

## ION-ASSOCIATION AND ION-SOLVATION BEHAVIOR OF METHY, PHENYL AND BENZYL TRIMETHYL AMMONIUM CHLORIDE IN DMSO-WATER MIXTURES AT 298K

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### ABSTRACT

An exhaustive study has been through of the ion-solvation and association of the Methyl trimethyl ammonium chloride (MTMAC), Phenyl trimethyl ammonium chloride (PTMAC) and Benzyl trimethyl ammonium chloride (BTMAC) in aqueous DMSO (DMSO) at 298K using conductance data. The ionic contributions to the limiting equivalent conductances have been analyzed by Shedlovsky equation. The Association Constant ( $K_A$ ) values increased rapidly with increasing organic solvent composition and maximum at 60-100% v/v DMSO in water. This increase is due to the formation of the additional association species i.e. contact ion pair (CIP). Strong association due to closer contact between the ions was found for all these electrolytes in this solvent medium. The strong ion-solvent interactions absorbed irregular trend in relative ionic conductance is observed. Standard free energy changes are all negative and are in the range 2-10 kJmol<sup>-1</sup>.

**Keywords:** Association Constant, Contact Ion Pair, Limiting Molar Conductance, Free Energy.

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### INTRODUCTION

Knowledge of the status of association of electrolytes in solution and of their contact with the solvent molecules is necessary for the favor of a proper understanding of their behavior in solution. The ion-solvent interaction or the behavior of the electrolytes during solution is informative since it is related to the nature of the movement of the species of electrolytes in a solution. The conductance behavior of electrolytes in binary solvent system is reported to be influenced by number of factors like temperature, density, viscosity of the solvent system, dielectric constant of the medium, ion-solvent interactions and solvent-solvent interactions. We have initiated a comprehensive program to study the solvation and association behavior of 1-1 electrolytes in different non-aqueous solvents by using measurements of various properties, though literature is abounding with such type.<sup>1-6</sup> Various type of relations exist between the solute and the solvent, but the solute-solute, solute-solvent and ion-solvent interactions are of current interest in all the branches of chemistry can better understanding of the nature of solute and solvent. The solution arrangement is of enormous importance in appreciative the nature and movement of bioactive molecules in a biological system.

In this paper, an attempt has been made to reveal the nature of various types of interactions existing in solutions of the Methyl trimethyl ammonium chloride (MTMAC), Phenyl trimethyl ammonium chloride (PTMAC) and Benzyl trimethyl ammonium chloride (BTMAC) in DMSO-water solvent mixture. These are under quaternary ammonium salts often used as disinfectants, surfactants, fabric softeners, and as antistatic agents (e.g. in shampoos). In liquid fabric softeners, the chloride salts are often used.<sup>7</sup> Spermicidal jellies also contain quaternary ammonium salts.<sup>8</sup> They are incompatible with many strong oxidizers and reducing agents, such as metal hydrides, alkali/active metals, and organometallics. The results have been discussed in terms of solvent properties like ion-solvent relations and solvent-solvent connections.

## EXPERIMENTAL

### Material and Methods

Distilled water re-distill and use. Dimethyl sulphoxide was purchase commencing Chemicals Ltd., Bombay. The densities of aqueous-organic solvent mixture are measured using a double stem pycnometer through a bulb. The viscosities of solvent system used in the present study were determined using Ubbelohde viscometer at 298K.

A digital conductivity bridge (ELICO model CM 180) equipped with a dip type conductivity cell has cell constant  $1.024 \text{ cm}^{-1}$  be used to compute the conductance of the solution. The conductivity cell was calibrated using standard saturated KCl solution. The accuracy of the use conductivity bridge is  $\pm 0.4 \mu\text{S}$ . Temperature is maintaining steady at 298K using a thermostat through accuracy of  $\pm 0.2^\circ\text{C}$ . To maintain the temperature below room temperature a frost bath equipped with a mechanical stirrer be presently used.

