

Electrochemical Studies on Ion Pairs Formation of Trimethylsulfonium Halides in Water at Different Temperatures

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Abstract- The conductance data of trimethylsulfonium halides (bromide and iodide) in water at various temperatures (25, 30, 35 and 40°C) are presented. The results were construed by applying the Fuoss-Onsager equation to obtain the parameters: equivalent conductance at infinite dilution (Λ_0), the distance of closest approach (a°) and association constant (K_A). In the light of the solvent separated-ion pair model, the K_A trend is discussed. A comparison was done between the value of a° and the sum of calculated electrostatic Stokes' radii R^+ and R^- . The thermodynamic functions (ΔH° , ΔG° , ΔS°) and the activation energy (ΔE_s) were determined; the Λ_0 values for trimethylsulfonium halides (Br⁻ and I⁻) were noticed to increase gradually with the dramatic increase in temperature referring to less solvation or higher ions mobility. Negative values of Gibbs free energy change ΔG° for trimethylsulfonium halides (Br⁻ and I⁻) indicate that the association process is preferable than the dissociation process. The positive value of (ΔH°) points to that the association process is endothermic. Entropy change (ΔS°) values for trimethylsulfonium halides (Br⁻ and I⁻) were positive which means that the solvation of ion-pair decreases emulated to that of the free ion.

Keywords- Trimethylsulfonium Halides, Limiting Equivalent Conductance (Λ_0), Ion Association, Activation Energy, Thermodynamic Functions

I. INTRODUCTION

Measuring the transport properties as conductance at low concentrations helps in exploring the ionic solvation besides obtaining reliable values of conductance at infinite dilution [1]. These properties are affected by (i) size of the ions, (ii) any modulation in the structure of the solvent and (iii) strong ion-solvent interactions.

Conductivity method is used to test the process water quality in those applications which require ultrapure water as in microelectronics, pharmaceutical, waste water treatment, sea water desalination, etc. [2,3]

The electrical conductivities study of dilute solutions whether for salts or complexes is considered important method for studying the ion-pair or multiple-ion association in aqueous solutions, non-aqueous or mixed ones [4-7]. Furthermore, measuring conductivity was used to study the solute-solvent

interaction of some electrolytic solutions and estimate the hydration free energy [8]. The aim of the present work is to determine trimethylsulfonium halides (Br⁻ and I⁻) conductance values that measured in water at various temperatures (25, 30, 35 and 40°C). The nature of the ion-ion and ion-solvent interaction for trimethylsulfonium salts were discussed by evaluating the limiting equivalent conductance (Λ_0), the association constant (K_A) and (a°) which expresses the solvation. The effect of temperature mutation on the association constant has been studied. Thus, the thermodynamic functions (ΔH° , ΔG° , ΔS°) and activation energy (ΔE_s) were obtained.

II. EXPERIMENTAL

All salts were highly purified reagent grade and used without further purification. where trimethylsulfonium bromide (Me₃S.Br) and trimethylsulfonium iodide (Me₃S.I) are Analar analytical reagent "BDH".



Conductivity water 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 at varied temperatures (25, 30, 35 and 40°C) amounted to $(2-7 \times 10^{-6})$ ohm⁻¹cm⁻¹.

All solutions were prepared by weight. trimethylsulfonium salts were weighed on microbalance which reads to ± 0.1 mg. Dilution into the cell was executed by dropping the solvent via weighing pipette. The experimental values of conductance were measured by Conductivity Bridge instrument model: Crison GLP31+ (Conductivity Measurement error $\leq 0.5\%$ and the reproducibility: $\pm 0.1\%$) and a cell with bright platinum electrodes has a cell constant for dilute solutions ($K=0.1$ cm⁻¹). The temperature is kept constant to within $\pm 0.1^\circ$ C using a water ultra thermostat. The dielectric constants ($D_{25^\circ} = 78.54$, ($D_{30^\circ} = 76.73$, ($D_{35^\circ} = 74.80$, ($D_{40^\circ} = 73.15$, respectively. In all calculations, the used solvent constants were taken as stated ⁹⁻¹¹, i.e., densities ($d_{25^\circ} = 0.99707$ g.cm⁻³, ($d_{30^\circ} = 0.99568$ g.cm⁻³, ($d_{35^\circ} = 0.99406$ g.cm⁻³, ($d_{40^\circ} =$

