RESEARCH ARTICLE

ELECTROCHEMICAL STUDIES ON ION PAIRS FORMATION OF TRIMETHYLSULFONIUM HALIDES IN N, N-DIMETHYLFORMAMIDE AT VARIOUS TEMPERATURES

Marwa A. Daghash and Nasr H. El-Hammamy*

Department of Chemistry, Faculty of Science, Alexandria University, Alexandria, P.O.426 Ibrahimia, Alexandria 21321, Egypt

ABSTRACT

The conductance data of trimethylsulfonium halides (bromide and iodide) in N, N-dimethylformamide 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_o), the distance of closest approach (a°) and association constant (K_A). After calculation of the electrostatic Stokes' radii (R^+ and R^-), their sum is likened to a° value. The thermodynamic functions (ΔH^o, ΔG^o, ΔS^o) and the activation energy (ΔE_s) were determined; Negative values of Gibbs free energy change ΔG^o for trimethylsulfonium halides (Bromide and Iodide) indicate that the association process is preferable than the dissociation process. The positive value of (ΔH^o) points to that the association process is endothermic. Entropy change (ΔS^o) values were positive which means that the solvation of ion-pair decreases emulated to that of the free ion.

Key words: Trimethylsulfonium halides, limiting equivalent conductance (Λ_o), ion association, activation energy and thermodynamic functions.

INTRODUCTION

The study of electrolyte solutions in N, N-dimethylformamide is of interest in organic electrolyte batteries, photoelectrochemical cells, electrodeposition, wet electrolyte capacitors or electroorganic synthesis (Barthel, 1983). A systematic investigation of the temperature dependence of the transport properties in this system has been lacking. The measurement of the electrical conductance of a non-aqueous electrolyte solution provides valuable information about its transport properties. Values of the equivalent or molar conductance of electrolyte at infinite dilution and ionic association constant can be obtained from conductance data as a function of concentration by using the appropriate equation. Several equations and approaches are available for the analysis of conductance data, depending on the precision required. The selection of an equation for the determination of Λ_o and K_A is open to debate. We used the Fuoss-Onsager conductance equation. N, N-dimethylformamide (DMF) is a versatile solvent for organic and inorganic substances. It is used as a solvent in peptide coupling for pharmaceuticals, in production of acrylic fibers and plastics, in the development and production of pesticides and in manufacture of adhesive, synthetic leathers, fibers, films and surface coatings (Chadwick, 2006). Also it is widely used as a solvent for electrochemical reactions, especially reductions (Juilliard, 1977). The aim of the present work is to determine trimethylsulfonium halides (bromide and iodide) conductance values that measured in N, N-dimethylformamide at various temperatures (25, 30, 35 and 40°C). The nature of the ion-ion and ion-solvent interaction for trimethylsulfonium halides were discussed by evaluating the limiting equivalent

Corresponding author: **Nasr H. El-Hammamy,**
Department of Chemistry, Faculty of Science, Alexandria University, Alexandria, P.O. 426 Ibrahimia, Alexandria 21321, Egypt.

conductance (Λ_o), 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^o, ΔG^o, ΔS^o) and activation energy (ΔEs) were obtained.

Experimental: All salts were highly purified reagent grade and used without further purification. where trimethylsulfonium bromide ($Me_3S.Br$) and trimethylsulfonium iodide ($Me_3S.I$) are Analar analytical reagent "BDH".

