



RESEARCH ARTICLE

ELECTRICAL CONDUCTANCE AND ION PAIR FORMATION OF TRIMETHYLSULFONIUM HALIDES IN ACETONITRILE-WATER MIXTURES AT 25°C

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ABSTRACT

Conductance of trimethylsulfonium halides (bromide and iodide) is measured at 25°C in acetonitrile-water mixtures (46.52<D<74.66). The conductance parameters derived from the Fuoss-Onsager conductance theory indicate that the equivalent conductance at infinite dilution (Λ_0) and (a°) solvation for trimethylsulfonium halides decreases with the decrease of the dielectric constants until a certain minimum and then increases again. The plot of $\log K_A$ versus $1/D$ is found to be linear indicating that the equation of association can be applied. The association constant is analyzed using the solvent separated –ion pair model.

INTRODUCTION

Acetonitrile has increased with opens up broad possibilities for studying biological objects (Kalugin, 2009) and for analytical practice (Roshal, 1998). A number of studies on binary mixture of acetonitrile (ACN) with water (W) have revealed that these solvent mix non-ideally and the binary mixture constitutes three distinct regions (Schnieder, 1964; Moreau, 1975; Visser, 1978). This may affect significantly the solvation of ions and ion-pair formation. Conductometric studies on a number of electrolytes have been carried out in ACN-W mixtures (Morinaga, 1982; Manaisah, 1986; Niazi, 1990; Hefter, 1984; Havlicka, 1987; Petrella, 1980). A few studies on NaClO_4 and $\text{C}_6\text{H}_5\text{COONa}$ are available in some mixture of these solvent systems (Manaisah, 1986; Niazi, 1990). NaClO_4 has been used as an electrolyte for maintaining constant ionic strength (Hefter, 1984) in potentiometry.

The influence of the solvent structure on the limiting ionic mobilities in water-organic solvent mixtures was recently the subject of a series of papers by Kay and Broadwater. They studied the conductometric behavior of several ions in water-dioxane ($\text{H}_2\text{O}-\text{D}$) (Kay, 1971) water-t-butyl alcohol ($\text{H}_2\text{O}-\text{t-BuOH}$) (Broadwater, 1970) and water-ethanol ($\text{H}_2\text{O}-\text{EtOH}$) (Kay, 1976) mixtures.

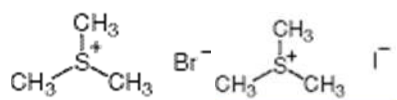
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In the light of these results, we thought it interesting to study the conductometric behaviour of ions in other aqueous mixtures where small additions of organic solvent cause a reduction in the long-range order of water. We therefore chose water-acetonitrile ($\text{H}_2\text{O}-\text{ACN}$) mixtures which are less structured than pure water. The structure-breaking properties of ACN in water-rich regions have been demonstrated by Armitage (Armitage, 1968) and co-workers by ultrasonic absorption. Excess volumes, mutual solubilities, and IR measurements, have been demonstrated by Moreau and Douheret (Moreau, 1975; Moreau, 1976) who have studied the dielectric, viscometric, and densimetric properties of $\text{H}_2\text{O}-\text{ACN}$ mixtures. In the present work, trimethylsulfonium halides (bromide and iodide) are selected as electrolytes with large cation size. The effect of cation size and anion size on the conductance of salts can be discussed from variation of Λ_0 , K_A and a° values. The conductance measurements in acetonitrile – water mixtures can also be analyzed using the Fuoss-Onsager equation (Fuoss, 1957) and the derived constants may then illustrate the electrolyte – solvent interaction.

Experimental: All salts were highly purified reagent grade and used without further purification. where trimethylsulfonium bromide ($\text{Me}_3\text{S.Br}$) and trimethylsulfonium iodide ($\text{Me}_3\text{S.I}$) are Analar analytical reagent "BDH".

Conductivity water: It was obtained by passing ordinary distilled water from a tin still over a 60 cm long Elgstat deionizer and guarded against contamination with atmospheric

CO₂ by sodalime tubes. Its specific conductance κ amounted to $(2-7 \times 10^{-6}) \text{ ohm}^{-1}\text{cm}^{-1}$.