0.99220 g.cm⁻³, respectively, the viscosities (η_{25°) = 0.8903 $\times 10^{-2}$ P, (η_{30°) = 0.7975 $\times 10^{-2}$ P and (η_{35°) = 0.7194 $\times 10^{-2}$ P, (η_{40°) = 0.6531 $\times 10^{-2}$ P, respectively.

III. RESULTS AND DISCUSSION

A. Conductance of trimethylsulfonium halides (bromide and iodide) in water at several temperatures:

The measured equivalent conductance data are shown in Tables (1-2). By plotting the extrapolation of Λ against $C^{1/2}$, an approximate value of Λ_0 was obtained. More precise values of Λ_0 were resulted from the following Fuoss-Kraus-Shedlovsky (F.K.S) equation:

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

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 $(CAS_{(z)}f^2)$ 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 equation¹². 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[13]:

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

where N is the number of experimental points.

Figures (1-2) displays the variation of J with a° for trimethylsulfonium halides (bromide and iodide) in water at 25, 30, 35 and 40°C. Through the knowledge of the average value of J , The average value of a° could be calculated by interpolation. This J value was obtained from the computer reading, where J is being a function of a° and has the following equation[12]:

$$J = \sigma_1 \Lambda_0 + \sigma_2, \quad (4)$$

Where σ_1 and σ_2 are the functions of J . The derived constants are represented in Tables (3-4) and it is observed that Λ_0 , K_A , a° for trimethylsulfonium bromide and trimethylsulfonium iodide increase with increasing the temperatures.

The values of Λ_0 decrease with increasing the size of the anion, in the order $\{\Lambda_0 \text{ trimethylsulfonium bromide} > \Lambda_0 \text{ trimethylsulfonium iodide}\}$, according to ionic equivalent conductance of anions.

K_A increases with decreasing the dielectric constant of the medium and increase with increasing the temperatures for the two salts; this was explained on the basis that, ionic mobility decrease as the dielectric constant of the medium decrease and hence the chance to form ion-pairs increases.

The values of K_A increases with increasing the size of the anion, in the order $\{K_A \text{ trimethylsulfonium iodide} > K_A \text{ trimethylsulfonium bromide}\}$, according to the electrostatic theory.

The trend of K_A in the present work was explained in the light of the U term as represented in the following equation [14]:

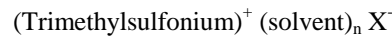
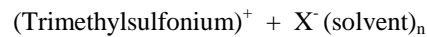
$$\ln K_A = \ln (4\pi N a^3 / 3000) + (e^2 / a^\circ DkT) + U \quad (5)$$

where,

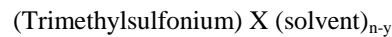
$$U = \Delta S / k - E_s / kT \quad (6)$$

$\Delta S / k$ is the entropy/Boltzmann constant ratio which explains the eventuality of the orientation of the solvent molecules around the free ions and E_s/kT is an energy relationship which includes the energy of the solvent molecules with respect to the free ions and ion-pairs. In case of trimethylsulfonium halides (bromide and iodide) in water, in Tables (5-6), the U term increases with increasing the temperature, i.e. the entropy term is more predominant than ion-dipole term but U term decreases with from bromide to iodide, i.e. the ion-dipole term is more predominant than entropy term.

Ultimately, the solvent separated ion-pair model can be applied [15]. In this model a multiple-step association was suggested as illustrated in the following scheme:



Condition (I) solvated pattern



Condition (II) Desolvated pattern

Where y = number of escaping solvent molecules from solvation.

