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Solvation Behaviour of Methyl Ammonium hydrochloride salts in DMF – Water Mixture at High Temperature (318 K)

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ABSTRACT

Conductance of Monomethyl Ammonium Hydrochloride, Dimethyl Ammonium Hydrochloride and Trimethyl Ammonium Hydrochloride have been studied in aqueous mixtures of DMF in a whole range of composition of mixtures at 318 K. The conductivity data have been analysed by the Debye – Huckel – Onsager and Krauss – Bay equations. The limiting molar conductance Λ_o *and ion dissociation constants Kc have been evaluated at all the solvent compositions. The dependencies of the limiting molar conductances* Λ_o *and Walden products* $\Lambda_o\eta_o$ *as a function of mixture composition were analyzed in the aspects of ion–solvent interactions.*

Keywords: Limiting molar conductance, ion dissociation constant, Debye – Huckel – Onsager, Krauss – Bay equation, Walden product.

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 the recent years as they are important from both fundamental and technological points of view [1-4]. It has also been established recently that selective solvation of ions by the components of a binary solvent mixture profoundly affects many chemical phenomenon such as solubilities, rates of reactions, phase separation, etc. In addition, such preferential solvation by solvent components around ions has been found to be of importance from a technological view point in the electro refining and electrowinning of metals. Thus, it is clear that conductance measurements find extensive applications in chemistry and chemical industry for obtaining important information concerning the behaviour of electrolytes [5], for analysis and quality control.

Survey of literature reveals that although lot of studies on solvation behaviour of various electrolytes have been carried out in single component and in mixed solvent systems, little attention has been paid to the behaviour of methyl ammonium hydrochloride salts in binary aqueous solutions of DMF. In view of these considerations, conductometric study of solute – solvent and solute – solute interactions in aqueous solution of DMF in the presence of mono, di and trimethyl derivatives have been undertaken. Also, the methyl derivatives of ammonium hydrochloride are of significant pharmaceutical applications [6]. The dimethyl derivative is used as an intermediate in the synthesis of analgesic (tramadol), antihypertensive (amlodipine), anti – diabetic drug (metformin), etc. The trimethyl derivative is used in manufacture of animal feed and also in pharmaceuticals. It is also used in performance chemicals & speciality chemicals [7].

MATERIALS AND METHODS

Monomethyl, Dimethyl and Trimethyl ammonium hydrochloride used were AR grade chemical (SD Fine Chem). These chemicals were used without further purification. The non – aqueous solvent DMF was purified as stated in the literature [8]. The water used was double-distilled, deionised water and filtered twice. The solvent mixtures (0% to 90% by weight) and solutions of various concentrations of electrolytes (0.02, 0.04, 0.06 and 0.08m by weights) were prepared by using digital electronic balance.

Conductance was measured by using precision digital conductivity meter and a dip type calibrated conductivity cell (cell constant = 0.1 cm^{-1}). All measurements were made in a thermostat maintained at 318 K with an accuracy of $\pm 0.05^{o}C$. The solution of known concentration was taken in a vessel and kept in a thermostat maintained at the desired temperature for approximately 10 – 15 minutes and its specific conductance was noted.

RESULTS AND DISCUSSION

Limiting Molal Conductance : Specific conductance (k) of Monomethyl, Dimethyl and Trimethyl ammonium hydrochloride in Water + DMF system at 318K were directly read from the instrument and molal conductance (Λ_m) was calculated from $\Lambda_m = 1000k/c$, where *c* is the molal concentration. Limiting molal conductance at infinite dilution ($\Lambda^0{}_m$) was determined for all the cases from the Debye Huckel Onsager equation [9].

$$\Lambda_m = \Lambda^{o}{}_{m} - (A - B\,\Lambda^{o}{}_{m})\sqrt{c} \qquad ....(1)$$

with usual notations. The intercept of the linear plot Λ_m vs $\sqrt{c}$ gave the Λ^0 m values. The resultant values are reported in table 1. It is found that Λ^0 m values decrease with increase in organic solvent component in the mixed solvent for all the three solvents. This may be attributed to the difference in solvation of ions which is responsible for the change in mobility of the ions and hence Λ^0 m values [10]. The Λ^0 m values for a given composition decrease from monomethyl to dimethyl to trimethyl ammonium salts.

