



REVIEW ARTICLE

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

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Conductance of trimethylsulfonium halides (bromide and iodide) is measured at 25°C in methanol-water mixtures (44.94<D<73.92). 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.

Keywords:

Trimethylsulfonium Halides, Electrical Conductance, Ion-Pair Formation.

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INTRODUCTION

In recent studies on the conductivity of several alkyl ammonium halides in methanol and ethanol, Kay and his co-workers (Kay, 1965) obtained values of association constant (K_A) higher than those expected by using the Bjerrum-Fuoss theory (Bjerrum, 1926). They explained their results on the basis of the hypothesis that the ion-pair association process is affected by the particular structure of the alcohol. Studies on various electrolytes in alcohol - dipolar aprotic solvent mixture such as methanol-acetonitrile (Conti, 1968), methanol-pyridine (Conti, 1968) and ethanol-acetone (Pistoia, 1968) gave surprising results for K_A values, which were explained by assuming that changes in alcohol structure affect K_A value much more than the change in dielectric constant. Miyoshi, (1972) measured the conductance of Bis (2,9-dimethyl 1,10 phenanthroline) copper 1 perchlorate in normal alcohols and ketones at 25°C. He found that the plot of $\log K_A$ versus $1/D$ give a curvature. This behaviour was also found in dioxane –water mixtures (Miyoshi, 1973), methanol –water mixtures (EI-Hammamy, 1989), ethanol –water mixtures (EI-Hammamy, 1995) and n-propanol –water mixtures (EI-Hammamy, 1991) at 25°C. It has been explained generally as being due to certain solute – solvent interaction. In the present work, trimethylsulfonium halides (bromide and iodide) are selected as electrolytes with large cation size.

The effect of cation size on the conductance of the salts can be discussed from variation of Λ_0 , K_A and a° values. The conductance measurements in methanol – water mixtures can also be analyzed using the Fuoss-Onsager equation (Fuoss, 1959) 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 ($\text{Me}_3\text{S}.\text{Br}$) and trimethylsulfonium iodide ($\text{Me}_3\text{S}.\text{I}$) 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 CO_2 by sodalime tubes. Its specific conductance $\%$ amounted to $(2-7 \times 10^{-6}) \text{ ohm}^{-1}\text{cm}^{-1}$.

Methanol: Analar analytical reagent methanol (BDH) was used without further purification. The specific conductance $\%$ for methanol were found to be $(1.47- 2.21 \times 10^{-6}) \text{ ohm}^{-1}\text{cm}^{-1}$.

Properties of Solvent Mixtures: Densities (d) of mixtures, viscosities (η) of mixtures and dielectric constants (D) of the

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methanol-water mixtures were used as reported in the literatures (El-Hammamy, 2013). 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 methanol - 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):

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

where N is the number of experimental points.

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 methanol-water mixtures were found to exhibit minima at 30 % methanol 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. N. G. Foster and E. S. Amis (Foster, 1956), have reported similar behavior in case of tetraethylammonium picrate in methanol - water and ethanol - water mixtures (Whoton, 1958) and for potassium chloride in methanol - water systems (Foster, 1955). Sadek et al. (1977), have obtained similar behavior for Λ_0 in case of s-alkylisothiuronium iodides in methanol - water mixtures at 25°C.

El - Hammamy et al. (2013); El-Hammamy, 1986; El-Hammamy, 1991, have obtained similar behavior for Λ_0 in case of N-N-diphenyl-s-alkylisothiuronium bromides in methanol-water (El-Hammamy, 1986) at 25°C, Co (II) complexes of acetone thiosemicarbazone halides in methanol - water (El-Hammamy, 1991) at 25°C, acetylcholine halides and perchlorate in methanol - water (El-Hammamy, 1989) at 25°C, s-acetylthiocholine halides and perchlorate in ethanol - water (El-Hammamy, 1995) at 25°C, and also in case of s-acetylthiocholine halides and perchlorate in methanol - water (El-Hammamy, 2013) at 25°C.