Thus, the association constant is given by the following expression:

$$K_A = K \sum \frac{[C_{(ion-pairs)}]}{[C_{(\text{trimethylsulfonium})^+}][C_{X^-(\text{solvent})_n}]} = K_1(1 + K_2) \quad (7)$$

where $K_A = K \Sigma$ is obtained from the conductance measurements and since $K_1 = 4 \pi N a^3 e^b / 3000$ then K_2 can be calculated and $b = e^2 / a^\circ DkT$

In case of trimethylsulfonium bromide and iodide in water at different temperatures, the results compiled in Tables (5-6) indicated that K_2 increases with increasing the temperature, i.e. Ion-pair favored the desolvated pattern (condition II) than the solvated pattern (condition I).

1) Radii of ions

The electrostatic radii R^+ and R^- are given by Stokes' equation:

$$R^\pm = 0.8194 \times 10^{-8} / \lambda_o^\pm \eta_o \quad (8)$$

Where λ_o^+ or λ_o^- are obtained from the intercept of the straight line, resulting from the plots of Walden product $\Lambda_o \eta_o$ versus the reciprocal of the molecular weight as previously discussed [16].

From the data in Tables (7-8), it could be noticed that; in case of water at 25, 30, 35 and 40°C, the values of a^o were greater than electrostatic radii ($R^+ + R^-$) obtained from stokes equation. This was due to the solvation of ions.

B. Thermodynamic studies of trimethylsulfonium halides (bromide and iodide) in water from conductance measurements:

It is evident from Tables (9-10) that the values of Λ_o increase regularly with increase in temperature for trimethylsulfonium bromide and iodide, indicating higher mobility of the ions in all solvent systems studied. This is due to the fact that the increase in thermal energy results in greater bond breaking and also variation in vibrational, rotational and translational energy of molecules lead to higher frequency and higher mobility of ions¹⁷. In addition, it is clear that the association constant (K_A) values increase with increase in temperature due to decrease in dielectric constant of the medium [18].

Since the conductance measurements of an ion depend on its mobility, it is quite reasonable to treat the conductance data similar to the one that employed for the processes taking place with change of temperature [19], i.e.

$$\Lambda_o = A e^{-\Delta E_s / RT}$$

or

$$\log \Lambda_o = \log A - (\Delta E_s / 2.303RT) \quad (9)$$

where A is the frequency factor, R is the ideal gas constant and ΔE_s is the Arrhenius activation energy of transport processes.

The values of ΔE_s have been computed from the slope ($-\Delta E_s / 2.303RT$) of the plot of $\log \Lambda_o$ vs. $1/T$ and recorded in Tables (9-10) and Figures (3, 4). From the tables, the activation energy ΔE_s is positive value for the two salts in all solvents. Their values indicate the higher mobility of the ions in solution and hence higher Λ_o values.

The free energy change ΔG^o for the association process is calculated from equation¹⁹

$$\Delta G^o = -RT \ln K_A \quad (10)$$

It is evident From Tables (9-10), that the free energy change (ΔG^o) values are negative for the two salts (Br^- and I^-) in all solvent systems studied. This means that the association process is favored over the dissociation process in all solvent systems.

The values of (ΔG^o) become more negative with increasing the temperature. The increase in (ΔG^o) values for the two salts favors the transfer of the released solvent molecules into bulk solvent and leads to a larger (ΔG^o) values. The strengthening to the interionic association at higher temperature is largely caused by a decrease in the permittivity of the solvent [20].

The enthalpy change (heat of association) (ΔH^o) is obtained from the slope of the plot of $\log K_A$ versus $1/T$ Figures (5-6). The values of (ΔH^o) were calculated, where the slope equals ($-\Delta H^o / 2.303R$). The positive values of (ΔH^o) for the two salts show that the association processes are endothermic in nature. It was observed that (ΔH^o) values decrease from bromide to iodide salts. Positive and high (ΔH^o) values can be attributed to the interaction between ions [20].

The entropy change (ΔS^o) was calculated, from Gibbs-Helmholtz equation;

$$\Delta G^o = \Delta H^o - T \Delta S^o \quad (11)$$

The positive values of (ΔS^o) for the two salts indicate the randomness of ions in all solvent systems studied. As presented in Tables (9-10), values of (ΔS^o) were positive because of the decrease in the solvation of ion-pair compared to that of the free ion²¹⁻²³. This may be attributed to increase in the degree of freedom upon association, mainly due to the release of solvent molecules.