The equivalent conductance values at zero conductance for all the systems under study show an overall decrease with increase in amount of co-solvent at all temperatures. This clearly indicates the role of the solvation of cation and solvent-solvent interaction involved in this conductivity measurements. In DMF-water system, Λ_m^0 for all the electrolytes is less than in water. This may be due to its low dielectric constant and huge molecular size. DMF has stronger bonds (ion-solvent interaction) with the cation. The preferential solvation of cations by the co-solvent is responsible for decrease in the conductance. The addition of aprotic, dipolar and protophilic co-solvent like DMF to water increases the coordination or three dimensional structure of the system or it acts as a structure former with water (DMF-$3H_2O$), thereby either solvation increases or captures more number of conducting ions with more compact structure formed, leading to the decrease in conduction.Also, the equivalent conductance values decreased as the size of the substituent ammonium cation increased irrespective of temperature considerations. The following order was found –

$$(CH_3)N^{+}H_2\text{-} > (CH_3)_2N^{+2}H\text{-} > (CH_3)_3N^{+3}$$

The Λ_m^0 values decreased with decrease in dielectric constant of the medium. The decrease was due to increase in ion-solvent interactions which increase with ionic size and hydrophobic solvation of cation.

Table 1. Values of Λ^0m (S cm^2 mol^{-1}) for Monomethyl, Dimethyl and Trimethyl Ammonium Hydrochloride Solution in DMF + H_2O Solvent Mixtures at 318K

% wt	$\Lambda^0 m_{MMAH}$	$\Lambda^0 m_{DMAH}$	$\Lambda^0 m_{TMAH}$
10	18.27	16.56	15.56
20	18.14	16.29	15.57
30	18.70	16.89	16.26
40	18.21	16.31	15.55
50	15.92	14.09	13.28
60	14.54	12.70	11.73
70	13.10	11.37	10.59
80	11.62	9.98	8.94
90	10.12	8.32	7.30

Dissociation constant : Kraus – Bay [11] equation was also tried.

$$\frac{1}{\Lambda m} = \frac{1}{\Lambda^0\ m} + \frac{c}{\Lambda^0\ m^2}\frac{\Lambda m}{K_c} \qquad \text{....... (2)}$$

A graph of $1/\Lambda_m$ versus $c\Lambda_m$ shows linear nature. The linearity indicates that the electrolyte forms ion-pairs in equilibrium with ions. The values of Λ^0_m and Kc are obtained from the intercept and slope of the above linear plot for all the three electrolytes at 318K temperature. The resultant values of Kc are reported in table 2. It is observed that the dissociation constant values increase with increase in percentage of the organic solvent component. Also, the values show a decrease from monomethyl to trimethyl ammonium hydrochloride.

The variation of Kc with percentage composition is primarily due to change in dielectric constant, and it also indicates that the electrolyte cause a reduction in thickness of the ionic atmosphere surrounding ionic species. It may reduce the repulsion between different ionic species by increasing the aggregation capacity. It may also be due to bulky organic molecules either entering the solvation shell or coming out of it during the movement of the solvated ion in the bulk of the solution.