The specific conductance $\mathcal{K}_o$ for N, N-dimethylformamide "BDH" at different temperatures (25, 30, 35 and 40°C) was found to be $(1.05- 1.72 \times 10^{-6})$ $ohm^{-1} cm^{-1}$. All solutions were prepared by weight. Salts were weighed on a 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 $\pm 0.1°C$ using a water ultra thermostat. The dielectric constants $(D25°) = 36.70$, $(D30°) = 35.88$, $(D35°) =34.95$, $(D40°) = 34.015$, respectively. In all calculations, the used solvent constants were taken as stated (Safonova, 2001), i.e., densities $(d25°) = 0.9443$ $g.cm^{-3}$, $(d30°) = 0.9397$ $g.cm^{-3}$, $(d35°) = 0.9350$ $g.cm^{-3}$, $(d40°) = 0.9304$ $g.cm^{-3}$, respectively, the viscosities $(\eta25°) = 0.8000 \times 10^{-2}$ P, $(\eta30°) = 0.7535 \times 10^{-2}$

P and $(\eta 35°) = 0.7070 \times 10^{-2}$ P, $(\eta 40°) = 0.6680 \times 10^{-2}$ P, respectively.

RESULTS AND DISCUSSION

Conductance of trimethylsulfonium halides (bromide and iodide) in N, N -dimethylformamide at various 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_o was obtained. More precise values of Λ_o were resulted from the following Fuoss-Kraus-Shedlovsky (F.K.S) equation:

$$\frac{1}{\Lambda S_{(z)}} = \frac{1}{\Lambda_\circ} + \frac{(C\Lambda S_{(z)}f^2)}{K_D \Lambda_\circ^2}, \qquad (1)$$

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:

$$z = \alpha\,(C\Lambda)^{1/2}/\,\Lambda_o^{3/2}, \qquad (2)$$

Where α is the limiting tangent (Onsager slope). The plot of $1/\Lambda S_{(z)}$ versus $(C\Lambda S_{(z)}f^2)$ gives $1/\Lambda_o$ as the intercept and $1/K_D\Lambda_o^2$ as the slope. More accurate values of Λ_o, $J_{(a)}$, $a°$ and K_A were obtained from Fuoss-Onsager equation (Fuoss, 1957). The starting Λ_o 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_o; ± 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):

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

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 N, N-dimethylformamide 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 (Fuoss, 1957):

$$J = \sigma_1\,\Lambda_\circ + \sigma_2, \qquad (4)$$

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_o, K_A, $a°$ for trimethylsulfonium bromide and trimethylsulfonium iodide increase with increasing the temperatures in N, N-dimethylformamide. The values of Λ_o increase with increasing the size of the anion, in the order {Λ_o trimethylsulfonium

iodide > Λ_o trimethylsulfonium bromide}, according to ionic equivalent conductance of anions in N, N-dimethylformamide at different temperatures. The values of K_A increases with increasing the size of the anion, in the order {K_A trimethylsulfonium iodide > K_A trimethylsulfonium bromide}, according to the electrostatic theory. K_A 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 (Robinson, 1959; El-Hammamy, 2010; El-Hammamy, 1984).
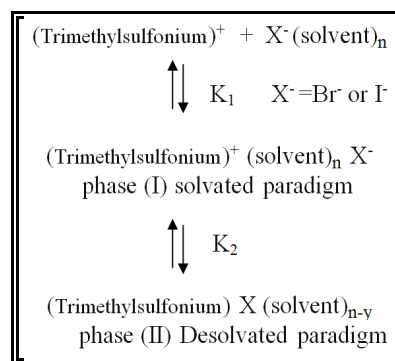
In the light of the U term, the association constant (K_A) is evaluated from the equation as follows (Accascina, 1967)**:**

$$\ln K_A = \ln(4\pi Na^{\circ3}/3000) + (e^2/a^\circ DkT) + U, \qquad (5)$$

where,

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

$\Delta S/k$ is the entropy/Boltzmann constant ratio which refers to the possibility of surrounding the free ions by the solvent molecules and E_s/kT Gilkerson (Gilkerson, 1956) is an energy relationship where the E_s parameter is the variance between the interaction energies of the solvent-ion and solvent-ion pairs. As shown in Tables (5-6) the U term (which denotes the change in the internal energy) increases slightly with increasing the temperature which means ion–dipole term for trimethylsulfonium halides (bromide and iodide) are less predominant than the entropy term. Ultimately, the solvent-separated ion pair model could be utilized (Evans, 1969) in which a multiple-stages association was proposed as shown in scheme:

$$
\boxed{
\begin{array}{c}
(\text{Trimethylsulfonium})^+ + \text{X}^-(\text{solvent})_n \\[4pt]
\updownarrow \quad K_1 \qquad \text{X}^- = \text{Br}^- \text{ or } \text{I}^- \\[4pt]
(\text{Trimethylsulfonium})^+ (\text{solvent})_n\,\text{X}^- \\
\text{phase (I) solvated paradigm} \\[4pt]
\updownarrow \quad K_2 \\[4pt]
(\text{Trimethylsulfonium})\,\text{X}\,(\text{solvent})_{n-y} \\
\text{phase (II) Desolvated paradigm}
\end{array}
}
$$

Where y = number of escaping solvent molecules from solvation.

Hence, the association constant K_A is specified by the expression:

$$K_A = K\ \Sigma\ \frac{[C_{(\text{ion-pairs})}]}{[C_{(\text{Trimethylsulfonium})^+}]\,[C_{\text{X}^-(\text{solvent})n}]} = K_1(1 + K_2) \qquad (7)$$

From the conductance measurements, K_A value is gained and since $K_1 = 4\pi N a^{\circ3} e^b/3000$ where $b = e^2/a^\circ DTk$ so K_2 value could be obtained. It is clearly noticed from Tables (5-6), K_2 values rises with the increase in temperature which is an

indication that the desolvated paradigm (Phase II) is more desired than the solvated paradigm (Phase I) for the ion-pair.

Radii of ions: The electrostatic radii R^+ and R^- are given by **Stokes' equation**:

$$R^{\pm} = 0.8194 \times 10^{-8}/\lambda_\circ^{\pm} \eta_\circ \quad , \qquad (8)$$

where η_o is the viscosity of pure solvent and 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 (El-Hammamy, 1984). From the data in Tables (7-8), it could be noticed that; in case of N, N-dimethylformamide 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.

Thermodynamic studies of trimethylsulfonium halides (bromide and iodide) in N, N-dimethylformamide from conductance measurements: Any rising in thermal energy affects the rotational, vibrational and translational energy of molecules which causes greater frequency and as a result, overstated ionic mobility. As seen in Tables (9-10), Λ_o values increase upon the increase in temperature in an indication of higher mobility of the ions or lower solvation (Dash, 2006). On increasing the temperature also, the association constant K_A values increase which is explicated by diminution the dielectric constant of the medium when the temperature increases (Coetzee, 1976). Svante Arrhenius (Arrhenius, 1889) combined the activation energy concepts and the Boltzmann distribution law into one equation:

$$\Lambda o = A e^{-(\Delta Es/RT)} \text{ or } \log \Lambda o = \log A - (\Delta Es/2.303RT), \qquad (9)$$

Where R is the ideal gas constant, A is the Arrhenius, pre-exponential, collision or frequency factor, ΔE_S is the Arrhenius activation energy (J/mol) and T is the temperature (absolute, Kelvin).

By plotting a graph between $\log \Lambda_o$ and $1/T$, as displayed in Figures (3, 4), straight lines are obtained with slope (-$\Delta ES/2.303R$) from which ΔE_S value is computed and recorded as seen in Tables (9,10). As shown, the activation energy (ΔEs) has a positive value which points to the high mobility of ions in the solution and thus high Λ_o values. The change in Gibbs free energy ΔG^o upon the process of association is obtained from equation (Coetzee, 1976):