The primary factors which administer the entropy of electrolytes ion association are: the size and shape of ions, orientation of the solvent molecules around the ions, ions charge density, and to what extent the molecules of solvent penetrate inside the space of ions [24].

El-Hammamy et al. [25], have measured the conductance of cobalt (III) salt, bromopentammine salts (chloride, bromide and perchlorate) in water at different temperatures 25 → 35°C. The results were analyzed using Fuoss-Edelson equation [26], from which the values of Λ_o , a and K_A were obtained for the salts at different temperatures. It was found that, Λ_o and a increase with increasing the temperature while K_A decreases with increasing the temperature, for all salts of cobalt (III) salt, bromopentammine, according to electrostatic attraction theory. Thus, from the plot of $\log \Lambda_o$ versus $1/T$ for all salts of cobalt (III) in water at different temperatures, the positive values of ΔE_s have been evaluated, and also ΔH^o , ΔG^o , ΔS^o for the salts. It was found that, negative values of ΔH^o , ΔG^o , ΔS^o in water at different temperatures; negative value of ΔH^o indicated that ion association processes were exothermic in nature in all solvents at all temperatures. The solvated radii were also increased with

temperature indicating a higher solvation process due to increase in the electronic clouds around the solvated molecules because of the increase in their vibrational and rotational motion. The limiting equivalent conductance and dissociation degree were also increased as the temperature increased, indicating higher solvation process [26]. The negative values of different thermodynamic parameters ΔH° , ΔG° , ΔS° , for all salts studied in the used solvent, indicated that exothermic association process was less energy-consuming and more stabilized [25].

El-Hammamy et al. [27], have measured the conductance of cobalt (III) salt, chloropentammine chloride, in water at different temperatures 40 \rightarrow 60°C. The results were analyzed using Fuoss-Edelson equation²⁶, from which the values of Λ_0 and K_A were obtained for the salt at different temperatures. It was found that, Λ_0 and K_A increase with increasing the temperature. Thus, from the plot of $\log \Lambda_0$ versus $1/T$ for the salt of cobalt (III) in water at different temperatures, the positive value of ΔE_S has been evaluated, and also ΔH° , ΔG° , ΔS° for the salt. It was found that, ΔH° and ΔS° are positive at a particular temperature but ΔG° is negative, this may be due to the increase in association of ions and thus solvation process was less. Endothermic solvation needs energy to break the bonds around free ion and ion-pairs, i.e., endothermic solvation process and ΔS° is constant but ΔG° decreases in the negative value with increasing the temperature.

El-Hammamy et al. [28], have measured the conductance of 1:1 s-acetylthiocholine salts (Cl^- , Br^- , I^- and ClO_4^-) in water at different temperatures (25,30,35°C). The results were analyzed using Fuoss-Onsager equation¹², from which the values of Λ_0 , K_A and a° (solvation) were obtained. It was found that, Λ_0 and a° increase with increasing the temperature while K_A decreases with increasing the temperature, for all salts of s-acetylthiocholine, according to electrostatic attraction theory. The limiting equivalent conductance and dissociation degree were also increased as the temperature increased, indicating higher solvation process²⁶. The negative values of different thermodynamic parameters ΔH° , ΔG° , ΔS° , for all salts studied in the used solvent, indicated that exothermic association process was less energy-consuming and more stabilized [29].

El-Hammamy et al.[30], have measured the conductance of sodium diethyldithiocarbamate in water at different temperatures (25, 30, 35 and 40°C). The results were also analyzed using Fuoss-Onsager equation¹², from which the values of Λ_0 , K_A and a° (solvation) were obtained. It was found that Λ_0 and K_A increase with increasing the temperature. Thus from the plot of $\log \Lambda_0$ versus $1/T$, in methanol and water at different temperature, ΔE_S values have been evaluated. Also ΔH° , ΔG° and ΔS° have been evaluated. It was found that values of ΔG° are negative indicating that ions association process is favored over dissociation process in both solvent systems. With increasing the temperature, the negative values of ΔG° increase due to releasing solvent molecules from solvation shell into the bulk solvent. The positive values of ΔH° indicate endothermic association process. ΔS° positive values are due to the randomness of ions in the solvent system studied.