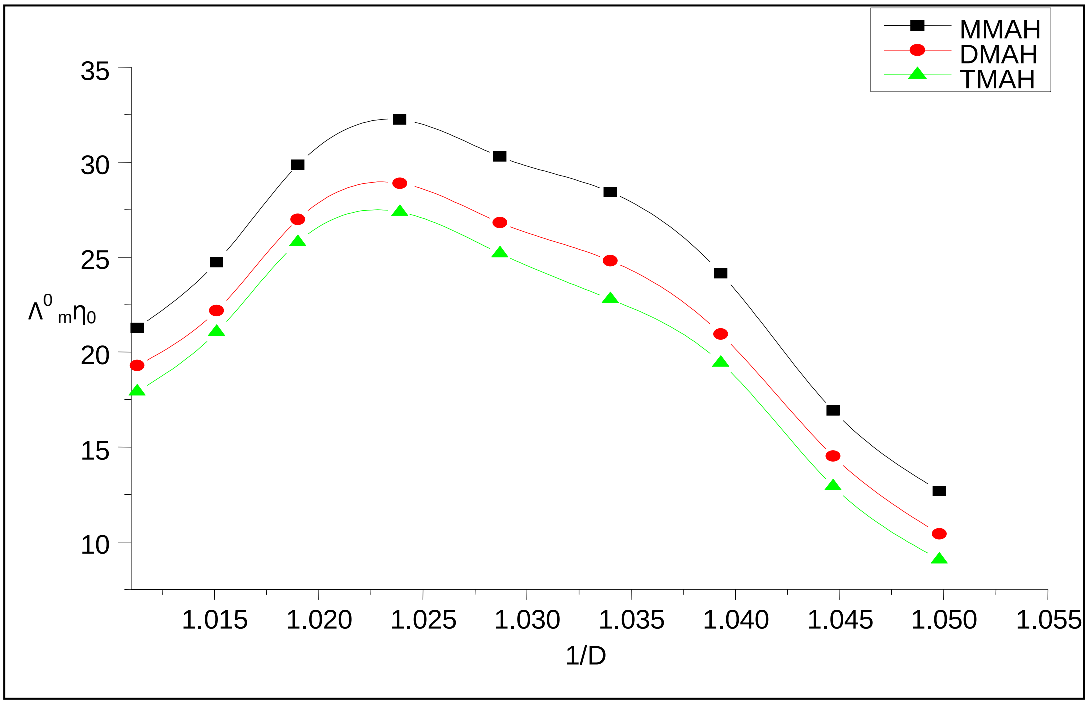
Table 2. Values of Kc for Monomethyl, Dimethyl and Trimethyl Ammonium Hydrochloride Solution in DMF + H_2O Solvent Mixtures at 318K

% wt	Kc_{MMAH}	Kc_{DMAH}	Kc_{TMAH}
10	0.026	0.020	0.018
20	0.057	0.049	0.046
30	0.138	0.121	0.121
40	0.296	0.313	0.308
50	0.442	0.436	0.436
60	0.453	0.565	0.552
70	0.670	0.593	0.588
80	0.829	0.702	0.678
90	0.965	0.782	0.685

Walden Product: The dependence of conductance on the viscosity of the medium is given by Walden's rule according to which the equivalent conductance of an electrolyte is inversely proportional to the viscosity of the medium. The Walden Product for all electrolytes under study at 318K is plotted as a function of 1/D of the composition (fig. 1). The graph was aimed to find out the effect of structure of the electrolytes on the properties of solution at constant temperature for all the three systems. It is observed that the curve for Walden Product passed through a maximum and as the strength of the electrolyte changed from monomethyl to trimethyl the magnitude of the maxima became less and less.

For DMF-water binary system the maxima occurred at 40% composition of DMF. It was also observed that the magnitude of Walden product was highest when the substituent group was monomethyl and as the substituent group became bulky there was separation in magnitudes of Walden product. The order found was NH_2 (CH_3) > - $NH(CH_3)_2$ > - $N(CH_3)_3$. It is also seen that the Walden product values increased slowly with the increase of amount of co solvent in water at a given temperature, reach a maximum and decrease further. These small variations of Walden product from one composition to the other in water-DMF mixture clearly informs about the preferential solvation of cation by DMF molecules. Thus, it depends on the viscosity of the medium, the exchange of ions with neighbouring solvent molecules and movement of ions through the holes in hydrogen bonded solvent mixtures.

Fig 1. Calculated Walden Product $\Lambda^0{}_m\eta_0$ (S $cm^2 mol^{-1}$) vs 1/D,System: DMF – Water, Temperature: 318K



APPLICATIONS

The methyl ammonium derivatives have significant use in the field of pharmacy. The present research work deals with the solvation behaviour of these derivatives in aqueous solvent of DMF. It gives us an insight in the solute – solvent and solvent – solvent interactions which is useful in the manufacturing processes on various drugs. The conductance measurements are useful in chemistry and chemical industry for obtaining important information regarding the behaviour of electrolytes, for analysis and quality control.

CONCLUSIONS

The limiting molar conductance values decrease with the increase in the substituent group i.e, from monomethyl to dimethyl to trimethyl ammonium salts. The equivalent conductance values at zero conductance for all the systems under study show an overall decrease with increase in amount of co-solvent at all temperatures. The dissociation constant values increase with increase in percentage of the organic solvent component. Also, the values show a decrease from monomethyl to trimethyl ammonium hydrochloride. It is observed that the curve for Walden Product passed through a maximum and as the strength of the electrolyte changed from monomethyl to trimethyl the magnitude of the maxima became less and less.

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