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

As observed in Tables (9,10), values of ΔG^o are negative for trimethylsulfonium halides (bromide and iodide) in N, N-dimethylformamide which is associated with a reaction that happens spontaneously; this means that the association process was chosen as favorite process better than dissociation in the solvent system studied. With increasing the temperature, an increase in negative values of ΔG^o was observed because of releasing solvent molecules from the solvation shell into the bulk solvent. The association between ions becomes more strength at high temperature where the permittivity of the solvent decreases (Kalugin, 2009). As resulted in Tables (9,10), the enthalpy change or heat of association (ΔH^o) has been calculated where ($-\Delta H^o/2.303R$) is the slope obtained

from plotting a graph of log KA versus 1/T as shown in Figures (5, 6). By applying the Van't Hoffs isochore expression:

$$d \ln KA/dT = \Delta H^o/RT^2 \quad , \qquad (11)$$

Then,
$$2.303 \log KA = -(\Delta H^o/R)(1/T) + \Delta S^o/R$$
or

$$\log KA = -(\Delta H^o/2.303R)(1/T) + \Delta S^o/2.303R \quad , \qquad (12)$$

ΔH^o positive values for trimethylsulfonium halides (bromide and iodide) in N, N-dimethylformamide refer to endothermic (endergonic) association process because the enthalpy of the products is higher than the enthalpy of the reactants of the system (Petrucci, 2007).

Gibbs-Helmholtz equation was applied to estimate ΔS^o values (The change of entropy) where:

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad , \qquad (13)$$

For trimethylsulfonium halides (bromide and iodide) in N, N-dimethylformamide, the positive values of ΔS^o reveal the disorder of ions (randomness). As obviously seen in Tables (9,10), the entropy change values (ΔS^o) were positive because the ion-pair solvation is diminished if they are matched to that of the free ion (Pura, 2007; Yokoyama, 1991; Pura, 2003). El-Hammamy et al. have measured the conductance of sodium dimethyldithiocarbamate salt in N, N-dimethylformamide at different temperatures (25, 30, 35 and 40°C). The results were analyzed using Fuoss-Onsager equation (Fuoss, 1959), from which the values of Λ_0, K_A and a^o (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 $1/T$, for sodium diethyldithiocarbamate in N, N-dimethylformamide at different temperature, ΔE_S values have been evaluated. Also ΔH^o, ΔG^o and, ΔS^o have been evaluated. It was found that values of ΔG^o are negative indicating that ions association process is favored over dissociation process in all solvent systems. With increasing the temperature, the negative values of ΔG^o increase due to releasing solvent molecules from solvation shell into the bulk solvent.

The positive values of ΔH^o indicate endothermic association process. Positive and high (ΔH^o) values can be attributed to the interaction between ions. ΔS^o positive values are due to the randomness of ions in the solvent system studied. El-Hammamy et al. have measured the conductance of sodium diethyldithiocarbamate salt in N, N-dimethylformamide at different temperatures (25, 30, 35 and 40°C). The results were analyzed using Fuoss-Onsager equation (Fuoss, 1959), from which the values of Λ_0, K_A and a^o (solvation) were obtained. It was reported that the increase in Λ_0 and K_A is involved with rising the temperature. ΔE_S values and thermodynamic functions have been evaluated. The negative value of ΔG^o for the association rate constants K_A indicates that the reaction is spontaneous and ion association process is energetically favored over dissociation process. The positive values of ΔH^o signalize a process or reaction in which the system absorbs energy from its surroundings (endothermic in nature). ΔS^o positive values are characteristic of the disorder of ions.