Acetonitrile: Analar analytical reagent acetonitrile (BDH) was used without further purification. The specific conductance κ for acetonitrile were found to be $(1.35- 2.12 \times 10^{-6}) \text{ ohm}^{-1}\text{cm}^{-1}$.

Properties of Solvent Mixtures: Densities (d) of mixtures, viscosities (η) of mixtures and dielectric constants (D) of the acetonitrile-water mixtures were used as reported in the literatures (Niazi, 1990; D'Aprano, 1969). All solutions were prepared by weight. Salts were weighed on a microbalance which reads to ± 0.1 mg. Dilution was carried out successively into the cell by siphoning the solvent by means of weighing pipette. Conductivity Bridge was model Crison GLP31+ and the cell with bright platinum electrodes was used. The cell constant was 0.1 cm^{-1} for dilute solutions.

RESULTS AND DISCUSSION

Conductance of trimethylsulfonium halides (bromide and iodide) in acetonitrile - water mixtures at 25°C was measured: The equivalent conductance Λ ($\Omega^{-1}\text{equiv}^{-1}\text{cm}^2$) is calculated at several concentrations (equiv/l). By plotting the extrapolation of Λ against $C^{1/2}$, an approximate value of Λ_0 was obtained. More precise values of limiting equivalent conductance Λ_0 were resulted from the following Fuoss-Kraus-Shedlovsky (F.K.S) equation:

$$\frac{1}{\Lambda S_{(z)}} = \frac{1}{\Lambda_0} + \frac{(C\Lambda S_{(z)} f^2)}{K_D \Lambda_0^2} \quad (1)$$

Where K_D is the dissociation constant and $S_{(z)}$ is a function of z called Shedlovsky's function that was tabulated by Daggett. The z value could be determined from the expression:

$$z = \alpha (C\Lambda)^{1/2} / \Lambda_0^{3/2} \quad (2)$$

Where α is the limiting tangent (Onsager slope). The plot of $1/\Lambda S_{(z)}$ versus $(C\Lambda S_{(z)} f^2)$ gives $1/\Lambda_0$ as the intercept and $1/K_D \Lambda_0^2$ as the slope. More accurate values of Λ_0 , $J_{(a)}$, a° and K_A were obtained from Fuoss-Onsager equation (Fuoss, 1957). The starting Λ_0 value was resulted from Fuoss-Kraus-Shedlovsky equation by the assist of specific computer program that was programmed on an IBM-PC. The desired accuracies in these calculations are ± 0.02 for Λ_0 ; ± 2 for (J less than 200), ± 5 for (J with values range from 200 to 1000) and ± 10 for (J more than 1000).

The standard deviation σ_Λ was calculated using the equation (Brown, 1982): where N is the number of experimental points

$$\sigma_\Lambda = \frac{\{\sum (\Lambda \text{ calculated} - \Lambda \text{ observed})^2\}^{1/2}}{(N-3)^{1/2}} \quad (3)$$

The data were analyzed by using the Fuoss – Onsager equation (Fuoss, 1957). It can be readily seen from Table (1) and Figure (1) that, Λ_0 for Trimethylsulfonium Bromide and Trimethylsulfonium Iodide, in acetonitrile-water mixtures were found to exhibit minima at 18 % acetonitrile for the two salts. The occurrence of minimum value of Λ_0 is unexpected behavior, since on decreasing the dielectric constant, the ionic mobility is hindered and ion-pair formation is more possible, so Λ_0 should decrease with the decrease of dielectric constant. The viscosity of the medium will affect the mobility of the ions. As the viscosity of the medium is increased, the ion mobility will decrease and then the ion mobility will increase as the viscosity of the medium decrease. This explains the unexpected behavior of Λ_0 as a function of the dielectric constant and the viscosity of the medium. A. E. Mahgoub and A. Lasson, (1975) have reported similar behavior for Λ_0 in case of rubidium iodide in acetonitrile – water mixtures at 25°C. The values of Λ_0 of lithium nitrate and sodium nitrate, in acetonitrile – water mixtures at 25°C (Sanchez, 1989), are found to decrease as the percentage of acetonitrile increase in the mixture up to a certain limit and then increase again. This is in accordance with our experimental observations.