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TABLE I. CONDUCTANCE OF TRIMETHYLSULFONIUM BROMIDE IN WATER AT DIFFERENT TEMPERATURES

Trimethylsulfonium Bromide at 25°C			
104C	C1/2	106 μ S	Λ
13.1011	0.0362	134.23	102.4566
11.6406	0.0341	121.33	104.2293
10.4985	0.0324	111.03	105.7573
9.5627	0.0309	102.53	107.2185
8.8442	0.0297	95.63	108.1268
8.1941	0.0286	89.35	109.0411
7.6282	0.0276	83.93	110.0246
7.1244	0.0267	78.93	110.7873
Trimethylsulfonium Bromide at 30°C			
5.2825	0.0230	63.24	119.7144
4.7716	0.0218	57.74	121.0074
4.3818	0.0209	53.50	122.0940
4.0331	0.0201	49.59	122.9555
3.7399	0.0193	46.34	123.9039
3.4760	0.0186	43.34	124.6805
3.2572	0.0180	40.84	125.3831
3.0705	0.0175	38.71	126.0683
Trimethylsulfonium Bromide at 35°C			
5.8232	0.0241	62.46	107.2591
5.2689	0.0230	57.76	109.6238
4.8715	0.0221	54.26	111.3815
4.5154	0.0212	51.06	113.0782
4.2176	0.0205	48.36	114.6604
3.9709	0.0199	46.06	115.9937
3.7460	0.0194	43.86	117.0821
3.5375	0.0188	41.76	118.0472
Trimethylsulfonium Bromide at 40°C			
10.8780	0.0330	158.46	145.6698
9.8247	0.0313	144.36	146.9346
9.0089	0.0300	133.16	147.8088
8.2155	0.0287	122.26	148.8156
7.6181	0.0276	113.96	149.5901
7.0969	0.0266	106.66	150.2902
6.6538	0.0258	100.36	150.8298
6.2597	0.0250	94.76	151.3799

* equiv L⁻¹ ** ohm⁻¹ equiv⁻¹ cm²

TABLE II. CONDUCTANCE OF TRIMETHYLSULFONIUM IODIDE IN WATER AT DIFFERENT TEMPERATURES

Trimethylsulfonium Iodide at 25°C			
104C	C1/2	106 μ S	Λ
10.6535	0.0326	106.73	100.1829
9.4679	0.0308	96.43	101.8492
8.5686	0.0293	88.53	103.3187
7.8156	0.0280	82.03	104.9556
7.2291	0.0269	76.53	105.8636
6.7228	0.0259	71.63	106.5477
6.2794	0.0251	67.63	107.7008
5.9050	0.0243	63.93	108.2636
Trimethylsulfonium Iodide at 30°C			
3.1467	0.0177	27.38	87.0099
2.8203	0.0168	25.34	89.8463
2.5872	0.0161	23.74	91.7571
2.3820	0.0154	22.26	93.4492
2.2037	0.0148	21.02	95.3830
2.0452	0.0143	19.83	96.9551
1.9144	0.0138	18.76	97.9904
1.7952	0.0134	17.85	99.4272
Trimethylsulfonium Iodide at 35°C			
6.1952	0.0249	65.66	105.9843
5.7008	0.0239	61.66	108.1588
5.2378	0.0229	57.56	109.8925
4.8829	0.0221	54.46	111.5315
4.5705	0.0214	51.56	112.8098
4.2839	0.0207	48.86	114.0524
4.0345	0.0201	46.56	115.4024
3.8253	0.0196	44.56	116.4856
Trimethylsulfonium Iodide at 40°C			
4.3600	0.0209	53.66	123.0706
3.9596	0.0199	49.56	125.1624
3.6066	0.0190	45.86	127.1526
3.3097	0.0182	42.66	128.8902
3.0655	0.0175	39.96	130.3523
2.8532	0.0169	37.56	131.6376
2.6607	0.0163	35.36	132.8928
2.4977	0.0158	33.46	133.9594