### General Procedure

The aqueous mixture of sulfonate was watered down to varying concentrations in the range 0.02M to  $4.0 \times 10^{-3} \text{ M}$  using diverse volumes of solvent / solvent system used are water - DMSO aqueous mixtures of these organic solvents in different proportions and the conductance values were measured in the temperature range 298K as in the series. These values are found to subsist reproducible with  $\pm 0.2\%$  error. The solvent systems used in this revision has conductance values in the range 0.014-0.0412mS. The solvent conductance values are subtracted from the conductance of the solution to get the conductance of the solute at each concentration from which the specific conductance was evaluated. Using these values the molar conductance value ( $\Lambda_m$ ) was calculated using the relation,  $\Lambda_m = (1000k)/C$  here k is the specific conductance and C is the molarity of the solute. The identical procedure was followed at varied compositions of solvent mixture within the range 0-100 % (v/v) and at 298K temperatures.

### Detection Method

The molar conductance ( $\Lambda_m$ ) value as a consequence resolute are analyze using Shedlovsky equation (1)<sup>9</sup>

$$\frac{1}{S \Lambda_m} = \frac{S f_{\pm}^2 K_A C \Lambda_m}{\Lambda_m^0 2} + \frac{1}{\Lambda_m^0} \quad (1)$$

$\Lambda_m$  be molar conductance via concentration C;  $\Lambda_m^0$  is the limiting molar conductance;  $K_A$  by the association invariable of the ion-pair;  $f_{\pm}$  be the indicate ionic activity coefficient, S be a part given via, equation (2-6)

$$S = \left[ \frac{\beta \sqrt{C \Lambda_m}}{4 \Lambda_m^0 3/2} + \sqrt{1 + \frac{\beta^2 C \Lambda_m}{4 \Lambda_m^0 3}} \right]^2 \quad (2)$$

$$\log f_{\pm} = \left[ \frac{-1.8246 \times 10^6 (C \alpha)^{1/2} / (\epsilon T)^{3/2}}{1 + 50.24 \times 10^8 R (C \alpha)^{1/2} (\epsilon T)^{1/2}} \right]^2 \quad (3)$$

$$\alpha = \frac{S \Lambda_m}{\Lambda_m^0} \quad (4)$$

$$\beta = \frac{8.20 \times 10^5 \Lambda_m^0}{(\epsilon T)^{3/2}} + \frac{82.5}{\eta (\epsilon T)^{1/2}} \quad (5)$$

Where R be the ion-size parameter which is equal to the Bjerrum critical distance q given by:

$$q = R = \frac{e^2}{2 \epsilon k T} \quad (6)$$

k is the Boltzmann's constant, and T is the temperature here Kelvin,  $\epsilon$  is dielectric constant and  $\eta$  be viscosity of the solvent; presented in Table-1.

Table-1: Viscosity ( $\eta_0$ ) in Poise and Dielectric Constant ( $\epsilon$ ) of the Aqueous-DMSO 298K

| 0% Dimethyl Sulphoxide |            | 20% Dimethyl Sulphoxide |            | 40% Dimethyl Sulphoxide |            | 60% Dimethyl Sulphoxide |            | 80% Dimethyl Sulphoxide |            | 100% Dimethyl Sulphoxide |            |
|------------------------|------------|-------------------------|------------|-------------------------|------------|-------------------------|------------|-------------------------|------------|--------------------------|------------|
| $\eta_0$               | $\epsilon$ | $\eta_0$                | $\epsilon$ | $\eta_0$                | $\epsilon$ | $\eta_0$                | $\epsilon$ | $\eta_0$                | $\epsilon$ | $\eta_0$                 | $\epsilon$ |
| 0.0063                 | 73.36      | 0.0099                  | 72.00      | 0.0119                  | 62.00      | 0.0127                  | 59.00      | 0.0132                  | 48.00      | 0.0096                   | 33.00      |

S is calculated using  $\Lambda_m^0$  obtained from the Onsager model by means of the plot of  $\Lambda_m$  against  $\sqrt{C}$ . The least-square analysis of the data ( $\Lambda_m$  and C) using the above equation (equations 1) is acceptable by means of linear correlation coefficient in the range 0.96-0.99.