Kawana and El -Hammamy (2002), have obtained similar behavior for Λ_0 in case of S -acetylthiocholine bromide in n-propanol - water mixtures at 25°C, which exhibits smooth curve and Λ_0 decrease with increasing n-propanol concentration, i.e., with decreasing dielectric constant of the medium. 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 methanol-water mixtures. The initial slight decreases in a° for the two salts in methanol-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 methanol (i.e. a° decrease to minimum value).

On increasing methanol content, depolymerization occurs and an increase of 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 methanol - water mixtures, may be explained on the basis that, the dielectric constant decreases with increasing the methanol 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):

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

$$\text{where, } U = \Delta S / k - E_s / kT \quad (5)$$

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

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

Wt%	D	10 ³ /D	Λ _s	J	a ⁺	K _A	log K _A	σ _A
Trimethylsulfonium Bromide								
10	73.92	13.5281		346.82	5.9		1.9215	0.0555
20	69.21	14.4487	125.96	365.45	5.7	83.482	1.9835	0.0332
30	64.59	15.4822	123.21	389.01	5.4	96.290	2.1672	0.0299
40	59.77	16.7308	120.48	475.37	5.5	146.98	2.2392	0.0113
50	54.76	18.2615	121.60	602.51	5.6	173.50	2.3370	0.0456
60	49.84	20.0642	122.72	778.97	5.7	217.32	2.4293	0.0660
70	44.94	22.2518	123.09	1039.4	5.8	268.76	2.5353	0.0795
			124.89			343.08		
Trimethylsulfonium Iodide								
10	73.92	13.5281	122.01	368.83	6.5	103.41	2.0145	0.0959
20	69.21	14.4487	119.24	385.42	6.3	120.26	2.0801	0.1212
30	64.59	15.4822	117.33	435.71	6.2	173.40	2.2390	0.0374
40	59.77	16.7308	120.10	532.57	6.3	230.36	2.3624	0.0308
50	54.76	18.2615	121.62	677.03	6.4	298.93	2.4755	0.0376
60	49.84	20.0642	122.78	876.12	6.6	369.71	2.5678	0.0475
70	44.94	22.2518	123.96	1168.1	6.7	459.29	2.6620	0.0306

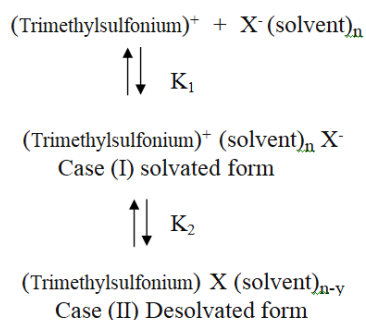
Table 2. Calculated values of K₂ and U for trimethylsulfonium bromide and trimethylsulfonium iodide in methanol – water mixtures at 25°C:

wt%	K _A	K ₁	K ₂	U
Trimethylsulfonium Bromide				
10				
20	83.482	1.8703	43.6345	3.7985
30	96.29	1.9313	48.8558	3.9091
40	146.98	1.9781	73.3024	4.3081
50	173.50	2.3052	74.2640	4.3210
60	217.32	2.7509	77.9988	4.3694
70	268.76	3.3540	79.1296	4.3836
	343.08	4.2192	80.3122	4.3982
Trimethylsulfonium Iodide				
10				
20	103.41	2.2212	45.5538	3.8406
30	120.26	2.2778	51.7958	3.9664
40	173.40	2.4335	70.2548	4.2662
50	230.36	2.7903	81.5562	4.4134
60	298.93	3.2679	90.4736	4.5160
70	369.71	3.9791	91.9128	4.5316
80	459.29	4.8728	93.2543	4.5459