* equiv L⁻¹ ** ohm⁻¹ equiv⁻¹ cm²

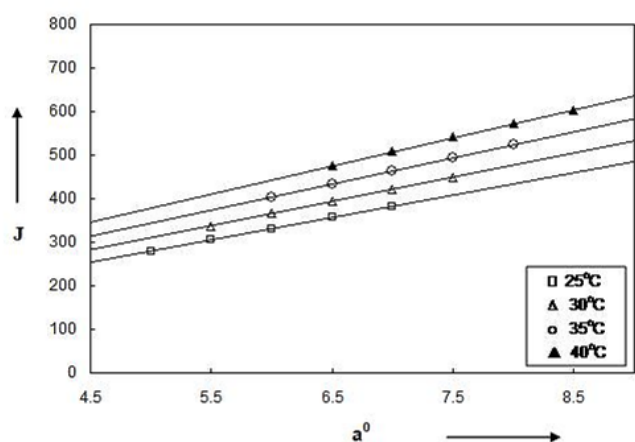


Figure 1. Variation of J and a° of Trimethylsulfonium bromide in water at different temperatures.

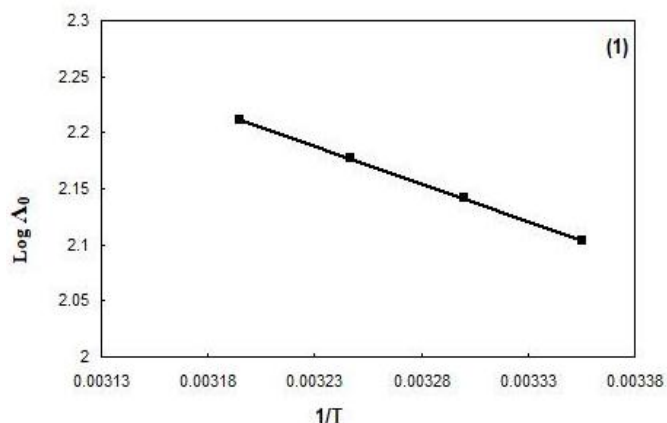


Figure 3. The variation of $\log \Lambda_0$ vs. $1/T$ for Trimethylsulfonium bromide in water at different temperatures.

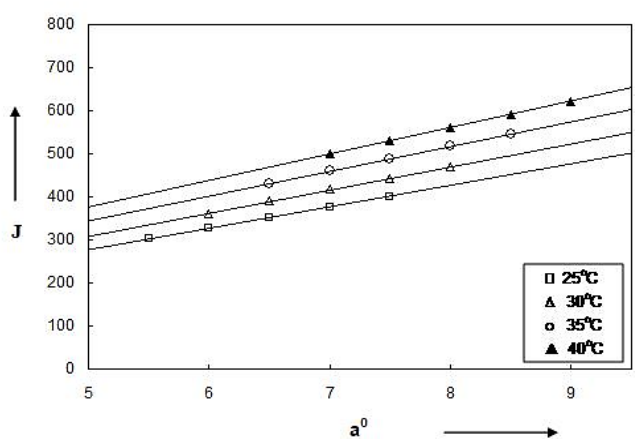


Figure 2. Variation of J and a° of Trimethylsulfonium iodide in water at different temperatures.

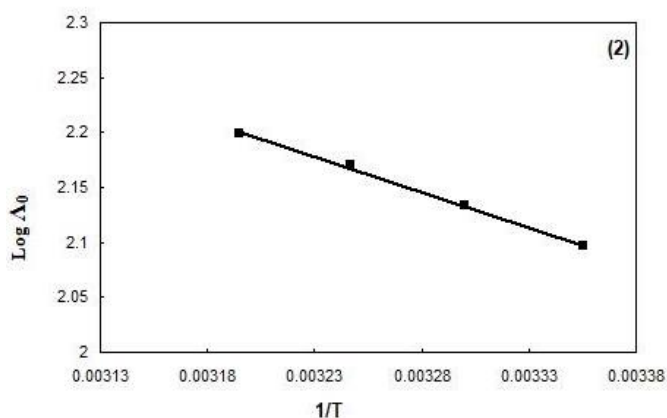


Figure 4. The variation of $\log \Lambda_0$ vs. $1/T$ for Trimethylsulfonium iodide in water at different temperatures.

