RESEARCH ARTICLE

ELECTRICAL CONDUCTIVITY AND THERMODYNAMIC STUDIES ON TRIMETHYLSULFONIUM HALIDES IN METHANOL AT DIFFERENT TEMPERATURES

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ABSTRACT

The conductance data of trimethylsulfonium halides (bromide and iodide) in methanol at different temperatures (25, 30, 35 and 40°C) are presented. Results were construed by applying the Fuoss-Onsager equation to determine the characteristic parameters: equivalent conductance at infinite dilution Λ_o, association constant K_A, the distance of closest approach of ions å. After calculation of the electrostatic Stokes' radii (R^+ and R^-), their sum is likened to å value. Thermodynamic functions such Gibbs free energy change ΔG^o, enthalpy change ΔH^o, change in entropy ΔS^o and the activation energy (ΔEs) were estimated.

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

INTRODUCTION

In a wide temperature range, conductivity measurements for electrolyte solution can give a detailed information for ion-ion and ion-solvent interactions (Yokoyama, 1989; Yokoyama, 1991). Primary alcohols (MeOH, EtOH, 1-PrOH and 1-BuOH) are polar solvents, having a lower relative permittivity than that of water. Alcohols associate in liquid by hydrogen bond. In the primary alcohols, ionic association is interpreted in terms of a multiple-step association process involving hydrogen bonded solvated of anions in the homologous series methanol through 1-pentanol by Matesich et al. (1970). Thus in this study, it was attempted to obtain some information on the association of trimethylsulfonium halides (bromide and iodide) in methanol solutions at different temperatures (25, 30, 35 and 40°C) by conductometric measurements. The limiting equivalent conductance and association constants for these salts in methanol solutions at (25, 30, 35 and 40°C) were determined by analyzing conductivity data terms of Fuoss-Onsager equation (Fuoss, 1957). The Thermodynamic functions ($\Delta H^0, \Delta G^0, \Delta S^0$) and activation energy (ΔEs) were calculated and compared according to interaction of solvent at different temperatures. Fuoss and Onsager (Fuoss, 1957), utilized the sphere in continuum model and the next equation was formulated:

$$\Lambda = \Lambda_\circ - S(C\gamma)^{1/2} + EC\gamma \log C\gamma + (J - B\Lambda_\circ)C\gamma - K_A C\gamma \Lambda f^2, \tag{1}$$

Where, Λ is the equivalent conductance ohm^{-1}equiv^{-1}cm^2, equivalent conductance at infinite dilution (Λ_o), C is the concentration (equiv/l) and ion association constant (K_A), γ is the degree of dissociation which is determined by the equation:

$$\gamma = \Lambda / \Lambda_\circ - S(C\Lambda / \Lambda_\circ)^{1/2}, \tag{2}$$

S and E are theoretically predicted constants, which depend on the dielectric constant of the medium, absolute temperature and the viscosity (D, T and η respectively). J term (which represents the ions and ion-solvent interactions) is given by the equation

$$J = \sigma_1 \Lambda_\circ + \sigma_2, \tag{3}$$

Where $\sigma_1 and \sigma_2$ are functions of the distance of closest approach of ions a° besides η and D. The aim of the present work is to study and understand the mobility and association process of the compound "trimethylsulfonium halides" by measuring its conductance in methanol at various temperatures (25, 30, 35 and 40°C) followed by determining the thermodynamic functions (ΔG^o, ΔH^o, ΔS^o and ΔE_s).

Experimental: All salts were highly purified reagent grade and used without further purification. where trimethylsulfonium bromide (Me$_3$S.Br) and trimethylsulfonium iodide (Me$_3$S.I) are Analar analytical reagent "BDH"**.** Methanol (B.D.H, Analar grade) was used without any further purification.

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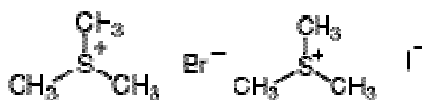
The specific conductance of purified methanol at 25, 30, 35 and 40°C was found to be in range of (1.47 -2.21 x 10^{-6}) ohm^{-1} cm^{-1}. The preparation of all solutions was performed by weight. Trimethylsulfonium halides were weighed on microbalance with a readability of ± 0.1 mg. By dropping the solvent via weighing pipette, dilution into the cell was carried out. Conductivity Bridge instrument model: Crison GLP31+ was used to measure the experimental values of conductance (the reproducibility is ±0.1% and Conductivity measurement error was ≤0.5%) and a cell with platinum electrodes has a cell constant (K=0.1 cm^{-1}) for dilute solutions. Using a water ultra thermostat, the temperature is kept constant to within ±0.1°C. Each measurement is taken three times and then the average of the three measurements is recorded. The solvent constants used in all calculations were taken as reported in references (El-Hammamy, 1984; El-Hammamy, 2011; EI-Hammamy, 2011), i.e., densities (d25°) = 0.7917 g/cm^3, (d30°) = 0.7862 g/cm^3, (d35°) = 0.7815 g/cm^3 and (d40°) = 0.7762 g/ cm^3 respectively. The viscosities (η25°) = 0.5448 ×10^{-2} Poise, (η30°) = 0.5030 ×10^{-2} Poise, (η35°) = 0.4620 ×10^{-2} Poise and (η40°) = 0.4220 ×10^{-2} Poise respectively. The dielectric constants (D25°) = 33.05, (D30°) = 31.62, (D35°) = 30.08 and (D40°) = 29.98 respectively.

