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Study of solvation behaviour of Dimethyl Ammonium Hydrochloride salt in various solvent mixtures

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ABSTRACT

Electrical conductivities of DMAH have been studied in aqueous mixtures of acetone, DMF and THF in a whole range of composition of mixtures at 298 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 in aqueous and partially aqueous media have received considerable attention in recent years as they are important from both fundamental and technological points of view [1-3]. Ion – solvent interactions, solvent – solvent interactions and other factors like density, viscosity, dielectric constant of the medium influence the conductance behaviour of electrolytes in mixed solvent systems. The ions are stabilized due to solvation by the ion - solvent interactions. The significance of conductance has prompted immense work in this field [4-6] but similar work on Dimethyl Ammonium Hydrochloride is lacking. Dimethyl Ammonium Hydrochloride $[(CH_3)_2NH.HCl]$ is a solid form of alkylamine and has extensive pharmaceutical applications [7], also it is used as an intermediate in the synthesis of analgesic (tramadol), anti – hypertensive (amlodipine), anti - diabetic drug (metformin), etc.

MATERIALS AND METHODS

Dimethyl ammonium hydrochloride used was AR grade chemical (SD Fine Chem). This chemical was used without further purification. The non – aqueous solvents acetone, THF and DMF were 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 298 K with an accuracy of $\pm 0.05^oC$. 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 dimethyl ammonium hydrochloride in water + acetone, water + THF and water + DMF system at 298K was 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 acetone to DMF to THF.

Table 1: Values of Λ^0m (S cm^2 mol^{-1}) for dimethyl Ammonium hydrochloride solution in acetone + H_2O, THF + H_2O and DMF + H_2O solvent Mixtures at 298K

% wt	Λ^0m $_{\text{Ac + water}}$	Λ^0m $_{\text{THF + water}}$	Λ^0m $_{\text{DMF + water}}$
10	15.54	13.26	13.35
20	14.17	10.80	12.36
30	13.35	8.80	11.37
40	14.65	8.92	10.80
50	12.42	8.53	9.16
60	12.25	8.26	7.88
70	11.84	7.84	7.54
80	11.66	4.66	6.71
90	11.42	----	6.19

Dissociation constant: Kraus – Bay equation was also tried.

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

The dissociation constant Kc is calculated from the slope of Kraus Bay linear plot of $1/\Lambda_m$ versus c Λ_m. 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 an increase from solvent THF to acetone to DMF.

Table 2: Values of Kc for Dimethyl Ammonium Hydrochloride Solution in Acetone + H_2O, THF + H_2O and DMF + H_2O Solvent Mixtures at 298K

Wt %	Kc $_{\text{Ac + water}}$	Kc $_{\text{THF + water}}$	Kc $_{\text{DMF + water}}$
10	0.0580	0.0500	0.0384
20	0.0705	0.0317	0.0741

30	0.0969	0.1021	0.1181
40	0.1734	0.0468	0.2325
50	0.1599	0.1123	0.3013
60	0.1914	0.2054	0.3894
70	0.2403	0.3963	0.6305
80	0.2988	0.1767	0.5590
90	0.3902	------	0.7340

The variation of Kc with percentage composition and solvent mixture is primarily due to change in dielectric constant and it also indicates that the electrolyte causes a reduction in thickness of the ionic atmosphere surrounding ionic species which reduces the repulsion between different ionic species. It may also be due to the bulky organic molecules either entering the solvation cell or coming out of it during the movement of the solvated ion in the bulk of the solution.

Walden Product: Walden product shows the dependence of conductance on the viscosity of the medium. The Walden product $\Lambda^0{}_m\eta_0$ is calculated at 298K temperature and for all % compositions as stated earlier and is shown in fig.1.

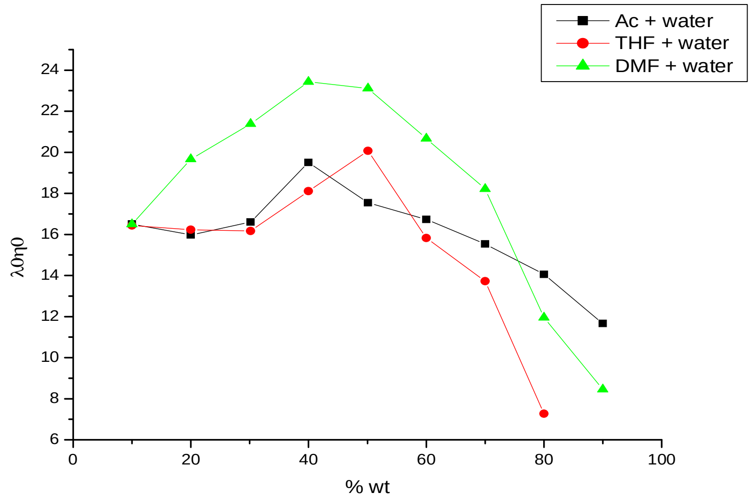

Figure 1: Calculated Walden Product, $\Lambda^0{}_m\eta_0$ (S cm^2mol^{-1})

It is seen that the Walden product increased with increase in amount of co-solvent with water. It is maximum at 40% for acetone and DMF and 50% for THF and decreases slowly further. This variation in the Walden product can be explained in terms of solvation of ions which suggest that the H^+ and DMAH ions are solvated to different extents in these solvent mixtures.

APPLICATIONS

The above research work is useful in studying the preferential solvation behaviour of Dimethyl Ammonium Hydrochloride in solvents such as acetone, DMF and THF. It has 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 pharmaceutical, electro refining and electro winning of metals. Thus, it is clear that conductance measurements find extensive applications in chemistry and chemical industry for obtaining important information concerning the behavior of electrolytes, for analysis and quality control.

CONCLUSIONS

From the above results it is concluded that the limiting molal conductance Λ^0 m values decrease with increase in organic solvent component in the mixed solvent for all the three solvents. The values for a certain composition also vary according to the solvent. It is maximum for acetone, then for DMF and is minimum for THF. The values for dissociation constant increase with increase in the solvent composition. But the dissociation constant show greater values for DMF followed by acetone and the lowest for THF. Walden product increases with increase in amount of co – solvent in water. A steady rise is seen in the values for DMF and Acetone with the maxima at 40% composition. A similar trend is seen for THF but the maxima is obtained at 50% composition.

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