TABLE III. THE CHARACTERISTIC PARAMETERS TRIMETHYLSULFONIUM BROMIDE IN WATER AT 25, 30, 35 AND 40°C DERIVED FROM FUOSS-ONSAGER EQUATION

Temperature	Λ° (ohm ⁻¹ equiv ⁻¹ cm ²)	J	K_A	a° (Å)	σ_Λ
25°C	126.91 ± 0.1958	325.51	440.24	6.0	0.0837
30°C	138.45 ± 0.1627	404.66	516.70	6.5	0.0749
35°C	150.30 ± 0.1328	476.21	645.11	7.0	0.1426
40°C	162.52 ± 0.1724	541.15	784.99	7.5	0.0356

TABLE IV. THE CHARACTERISTIC PARAMETERS FOR TRIMETHYLSULFONIUM IODIDE IN WATER AT 25, 30, 35 AND 40°C DERIVED FROM FUOSS-ONSAGER EQUATION

Temperature	Λ° (ohm ⁻¹ equiv ⁻¹ cm ²)	J	K_A	a° (Å)	σ_Λ
25°C	124.83 ± 0.4014	333.28	471.39	6.5	0.1897
30°C	136.01 ± 0.1554	417.70	576.10	7.0	0.1885
35°C	147.86 ± 0.1295	489.97	675.48	7.5	0.1521
40°C	158.24 ± 0.1036	564.38	812.88	8.0	0.0608

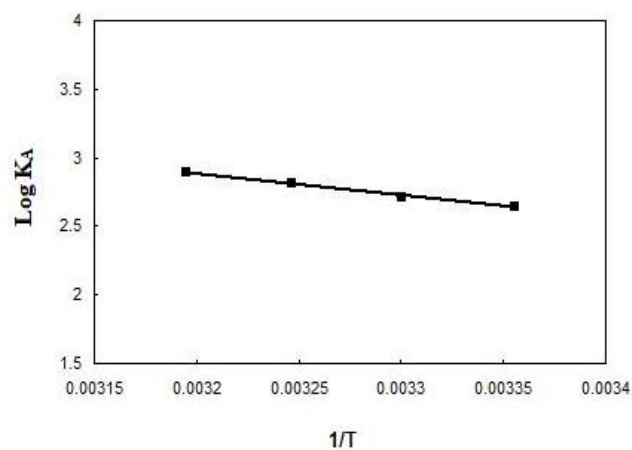


Figure 5. The variation of $\log K_A$ vs. $1/T$ for Trimethylsulfonium bromide in water at different temperatures.

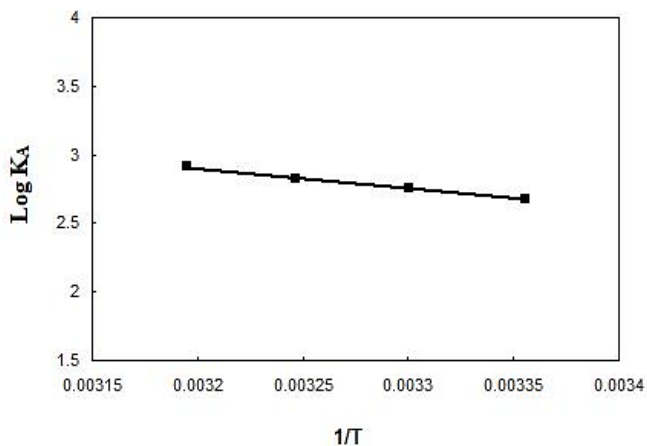


Figure 6. The variation of log K_A vs. $1/T$ for Trimethylsulfonium iodide in water at different temperatures.