Table 1. Conductance of trimethylsulfonium bromide in DMF at different temperatures:

10^4C	$C^{1/2}$	$10^6\mathcal{H}$	Λ
Trimethylsulfonium Bromide at 25°C			
6.1422	0.0248	81.15	132.1175
5.4865	0.0234	74.05	134.9655
4.9779	0.0223	68.25	137.1052
4.5405	0.0213	63.25	139.3004
4.2033	0.0205	59.25	140.9601
3.9023	0.0198	55.75	142.8619
3.6339	0.0191	52.45	144.3326
3.3935	0.0184	49.35	145.4241
Trimethylsulfonium Bromide at 30°C			
4.9129	0.0222	70.15	142.7864
4.4426	0.0211	64.55	145.2975
4.0627	0.0202	59.85	147.3145
3.7554	0.0194	56.05	149.2493
3.4896	0.0187	52.55	150.5887
3.2632	0.0181	49.65	152.1478
3.0549	0.0175	46.95	153.6831
2.8592	0.0169	44.35	155.1085
Trimethylsulfonium Bromide at 35°C			
6.3630	0.0252	113.13	177.7933
5.7677	0.0240	103.23	178.9764
5.2561	0.0229	94.63	180.0360
4.8176	0.0219	87.23	181.0638
4.4539	0.0211	80.93	181.7020
4.1469	0.0204	75.73	182.6147
3.8757	0.0197	70.93	183.0103
3.6301	0.0191	66.73	183.8229
Trimethylsulfonium Bromide at 40°C			
2.9552	0.0172	53.98	182.6599
2.7019	0.0164	49.68	183.8703
2.4853	0.0158	45.98	185.0026
2.2979	0.0152	42.78	186.1678
2.1327	0.0146	39.92	187.1802
2.0003	0.0141	37.58	187.8685
1.8771	0.0137	35.40	188.5803
1.7660	0.0133	33.45	189.4031

* equiv L^{-1}　　** ohm^{-1} equiv^{-1} cm^2

Table 2. Conductance of trimethylsulfonium iodide in DMF at different temperatures:

10^4C	$C^{1/2}$	$10^6\mathcal{H}$	Λ
Trimethylsulfonium Iodide at 25°C			
2.2724	0.0151	28.45	125.1926
2.0468	0.0143	26.25	128.2466
1.8577	0.0136	24.35	131.0727
1.7093	0.0131	22.75	133.0909
1.5798	0.0126	21.35	135.1367
1.4689	0.0121	20.15	137.1770
1.3713	0.0117	19.05	138.9189
1.3154	0.0115	18.39	139.8023
Trimethylsulfonium Iodide at 30°C			
0.6819	0.0083	9.60	140.7725
0.6141	0.0078	8.83	143.7718
0.5601	0.0075	8.19	146.1994
0.5159	0.0072	7.65	148.2681
0.4773	0.0069	7.17	150.1908
0.4448	0.0067	6.76	151.9593
0.4157	0.0064	6.38	153.4588
0.3890	0.0062	6.03	154.9777
Trimethylsulfonium Iodide at 35°C			
1.1511	0.0107	20.45	177.6412
1.0402	0.0102	18.62	179.0001
0.9544	0.0098	17.20	180.2048
0.8755	0.0094	15.87	181.2663
0.8124	0.0090	14.80	182.1681
0.7723	0.0088	14.12	182.8103
0.7251	0.0085	13.32	183.6741
0.6793	0.0082	12.53	184.4462
Trimethylsulfonium Iodide at 40°C			
0.6586	0.0081	12.83	194.7967
0.5946	0.0077	11.64	195.7548
0.5463	0.0074	10.74	196.5834
0.5003	0.0071	9.87	197.2794
0.4625	0.0068	9.15	197.8320
0.4298	0.0066	8.53	198.4390
0.4014	0.0063	7.99	199.0412
0.3770	0.0061	7.52	199.4463

* equiv L^{-1}　　** ohm^{-1} equiv^{-1} cm^2

Table 3. The characteristic parameters for trimethylsulfonium bromide in DMF at 25, 30, 35 and 40°C derived from Fuoss–Onsager equation:

Temperature	$\Lambda_\circ$ (ohm^{-1} equiv^{-1} cm^2)	J	K_A	a° (Å)	σ_Λ
25°C	176.84 ± 0.1253	2667.7	631.47	6.5	0.1755
30°C	185.16 ± 0.1197	3027.0	732.57	7.0	0.1489
35°C	196.30 ± 0.3773	3427.1	811.58	7.5	0.1067
40°C	203.95 ± 0.3580	3833.6	886.41	8.0	0.0874