M. S. k. Niazi and A. Khan, (1992) have reported similar behavior for Λ_0 in case of sodium perchlorate and sodium benzoate in acetonitrile – water mixtures. The values of Λ_0 for both salts, in acetonitrile – water mixtures, decreased with increasing the percentage of acetonitrile in the mixture, up to 22.7 mole percentage for sodium perchlorate and 10.0 mole percentage for sodium benzoate. Above these limits Λ_0 increased with further addition of acetonitrile. El-Hammamy et al., (2016) have measured the conductance of sodium diethyldithiocarbamate in acetonitrile-water mixtures at 25°C. The values of Λ_0 are found to decrease as the percentage of acetonitrile increase in the mixture up to a certain limit 30% and then increase again. The plot of a° , J versus $1/D$ the dielectric constant in Figures (2, 3) shows a minimum at specific dielectric constant for the two studied salts in acetonitrile-water mixtures. The initial slight decreases in a° for the two salts in acetonitrile-water mixtures, can be explained on the basis that, the strength of hydrogen bonds between ions and water molecules was strongly affected by adding small amounts of acetonitrile. On increasing acetonitrile content, water-water interactions are broken down and replaced by weaker acetonitrile-water interactions. This was in agreement with the measured endothermic heat of mixing (Accascina, 1967) and then a slight increase in a° values was observed. The increase in $\log K_A$ vs. $1/D$ plots, shown in Figure (4), for trimethylsulfonium bromide and trimethylsulfonium iodide in acetonitrile – water mixtures, may be explained on the basis that, the dielectric constant decreases with increasing the acetonitrile content as shown in Table (2). This increase in $\log K_A$ versus $1/D$ plots shows the dominance of electrostatic interaction and may be due to solute – solvent interaction. The trend of K_A in the present work was explained in the light of the U term as represented in the following equation (Accascina, 1967):

$$\ln K_A = \ln (4\pi N a^3 / 3000) + (e^2 / a^\circ kT) + U \quad (4)$$

where,

$$U = \Delta S / k - E_s / kT \quad (5)$$

The factor E_s/kT introduced by Gilkerson (1956) indicates the ion-dipole interaction energy, which differs when ion pairs are taken into consideration. The entropy term $\Delta S/k$ refers to the entropy change due to various arrangements of solvent molecules around free ion and ion pairs.

Table 1. Characteristic parameters for trimethylsulfonium bromide and trimethylsulfonium iodide in acetonitrile - water mixtures at 25°C

Wt%	D	10 ³ /D	Λ_{∞}	J	a°	K_A	log K_A	σ_A
Trimethylsulfonium Bromide								
10	74.66	13.3940	141.43	389.96	6.2	107.32	2.0306	0.0971
20	70.48	14.1884	134.25	403.30	6.1	122.27	2.0873	0.0705
30	65.78	15.2021	148.49	552.38	6.3	179.57	2.2542	0.0559
40	60.20	16.6112	155.81	727.25	6.4	247.30	2.3932	0.0479
50	55.70	17.9533	162.51	920.49	6.5	316.29	2.5001	0.0787
60	50.77	19.6966	169.30	1210.2	6.6	394.46	2.5960	0.0972
70	46.52	21.4961	176.32	1590.2	6.7	476.11	2.6777	0.0443
Trimethylsulfonium Iodide								
10	74.66	13.3940	138.88	425.66	6.7	208.06	2.3181	0.0381
20	70.48	14.1884	131.61	455.03	6.6	243.3	2.3861	0.0488
30	65.78	15.2021	147.41	599.78	6.8	283.62	2.4527	0.0495
40	60.20	16.6112	154.57	772.53	6.9	333.05	2.5225	0.0295
50	55.70	17.9533	161.34	978.41	7.0	382.04	2.5821	0.0800
60	50.77	19.6966	167.65	1290.8	7.1	457.39	2.6602	0.0489
70	46.52	21.4961	175.01	1679.6	7.2	540.43	2.7327	0.0099