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

wt %	Λ _s η _v ⁽¹⁾	λ _v ⁻ η _v ⁽¹⁾	λ _v ⁺ η _v ⁽¹⁾	R ⁻ (²)	R ⁺ (²)	R ⁺ +R ⁻ (²)	a ^o (²)
Trimethylsulfonium Bromide							
10	1.4554	0.8961	0.5508	0.9143	1.4874	2.4017	5.9
20	1.6990	1.0461	0.6428	0.7832	1.2747	2.0579	5.7
30	1.8553	1.1423	0.7041	0.7172	1.1637	1.8810	5.4
40	1.9310	1.1889	0.7379	0.6891	1.1103	1.7995	5.5
50	1.8874	1.1621	0.7225	0.7050	1.1340	1.8391	5.6
60	1.7195	1.0587	0.6603	0.7739	1.2407	2.0147	5.7
70	1.5299	0.9419	0.5860	0.8698	1.3980	2.2679	5.8
Trimethylsulfonium Iodide							
10	1.4098	0.8673	0.5508	0.9446	1.4874	2.4321	6.5
20	1.6443	1.0116	0.6428	0.8099	1.2747	2.0846	6.3
30	1.8068	1.1116	0.7041	0.7370	1.1637	1.9008	6.2
40	1.9071	1.1733	0.7379	0.6983	1.1103	1.8087	6.3
50	1.8705	1.1508	0.7225	0.7120	1.1340	1.8461	6.4
60	1.7152	1.0552	0.6603	0.7764	1.2407	2.0172	6.6
70	1.5185	0.9342	0.5860	0.8770	1.3980	2.2751	6.7

(1) ohm⁻¹ equiv⁻¹ cm² p(2) Å^o



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:

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

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

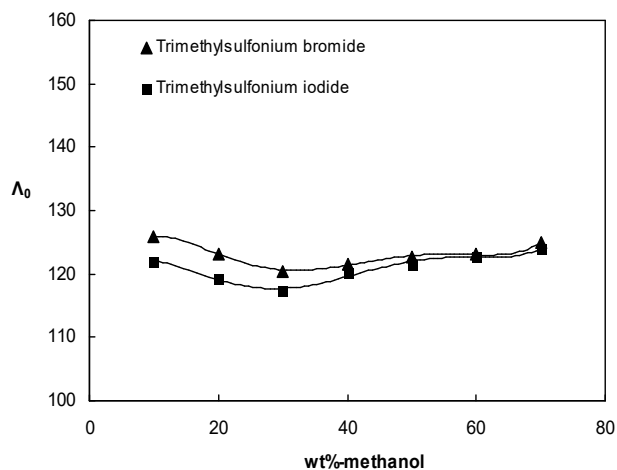


Figure 1. Variation of Λ_0 of Trimethylsulfonium Salts with the composition of methanol - water mixtures

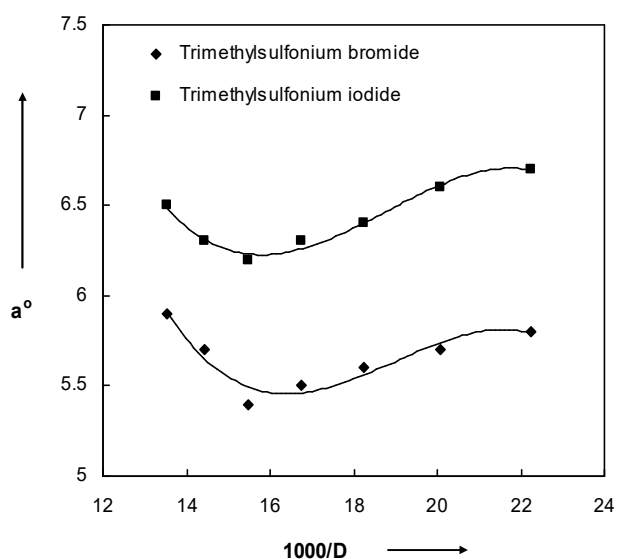


Figure 2. Variation of a° with dielectric constant of Trimethylsulfonium Salts in methanol - water mixtures

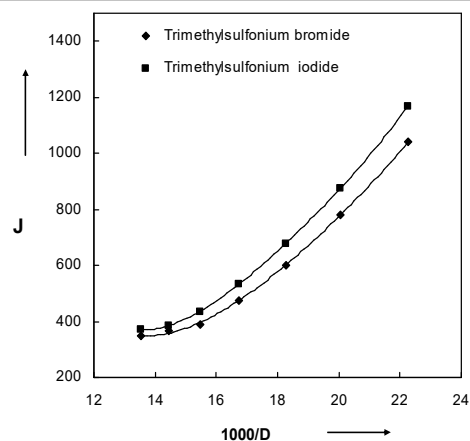


Figure 3. Variation of J with dielectric constant of Trimethylsulfonium Salts in methanol - water mixtures.