Table 4. The characteristic parameters for trimethylsulfonium iodide in DMF at 25, 30, 35 and 40°C derived from Fuoss–Onsager equation:

Temperature	$\Lambda_\circ$ (ohm^{-1} equiv^{-1} cm^2)	J	K_A	a° (Å)	σ_Λ
25°C	180.57 ± 0.1687	2923.0	686.96	7.0	0.1468
30°C	188.16 ± 0.1442	3257.8	778.09	7.5	0.0817
35°C	197.63 ± 0.2602	3689.8	848.94	8.0	0.1164
40°C	207.44 ± 0.1420	4090.5	943.88	8.5	0.0681

Table 5. Calculated values of K_2 and U for trimethylsulfonium bromide in DMF at 25, 30, 35 and 40°C:

Temperature	K_A	K_1	K_2	U
25°C	631.47	7.2474	86.1299	4.4674
30°C	732.57	7.7543	93.4727	4.5483
35°C	811.58	8.4092	95.5106	4.5696
40°C	886.41	9.1629	95.7386	4.5720

Table 6. Calculated values of K_2 and U for trimethylsulfonium iodide in DMF at 25, 30, 35 and 40°C:

Temperature	K_A	K_1	K_2	U
25°C	686.96	7.6539	88.7528	4.4970
30°C	778.09	8.2397	93.4314	4.5478
35°C	848.94	8.9683	93.6600	4.5502
40°C	943.88	9.7936	95.3766	4.5682

Table 7. Calculations of the radii of the ions for trimethylsulfonium bromide in DMF at 25, 30, 35 and 40°C:

Temperature	$\Lambda_\circ$ [1]	$\lambda_\circ^- \eta_\circ$ [2]	$\lambda_\circ^+ \eta_\circ$ [2]	$\lambda_\circ^-$ [1]	$\lambda_\circ^+$ [1]	Av. $\lambda_\circ^+$	R^+ (A°)	R^- (A°)	$R^+ + R^-$	a° (A°)
25°C	176.84	0.3649	1.0702	45.62	131.22	133.775	0.7656	2.2451	3.0108	6.5
30°C	185.16	0.3771	1.0344	50.05	135.11	137.29	0.7920	2.1727	2.9648	7.0
35°C	196.30	0.3922	1.0086	55.48	140.82	142.66	0.8124	2.0890	2.9014	7.5
40°C	203.95	0.4233	0.9552	63.37	140.58	142.995	0.8578	1.9356	2.7935	8.0

(1) ohm^{-1}equiv^{-1}cm^2 (2) ohm^{-1}equiv^{-1}cm^2 p

Table 8. Calculations of the radii of the ions for trimethylsulfonium iodide in DMF at 25, 30, 35 and 40°C:

Temperature	$\Lambda_\circ$ [1]	$\lambda_\circ^- \eta_\circ$ [2]	$\lambda_\circ^+ \eta_\circ$ [2]	$\lambda_\circ^-$ [1]	$\lambda_\circ^+$ [1]	Av. $\lambda_\circ^+$	R^+ (A°)	R^- (A°)	$R^+ + R^-$	a° (A°)
25°C	180.57	0.3539	1.0702	44.24	136.33	133.775	0.7656	2.3152	3.0808	7.0
30°C	188.16	0.3668	1.0344	48.69	139.47	137.29	0.7920	2.2334	3.0255	7.5
35°C	197.63	0.3756	1.0086	53.13	144.50	142.66	0.8124	2.1814	2.9938	8.0
40°C	207.44	0.4143	0.9552	62.03	145.41	142.995	0.8578	1.9775	2.8353	8.5