Table 2. Calculated values of K_2 and U for trimethylsulfonium bromide and trimethylsulfonium Iodide in acetonitrile – water mixtures at 25°C

wt%	K_A	K_1	K_2	U
Trimethylsulfonium Bromide				
10	107.32	2.0150	52.2595	3.9751
20	122.27	2.1057	57.0656	4.0615
30	179.57	2.4356	72.7249	4.3003
40	247.30	2.8283	86.4356	4.4709
50	316.29	3.2527	96.2364	4.5771
60	394.46	3.8568	101.2744	4.6276
70	476.11	4.5744	103.0801	4.6451
Trimethylsulfonium Iodide				
10	208.06	2.3233	88.5536	4.4948
20	243.30	2.4163	99.6871	4.6120
30	283.62	3.1899	103.407	4.6482
40	333.05	3.6375	104.027	4.6542
50	382.04	4.2681	106.163	4.6743
60	457.39	5.0107	106.855	4.6807
70	540.43			

Table 3. Calculations of radii of the ions for trimethylsulfonium bromide and trimethylsulfonium iodide in acetonitrile - water mixtures at 25°C:

wt %	$\Lambda_{\infty} \eta_{\infty}^{(1)}$	$\lambda_{\infty}^{-} \eta_{\infty}^{(1)}$	$\lambda_{\infty}^{+} \eta_{\infty}^{(1)}$	$R^{- (2)}$	$R^{+ (2)}$	$R^{+}+R^{- (2)}$	$a^{\circ (2)}$
Trimethylsulfonium Bromide							
10	1.3860	0.8533	0.5281	0.9601	1.5514	2.5116	6.2
20	1.3035	0.8026	0.4963	1.0209	1.6509	2.6718	6.1
30	1.3542	0.8338	0.5188	0.9827	1.5792	2.5620	6.3
40	1.3150	0.8096	0.5036	1.0120	1.6269	2.6389	6.4
50	1.2171	0.7494	0.4663	1.0933	1.7570	2.8503	6.5
60	1.1089	0.6827	0.4243	1.2001	1.9310	3.1311	6.6
70	1.0103	0.6220	0.3870	1.3172	2.1170	3.4342	6.7
Trimethylsulfonium Iodide							
10	1.3610	0.8373	0.5281	0.9785	1.5514	2.5300	6.7
20	1.2779	0.7862	0.4963	1.0421	1.6509	2.6931	6.6
30	1.3443	0.8271	0.5188	0.9906	1.5792	2.5699	6.8
40	1.3045	0.8026	0.5036	1.0209	1.6269	2.6478	6.9
50	1.2084	0.7434	0.4663	1.1021	1.7570	2.8591	7.0
60	1.0981	0.6755	0.4243	1.2128	1.9310	3.1439	7.1
70	1.0028	0.6169	0.3870	1.3281	2.1170	3.4451	7.2

(1) $\text{ohm}^{-1} \text{equiv}^{-1} \text{cm}^2 \text{p}$ (2) A°

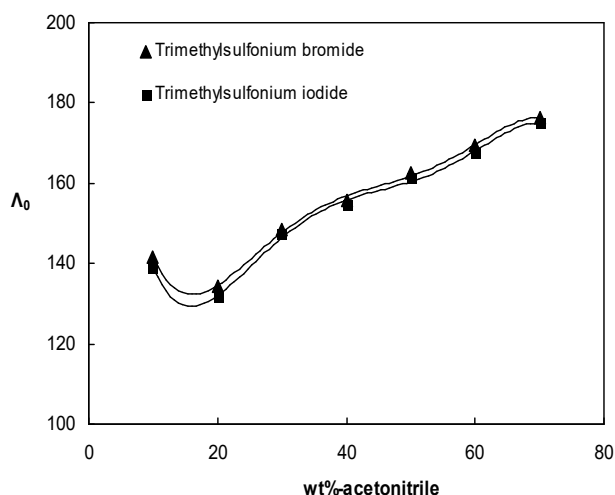


Figure 1. Variation of Λ_0 of trimethylsulfonium salts with the composition of acetonitrile - water mixtures