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).

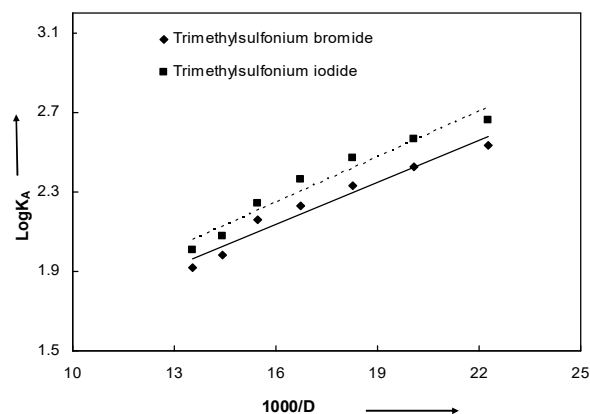


Figure 4. Variation of $\log K_A$ with dielectric constant of Trimethylsulfonium Salts in methanol - water mixtures

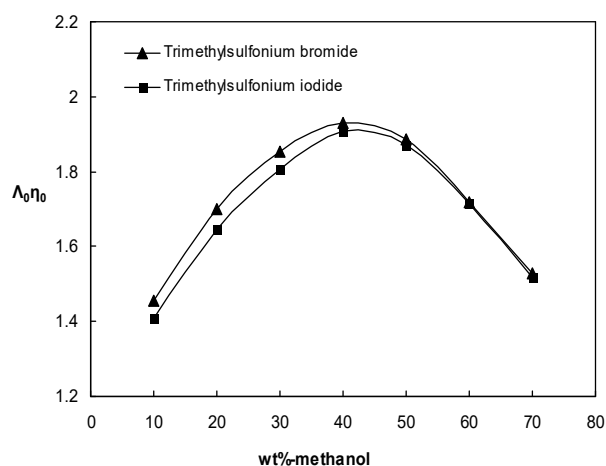


Figure 5. Variation of Walden Product with composition of methanol - water mixtures

Figure (5) shows that, the Walden Product $\Lambda_0 \eta_0$, as a function of solvent composition for trimethylsulfonium bromide and iodide in methanol-water mixtures at 25°C, the values of $\Lambda_0 \eta_0$ increase with the increase in wt% up to about 40% and then it

decrease rapidly. The variation of Walden Product $\Lambda_0\eta_0$ reflects the change of total solvation (Raju, 1982). The decrease of the Walden product indicates the increase of the hydrophobic solvation with increasing concentration of methanol (70%).

Radii of ions

The electrostatic radii R^+ and R^- were calculated by using

Stokes' equation:

$$R^\pm = 0.8194 \times 10^{-8} / \lambda_0^\pm \eta_0 \quad (7)$$

The application of Stokes' equation depends on the determination of the ionic conductance. According to Fuoss assumption (Fuoss, 1958), the ionic equivalent conductance for cations and anions in methanol-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 methanol-water mixtures due to the solvation of ions. Hughes and Hartly (Hughes, 1933), observed the same trend in electrostatic radii for Li^+ , Na^+ , K^+ , $\text{N}(\text{C}_2\text{H}_5)_4^+$, Cl^- , Br^- , I^- , ClO_4^- and picrate ions in alcohol-water and in acetone-water mixtures.

Kortium and Welier (Kortium, 1950), calculated R 's for perchlorate ion (P_i) in both alcohol and water solutions. The results were: $R_{\text{P}_i^-}(\text{H}_2\text{O}) = 3.33 \text{ \AA}$, in (MeOH) = 3.7 \AA and in (EtOH) = 3.8 \AA . The authors also found that R 's for Li^+ in ethanol-water increases from water to ethanol. 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, \hat{a} was always greater except in case of rich methanol content. This behavior can be explained using Nightingale's (Nightingale, 1959) conclusion, for water and mixed aqueous solvents of high dielectric constant and high viscosity, Stokes' equation gives inappropriate small value due to discontinuity of the medium.

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 methanol-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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