(1) ohm^{-1}equiv^{-1}cm^2 (2) ohm^{-1}equiv^{-1}cm^2 p

Table 9. Thermodynamic parameters of trimethylsulfonium bromide in DMF at different temperatures:

T (°K)	$\Lambda_\circ$ (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	176.84	631.47	7.55	17.39	-15.98	112.00
303	185.16	732.57			-16.62	112.28
308	196.30	811.58			-17.16	112.19
313	203.95	886.41			-17.66	112.03

Table 10: Thermodynamic parameters of trimethylsulfonium iodide in DMF at different temperatures:

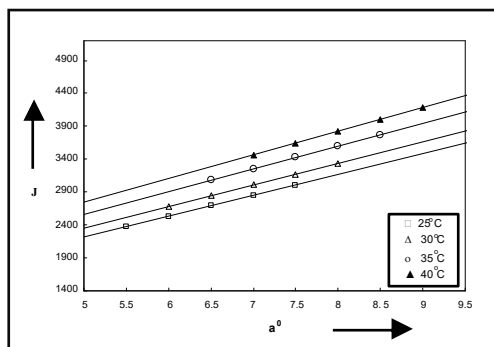| T (°K)	$\Lambda_\circ$ (ohm^{-1} equiv^{-1} cm^2)	K_A	ΔE_s° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔG° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K^{-1})
298	180.57	686.96	7.21	16.14	-16.19	108.49
303	188.16	778.09			-16.77	108.64
308	197.63	848.94			-17.27	108.49
313	207.44	943.88			-17.83	108.54

Figure 1: Variation of J and a° of trimethylsulfonuim bromide in DMF at different temperatures.
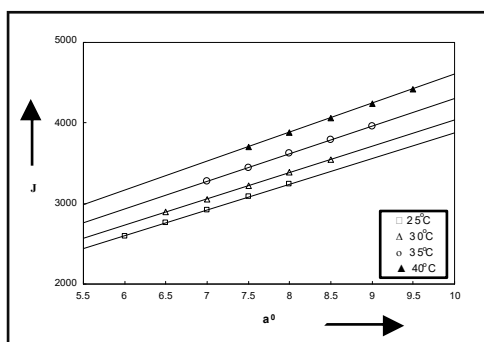

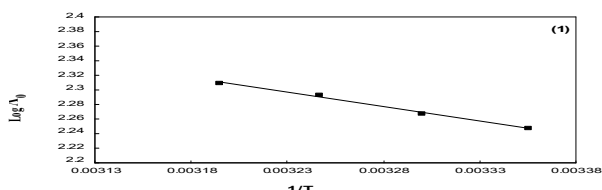**Figure 2: Variation of J and a° of trimethylsulfonuim iodide in DMF at different temperatures.**

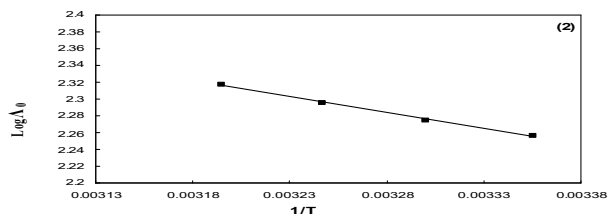**Figure 3. The variation of log Λ_0 vs. 1/T for trimethylsulfonium bromide in DMF at different temperatures**

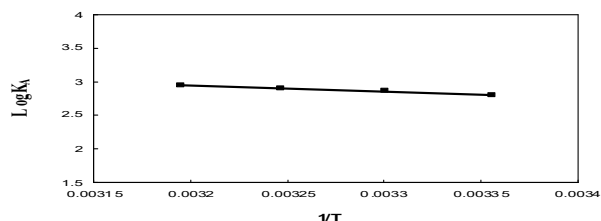**Figure 4: The variation of log Λ_0 vs. 1/T for trimethylsulfonium iodide in DMF at different temperatures**