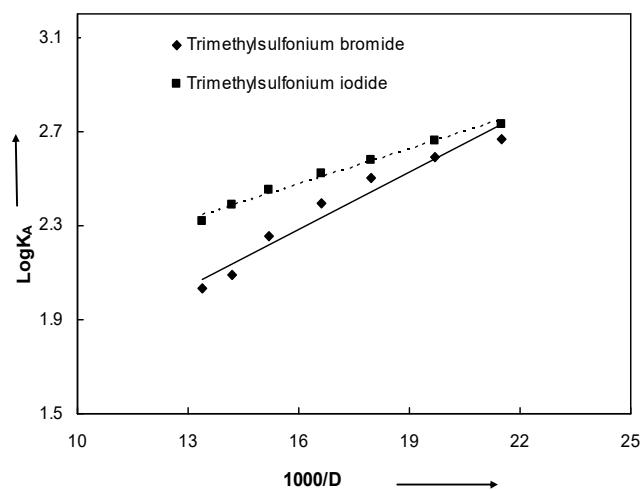


Figure 4. Variation of $\log K_A$ with dielectric constant of Trimethylsulfonium Salts in acetonitrile-water mixtures

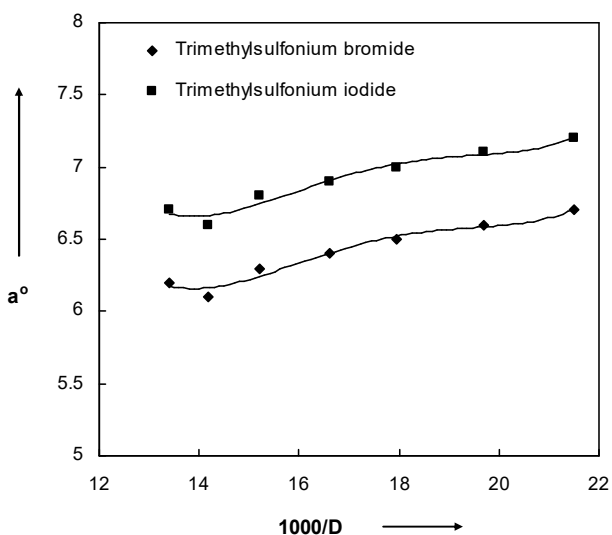


Figure 2. Variation of a° with dielectric constant of trimethylsulfonium salts in acetonitrile - water mixtures.

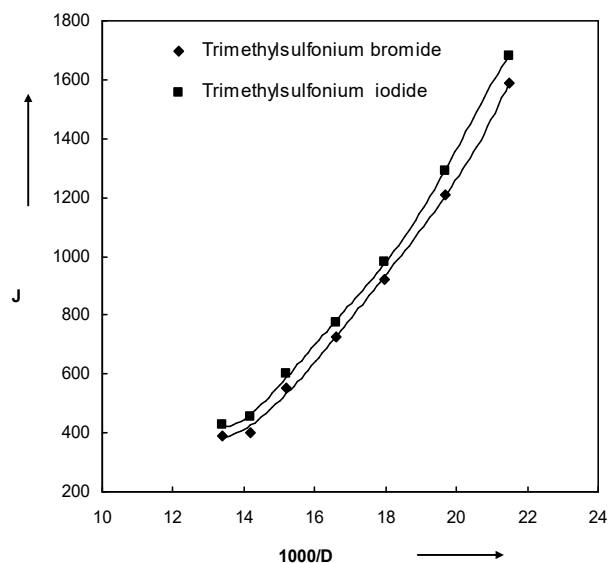


Figure 3. Variation of J with dielectric constant of trimethylsulfonium salts in acetonitrile - water mixtures.

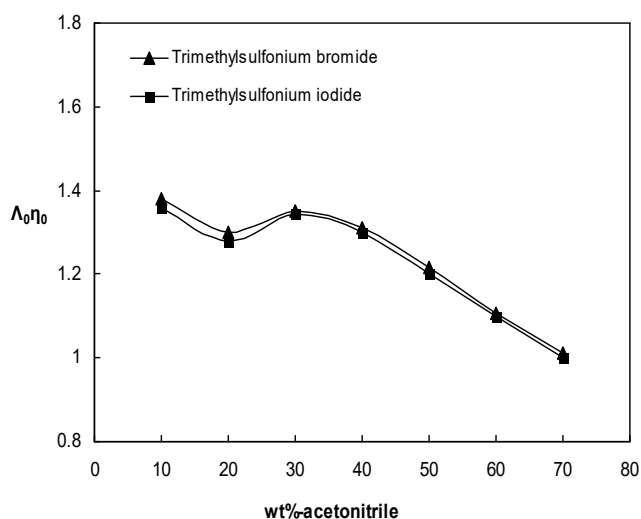
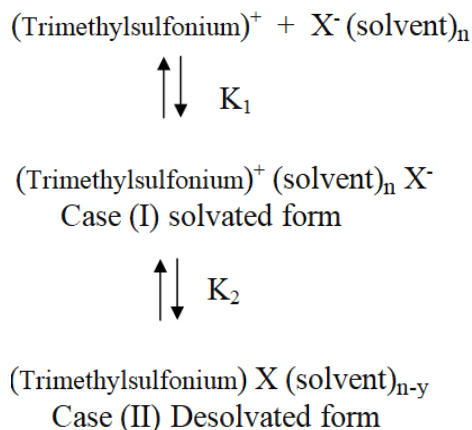