TABLE V. CALCULATED VALUES OF K_2 AND U FOR TRIMETHYLSULFONIUM BROMIDE IN WATER AT 25, 30, 35 AND 40°C

Temperature	K_A	K_1	K_2	U
25°C	440.24	1.7875	245.2857	5.5064
30°C	516.70	2.0893	246.3018	5.5106
35°C	645.11	2.4336	264.0844	5.5800
40°C	784.99	2.8112	278.2338	5.6320

TABLE VI. CALCULATED VALUES OF K_2 AND U FOR TRIMETHYLSULFONIUM IODIDE IN WATER AT 25, 30, 35 AND 40°C

Temperature	K_A	K_1	K_2	U
25°C	471.39	2.0740	226.2802	5.4261
30°C	576.10	2.4115	237.8936	5.4760
35°C	675.48	2.7936	240.7905	5.4880
40°C	812.88	3.2106	252.1830	5.5341

TABLE VII. CALCULATIONS OF THE RADII OF THE IONS FOR TRIMETHYLSULFONIUM BROMIDE IN WATER AT 25, 30, 35 AND 40°C

Temperature	$\Lambda_s^{(1)}$	$\lambda^- \eta_s^{(2)}$	$\lambda^+ \eta_s^{(2)}$	$\lambda_s^{-(1)}$	$\lambda_s^{+(1)}$	$Av \lambda_s^+$	$R^+ (A^\circ)$	$R^- (A^\circ)$	$R^+ + R^-$	$a^\circ (A^\circ)$
25°C	126.91	0.7002	0.4309	78.65	48.26	48.405	1.9013	1.1702	3.0715	6.0
30°C	138.45	0.6858	0.4145	86.0	52.45	51.98	1.9766	1.1947	3.1713	6.5
35°C	150.30	0.6762	0.4023	94.0	56.30	55.93	2.0364	1.2117	3.2481	7.0
40°C	162.52	0.6674	0.3865	102.2	60.32	59.18	2.1200	1.2276	3.3476	7.5

TABLE VIII. CALCULATIONS OF THE RADII OF THE IONS FOR TRIMETHYLSULFONIUM IODIDE IN WATER AT 25, 30, 35 AND 40°C

Temperature	$\Lambda_s^{(1)}$	$\lambda^- \eta_s^{(2)}$	$\lambda^+ \eta_s^{(2)}$	$\lambda_s^{-(1)}$	$\lambda_s^{+(1)}$	$Av \lambda_s^+$	$R^+ (A^\circ)$	$R^- (A^\circ)$	$R^+ + R^-$	$a^\circ (A^\circ)$
25°C	124.83	0.6791	0.6791	76.28	48.55	48.405	1.9013	1.2065	3.1079	6.5
30°C	136.01	0.6738	0.6738	84.50	51.51	51.98	1.9766	1.2159	3.1925	7.0
35°C	147.86	0.6640	0.6640	92.30	55.56	55.93	2.0364	1.2340	3.2705	7.5
40°C	158.24	0.6544	0.6544	100.2	58.04	59.18	2.1200	1.2521	3.3721	8.0

TABLE IX. THERMODYNAMIC PARAMETERS OF TRIMETHYLSULFONIUM BROMIDE IN WATER AT DIFFERENT TEMPERATURES

T(K)	Λ_s (ohm ⁻¹ equiv ⁻¹ cm ²)	K_A	ΔE_s° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔG° (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹ K ⁻¹)
298	126.91	440.24	12.79	30.33	-15.08	152.41
303	138.45	516.70			-15.74	152.06
308	150.30	645.11			-16.57	152.29
313	162.52	784.99			-17.35	152.34

TABLE X. THERMODYNAMIC PARAMETERS OF TRIMETHYLSULFONIUM IODIDE IN WATER AT DIFFERENT TEMPERATURES

T (K)	Λ_s (ohm ⁻¹ equiv ⁻¹ cm ²)	K_A	ΔE_s° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔG° (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹ K ⁻¹)
298	124.83	471.39	12.34	27.83	-15.25	144.58
303	136.01	576.10			-16.01	144.70
308	147.86	675.48			-16.69	144.54
313	158.24	812.88			-17.44	144.63