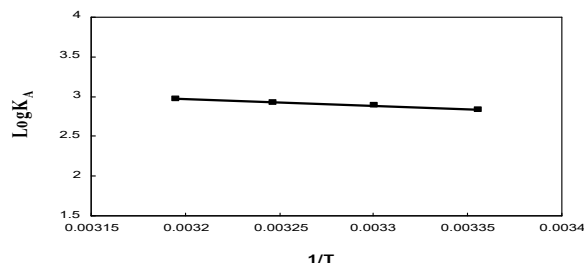**Figure 5: The variation of log K_A vs. 1/T for trimethylsulfonium bromide in DMF at different temperatures**

Figure 6: The variation of log K_A vs. 1/T for trimethylsulfonium iodide in DMF at different temperatures.

REFERENCES

Accascina, F., D'Aprano A. and Triolo, R. 1967. J. Phys. Chem., 71, 3469.

Arrhenius, S. A. 1889. Z. Phys. Chem., 4, 96.

Barthel, J., Gores, H. J., Schmeer G. and Wachter, R. 1983. Non-aqueous Electrolyte Solutions in Chemistry and Technology, Topics in Current Chemistry, ed. F. L. Boschke, Springer Verlag, Heidelberg, vol. 111, pp. 33È144.

Brown, G. W. 1982. Am. J. Dis. Child., 136, 937.

Chadwick, S. S. 2006. Encyclopedia of industrial chemistry: Wiley-VCH: Weinheim.

Coetzee J. F. and Ritchie, C. D. 1976. "Solute-Solvent Interaction", Marcel-Dekker, New York, vol. 2.

Dash, U. N., Mohatra J. R. and Lal, B. 2006. *J. Molecular Liquids,* 124, 13.

EI-Hammamy, N. H., El-Kholy, M. M., G. A. Ibrahim and A. I. Kawana, 2010. *J. Adv. Appl. Sci. Res.,* 1(3), 168.

El-Hammamy, N. H., Amira, S. A. Abou El-Enein and F. M. Abd El-Halim, Indian J. Chem., 23, 43(1984).

El-Hammamy, N. H., Hasanien, A. A., Amira M. F. and Abd El-Halim, F. M. 1984. *J Electrochem. Soc., India*, 33, 43.

El-Hammamy, N.H., Kawana, A.I., Daghash M. A. and Morshidy, M. H. under publication.

El-Hammamy, N.H., Kawana, A.I., Daghash M. A. and Sh, N. H. Zayed, under publication.

Evans D. F. and Gardam, P. 1956. J. Phys. Chem., 73, 158.

Fuoss R.M. and Onsager, L. 1957. J. Phys. Chem., 61, 668;

Fuoss, R.M. 1959. J. Am. Chem. Soc., 81, 2659.

Gilkerson, W. R. 1956. *J. Chem Phys.*, 25, 1199.

Juilliard, J. 1977. Pure Appl. Chem., 49, 885.

Kalugin, O.N., Agieienko, V.N., OtroshKo N. A. and Moroz, V.V. 2009. *Russian J. Phys. Chem. A*, 83, 231.

Petrucci, R. H., Harwood, W. S., Herring F. G. and Madura, J. D. 2007. General Chemistry: Principles and Modern Applications. 9th Ed. Pearson Prentice Hall Inc., New Jersey.

Pura S. and Atun, G. 2003. J. Solution Chem., 32, 341.

Pura, S. 2007. J. Molecular Liquids, 136, 64.

Robinson R. A. and Stokes, R. H. 1959. "Electrolyte solutions". Butterworths, 2nd ed, London.

Safonova, L. P., Sakharov, D. V., Shmukler L. E. and Kolker, A. M. 2001. Phys. Chem. Chem. Phys., 3, 819.

Yokoyama H. and Kon, H. 1991. J. Phys. Chem., 95, 8956.

****