquo-organic mixture and attained a maximum value in 100 % organic solvent. KA value is maximum in 100% DMSO. The Λ° values decrease up to 40-60% MeOH and thereafter increase slightly. It is the same case with free energy change ($-\Delta GA$). When organic solvent is added to water, there is sudden fall in Λ° values to the extent of about 30 to 40 units of conductance and later only slight variation is observed which is due to solvent-solvent and ion-ion interactions which might be attributed to the increase in the three dimensional structure of water in association with methanol. Differences in ionic conductance indicate that, the ions are more solvated in solutions of lower dielectric constant. The extent of ion-ion interactions are expressed in terms of ion-pair association constant (KA). Experimental statistics indicates that $KA > 1$, signifying that part of ion which exists as ion-pairs is superior to free ions and ion-pair formation is more viable in organic solvent than in water.

Limiting molar conductance values depend on composition of solvent too. At each temperature, these values are highest in pure water. Through the adding of MeOH and DMSO to water, they steadily decline up to 80%. Composition of methanol 80 % (v/v) and DMSO to Sodium stearate again rise up to 100%. The decrease Λ° up to 80% is due to increase in percentage of Methanol and DMSO might be due to spin down in dielectric constant of medium. On addition of co-solvent to water, solvent-solvent interaction improved.

As conductivity increase by increase in temperature, it is consider that this variation has to go after Arrhenius relation analogous to rate process. KA values determined at different temperatures are nearly constant which indicate that the process if in pair formation cannot be group as exothermic or endothermic progression. Standard free energy change convoy by ion pairing is designed with $\Delta G^\circ A = -RT \ln KA$ and is displayed in Table 2.

Table 2. Free energy change $-\Delta GA$ Values in KJ mole⁻¹ Sodium stearate in Aq-MeOH and Aq-DMSO organic mixtures.

% Organic Component	Aq MeOH				Aq DMSO			
	298 K	308 K	313 K	318 K	298 K	308 K	313 K	318 K
0	3.72	3.66	3.88	4.10	3.72	3.66	3.88	4.10
20	4.03	4.24	4.71	5.07	3.88	4.54	4.68	4.83
40	4.10	4.60	4.52	4.72	6.00	6.04	5.96	6.32
60	5.52	5.44	6.25	6.23	6.57	7.34	7.40	7.86
80	5.89	5.84	5.70	6.08	7.88	8.57	8.75	8.69
100	2.47	6.06	6.03	6.46	7.19	7.69	7.79	8.20

These are all negative values signifying spontaneous ion pairing which steadily rise in the ratio of organic component of solvent system that is liable as ion-pairs are more stabilize in low dielectric medium.

4. CONCLUSION

It is concluded that, ion-ion relations and free energy change are strong in high percentage of 80% aq-MeOH and aq-DMSO composition.

ACKNOWLEDGEMENT

The author wishes to thank anonymous support given by Govt. Degree College for Women, Gajwel, Siddipet, and Telangana-506001.

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