## RESULTS AND DISCUSSION

The conductance of methyl trimethyl ammonium chloride (MTMAC), phenyl trimethyl ammonium chloride (PTMAC), Benzyl trimethyl ammonium chloride (BTMAC) is determined in DMSO in the presence of water at different compositions. A scan at the data presented in Table-1 indicates that in all solvent mixtures,  $\Lambda_m^0$  values are maximum in pure water and addition of organic solvent DMSO decreases the  $\Lambda_m^0$  values. This may be attributed to the component in the dielectric constant of the medium due to the addition of organic component to water. If it is so the conductance would decrease and reach a minimum value in 100% organic solvent. In each solvent system, when organic component is added to water at the initial addition there is a steep fall in  $\Lambda_m^0$ , thereafter it decreases slowly up to 100% (v/v) organic solvent. The viscosity values of these solvent systems also vary in a similar fashion. For example in water-DMSO system above table, the viscosity changes from 0.0063cp in pure water to 0.0099cp in 20% (v/v) DMSO, then increase gradually up to 100% DMSO. On adding DMSO to water at the initial stages the three-dimensional structure of water increases giving a larger solvent frame. Due to this the size of the solvent shell increases capturing more number of conduction ions leading to a decrease in the conductance. This trend indicates strong solvent-solvent interactions between water and DMSO. The  $\Lambda_m^0$  values appear to decrease with increase in viscosity values. A similar trend in  $\Lambda^0$  and  $\eta$  is observed in earlier studies also.<sup>10-13</sup> This suggests that besides hydrodynamic viscous force, the structural effects and specific solvation of the ions also play a significant role. It is also clear that for all the electrolytes the higher  $\Lambda_m^0$  values in 100% water compared to *aqua*-organic solvent system indicate higher degree of freedom of ions in polar water of higher dielectric constant.

The structural effect and also the influence of the extent of solvation on the conductance of electrolytes can be understood by comparing the factor Walden product ( $\Lambda^0\eta$ ) which is the product of the limiting molar conductance and the viscosity of the solvent. A constant Walden product is expected for a given electrolyte at different compositions of a binary solvent mixture provided constant ion-solvent interactions exist at all compositions. The variation in the Walden product as a function of the solvent is generally regarded as an index of variable of specific ion-solvent interactions including structural effects shown in Table -2.

In the present case, there is a sharp decrease in these values due to an increase in the proportion of organic component of the solvent system. This is attributed to increased ion-solvent interactions due to the addition of DMSO to water as our previous papers.<sup>14,15</sup>

By assuming perfect stick of the solvent at the surface of the ion, Walden modified the stokes law.<sup>16,17</sup> It is proposed a relationship in which the conductance  $\Lambda_i^0$  of a hydrodynamic entity (solvated ion) of radius  $r_s^i$  and charge  $Z_i$  in a medium of viscosity  $\eta$  are related as:

$$\eta \Lambda_i^0 = \frac{0.82|Z_i|}{r_s^i} \quad (7)$$

For a 1:1 electrolyte ( $Z_+ = Z_- = 1$ ) the above equation becomes:

$$\eta^{\wedge 0} = 0.82 \left[ \frac{1}{r_s^+} + \frac{1}{r_s^-} \right] \quad (8)$$

Table-2: Limiting Molar Conductance ( $\text{mho cm}^2 \text{mol}^{-1}$ ), Association Constant ( $K_A$ ) Values of Methyl Trimethyl Ammonium Chloride (MTMAC), Phenyl Trimethyl Ammonium Chloride (PTMAC) and Benzyl Trimethyl Ammonium Chloride (BTMAC) in Binary Aqueous-DMSO Mixtures.