Figure 5. Variation of Walden Product with composition of acetonitrile-water mixtures.

From Table (2), it is evident that U increases as the acetonitrile weight percentage increases. This approves that, the entropy term increases with increasing weight percentage of acetonitrile. Eventually, the solvent separated ion-pair model can be applied (Evans, 1969). The association steps are illustrated in the following scheme:



Where y = number of escaping solvent molecules from solvation.

Thus, the association constant K_A is obtained from the conductance measurements according to the equation:

$$K_A = K \frac{[C_{(\text{ion-pairs})}]}{[C_{(\text{Trimethylsulfonium}^+)}][C_{X^- (\text{solvent})}]} = K_1(1 + K_2) \quad (6)$$

where $K_1 = 4 \pi N a^3 e^b / 3000$ and $b = e^2 / a^0 D T k$ then K_2 can be calculated.

From the data given in Table (2), it was clear that the values of K_2 increase with decreasing the dielectric constant. This means; as the dielectric constant decreases, the ion-pair prefers the desolvated form (II) more than solvated form (I).

Figure (5) shows that, the Walden Product $\Lambda_0 \eta_0$, as a function of solvent composition for trimethylsulfonium bromide and iodide in acetonitrile-water mixtures at 25°C, varies in the usual manner, i.e. decreases with decreasing the dielectric constant. This is in accordance with general finding on several small sizes (Uni-Univalent) (Lind, 1961; Kunze, 1963) and (Bi-Bivalent) (Atkinsen, 1964) systems and can be attributed to ion-solvent relaxation drag (Fuoss, 1959; Zwanzig, 1963).

Radii of ions: The electrostatic radii R^+ and R^- were calculated by using Stokes' equation:

$$R^\pm = 0.8194 \times 10^{-8} / \lambda_\infty^\pm \eta_0, \quad (7)$$

The application of Stokes' equation depends on the determination of the ionic conductance. According to Fuoss assumption³², the ionic equivalent conductance for cations and anions in acetonitrile-water mixtures can be calculated as transport number is independent on the solvent composition. These values are summarized in Table (3).

From Table (3) It can be seen easily that, for trimethylsulfonium bromide and iodide R^+ and R^- increase on decreasing the dielectric constant. On comparing the summation of electrostatic radii ($R^+ + R^-$) with the closest distance of approach \hat{a} , which was previously derived using Fuoss Onsager equation, one can observe that \hat{a} is always larger than electrostatic radii ($R^+ + R^-$), obtained from Stokes' equation in acetonitrile-water mixtures due to the solvation of ions.

Conclusion

This paper aims to shed light on the association process of the organic compound: trimethylsulfonium halides (bromide and iodide); which has been interpreted by solvent separated – ion pair model. Moreover, the limiting equivalent conductance (Λ_0) of trimethylsulfonium halides in mixtures of acetonitrile-water at 25°C was discussed in details. By plotting the extrapolation of Λ against $C^{1/2}$, preliminary values of Λ_0 were estimated. Consequently, more precise values of Λ_0 were resulted by applying Fuoss-Kraus-Shedlovsky equation. Finally, more accurate values of Λ_0 , J (function of a), \hat{a} and K_A

were obtained from Fuoss-Onsager equation. A comparison between the summation of electrostatic radii ($R^+ + R^-$) and the closest distance of approach \hat{a} was done; it was observed that \hat{a} is always larger than electrostatic radii ($R^+ + R^-$) due to the solvation of ions.

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