| % DMSO | Methyl Trimethyl Ammonium Chloride |       | Phenyl Trimethyl Ammonium Chloride |       | Benzyl Trimethyl Ammonium Chloride |       |
|--------|------------------------------------|-------|------------------------------------|-------|------------------------------------|-------|
|        | $\Lambda_s^0$                      | $K_A$ | $\Lambda_s^0$                      | $K_A$ | $\Lambda_s^0$                      | $K_A$ |
| 0      | 131.26                             | 4.86  | 122.79                             | 3.65  | 118.61                             | 5.20  |
| 20     | 91.94                              | 10.82 | 87.22                              | 6.49  | 76.73                              | 8.30  |
| 40     | 74.33                              | 13.67 | 58.87                              | 9.39  | 57.36                              | 18.04 |
| 60     | 62.87                              | 27.67 | 30.24                              | 5.66  | 53.45                              | 31.31 |
| 80     | 46.69                              | 37.04 | 28.04                              | 10.03 | 48.53                              | 46.25 |
| 100    | 48.65                              | 42.11 | 38.35                              | 11.30 | 42.41                              | 61.36 |

$\Lambda_s^0$  = Shedlovsky model  $K_A$  = Association constant commencing from Shedlovsky equation

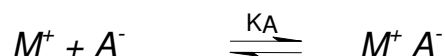
For any electrolyte, the factor  $\frac{0.82}{\eta^{\wedge 0}}$ , which is equal to  $\left[ \frac{1}{r_s^+} + \frac{1}{r_s^-} \right]$  is a measure of the hydrodynamic radii of

the ions. This hydrodynamic radius is the efficient radius of an ion in a solution by assuming that it is a body moving all the way through the solution and resisted by the viscosity of the solution. This hydrodynamic radius includes all the solvent molecules attached to the ion. This factor can be used to obtain information on ion-solvent interaction. These values calculated in the present study are also recorded in Table-3.

Table-3: Computed Values of Change in Free Energy Accompanied as a Result of Association ( $-\Delta G_A^0$ ) ( $\text{kJmol}^{-1}$ ) and Walden Product ( $\Lambda_s^0 \eta_0$ ) Values of Methyl, Phenyl, and Benzyl in Water-DMSO Mixtures at Different Compositions (v/v).

| % DMSO | Methyl Trimethyl Ammonium Chloride |                 | Phenyl Trimethyl Ammonium Chloride |                 | Benzyl Trimethyl Ammonium Chloride |                 |
|--------|------------------------------------|-----------------|------------------------------------|-----------------|------------------------------------|-----------------|
|        | $\Lambda_s^0 \eta_0$               | $-\Delta G_A^0$ | $\Lambda_s^0 \eta_0$               | $-\Delta G_A^0$ | $\Lambda_s^0 \eta_0$               | $-\Delta G_A^0$ |
| 0      | 100.84                             | 3.23            | 104.94                             | 3.23            | 101.37                             | 4.11            |
| 20     | 111.53                             | 2.28            | 118.61                             | 4.66            | 104.35                             | 5.28            |
| 40     | 75.45                              | 3.81            | 87.65                              | 5.58            | 85.40                              | 7.21            |
| 60     | 61.98                              | 5.27            | 71.98                              | 4.38            | 77.18                              | 8.28            |
| 80     | 53.74                              | 5.62            | 56.70                              | 5.75            | 69.17                              | 9.26            |
| 100    | 48.01                              | 5.63            | 38.01                              | 6.07            | 58.60                              | 1063            |

In DMSO-water system maximum ion-solvent interaction as indicated by higher hydrodynamic radii is observed in 60% aqueous-DMSO, with all the three electrolytes. A comparison of viscosity data suggests that this is the composition where the viscosity of the solvent mixture is minimum indicating maximum solvent-solvent interaction. In Aqueous mixture, the ions are within equilibrium by means of the ion-pairs



These values are evaluated for the three electrolytes applying linear smallest amount square analysis using Shedlovsky model, the association constant  $K_A$  of the ion-pair have been evaluating and presented in Table -2 along with  $\Lambda_m^0$  values.

This data indicates that for each electrolyte  $K_A > 1$  suggesting that the fraction of ions which exist as ion-pairs is higher than the free ions.

This trend suggests that ion-pair formation is controlled not solely by the dielectric constant of the medium but also by viscosity of it. These ion-pairs are neutral entities and do not contribute to

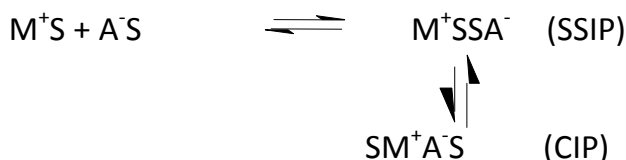
conductance. According to Bjerrum, it is simply short-range coulombic relations that lead to ion-pair structure. He further stated that ion-pair formation occurs when an ion of one kind of charge e.g. a negative ion, enter a sphere of radius  $q_i$  drawn in the region of a reference ion of the opposite charge i.e. a positive ion. This stricture  $q_i$  is a function of dielectric constant of the medium and is given:

$$\text{by } \frac{|Z_+ Z_-| e^2}{2\epsilon k_B T}. \quad (9)$$

These values calculated for every solvent system are presented into Table-2.  $K_A$ , the association constant of the ion-pair has been calculated from the Shedlovsky's treatment of conductance data and presented in Tables-2.  $K_A$  values are strongly dependent on the dielectric constant of the system. In general, a medium of lesser dielectric constant is more constructive for ion-pair formation. Table-1 indicates that the association constants are minimum in 100% water. Addition of organic solvent which decreases the dielectric constant of the medium gradually increases the  $K_A$  values. These values become maximum around 60-80% (v/v) organic solvent and then decrease. A similar trend is observed in other systems also. At a given temperature the  $K_A$  values of each electrolyte in DMSO more than Water, indicating that the ion-pairs are relatively more stable in DMSO than in water. Those  $K_A$  values are used to calculate the standard free energy change ( $\Delta G_A^0$ ) accompanied by the association process using the relation.

$$\Delta G_A^0 = -RT \ln K_A \quad (10)$$

These values are calculated in each solvent system and recorded in Tables - 3. These are all negative and are in the range of 2-10 kJmol<sup>-1</sup>. As expected these  $\Delta G_A^0$  are higher in DMSO system. This is true with all the salts. This observation supports the fact that the ion-pairs of all the three electrolyte systems are more stable in DMSO than in other solvents. Ion-solvent interactions, in general, affect the extent of ion-association in several ways. These interactions stabilize not only the free ions but also ion-pairs to different extents. The ion-pair formation i.e. association equilibrium in solution is governed by the relative stabilities of the ions and ion-pairs. Therefore  $K_A$  changes with the changes in ion-solvent interactions. The association of solvent molecules with ions may lead to formation of different types of ion-pairs namely 'solvent separated ion-pairs' (SSIP) and 'contact ion-pairs' (CIP). Thus this equilibrium may be represented as:



Thus in SSIP, there is large separation between  $M^+$  and  $A^-$  hence weak association while in CIP, there is strong association due to closer contact between the ions. These ion-solvation interactions may change the solvent structure also. Therefore, main effect of ion-solvation on ion-pair formation is either to decrease  $K_A$  due to the formation of the extra associated species i.e. CIP (contact ion pair).

### CONCLUSION

In pure solvents (Water, DMSO) the  $K_A$  principles of the three electrolytes used are in the order BTMAC > MTMAC > PTMAC suggesting that the ion-pair in Benzyl salt is more stable than the other two salts.

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