Results and discussion

A-   Conductance of trimethylsulfonium halides (bromide and iodide) in methanol at different temperatures:

In order to get the best value of equivalent conductance at infinite dilution (Λ_o), three steps are done. First step, is determining an approximate value of Λ_o by plotting the equivalent conductance (Λ) against ($C^{1/2}$) which gives a straight line and the intercept = Λ_o. The value Λ is calculated from equation (Sivasankar, 2008):

$$\Lambda = \frac{1000* \varkappa}{C} ,$$

(4)

In which $\varkappa$ is the specific conductance (ohm^{-1} cm^{-1}) and C is the concentration (equiv L^{-1}). In Tables (1-2) the measured equivalent conductance data are represented. Secondly, more rigorous Λ_o values were gained by applying Fuoss, Kraus and Shedlovsky (F.K.S) equation:

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

(5)

K_D: the dissociation constant and $S_{(z)}$ is the Shedlovsky's extrapolation function which was represented in table by Daggett (Daggett, 1951) for various z values. The linear interpolation in the table was executed to give $S_{(z)}$ for any z in a range of $0.000 \leq z \leq 0.209$ where z can be calculated from the formula**:**

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

(6)

Where α is the limiting Onsager slope. By plotting a graph between $1/\Lambda S_{(z)}$ and ($C\Lambda S_{(z)}f^2$), straight line was obtained with intercept ($1/\Lambda_o$) and slope ($1/ K_D\Lambda_o^2$). Third and last step is calculating the most accurate and precise values of Λ_o, $J_{(a)}$, å and K_A from Fuoss-Onsager equation (Fuoss, 1957) through the assistance of special computer program (has been developed by Fortran programming) on an IBM-PC, starting by Λ_o value which was taken out from (F.K.S) equation. The agreeable accuracies in these reckonings are ± 0.02 for Λo; ± 2 for "J values lower than 200", ± 5 for "J = 200 – 1000" and ± 10 for "J greater than 1000".

The standard deviation of the measured equivalent conductance σ_Λ was calculated using the expression (Brown, 1982):

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

(7)

where N is the number of experimental points.

Figures (1-2) displays the linear correlation between å and J, from which the average value of å can be estimated using interpolation by knowing average of J value.

From Tables (3-4), it can be noticed that Λ_o values rise with accretion of the temperature. The same trend is obtained for K_A values which increase with the temperature increment; this can be illustrated as follows: on increasing the temperature, the dielectric constant of solvents decreases as reported in literature (El-Hammamy, 1984; El-Hammamy, 2011; EI-Hammamy, 2011).
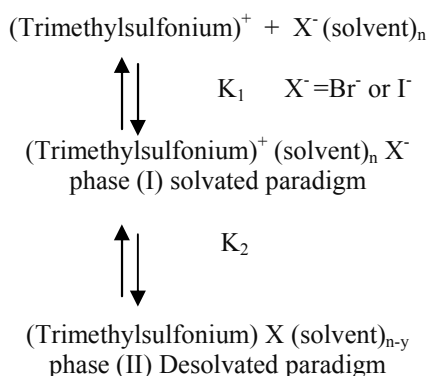
Consequently, ion association process takes place. In the light of the U term, the association constant (K_A) is evaluated from the equation as follows (Accascina, 1967)**:**

$$\ln K_A = \ln (4\pi Na^{\circ 3}/3000) + (e^2 / a^{\circ}DkT) + U \tag{8}$$

where,

$$U = \Delta S / k - E_s / kT \tag{9}$$

$\Delta S / k$ 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:

$$(\text{Trimethylsulfonium})^+ + X^- (\text{solvent})_n$$

$$K_1 \quad X^- = Br^- \text{ or } I^-$$

$$(\text{Trimethylsulfonium})^+ (\text{solvent})_n X^-$$
phase (I) solvated paradigm

$$K_2$$

$$(\text{Trimethylsulfonium}) X (\text{solvent})_{n-y}$$
phase (II) Desolvated paradigm

Where y = number of escaping solvent molecules from solvation.

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

$$K_A = K \; \Sigma \; \frac{[C_{(\text{ion-pairs})}]}{[C_{(\text{Trimethylsulfonium})^+}][C_{X^- (\text{solvent})n}]} = K_1 (1 + K_2) \tag{10}$$

From the conductance measurements, K_A value is gained and since $K_1 = 4\pi N a^{\circ 3} e^b /3000$ where $b = e^2 / a^{\circ}DTk$ so K_2 value could be obtained. It is clearly noticed from Tables (El-Hammamy, 1984; El-Hammamy, 2011; EI-Hammamy, 2011), 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

Using Stokes' equation (Robinson, 1959), the electrostatic radius for positive and negative ions (R^+ and R^-) can be calculated by knowing the viscosity and the limiting equivalent conductivities of ions as follows**:**

$$R^{\pm} = 0.8194 \times 10^{-8}/ \lambda_{\circ}^{\pm} \eta_{\circ} \; , \tag{11}$$

Where λ_o^+ or λ_o^- are the limiting ionic equivalent conductance of positive and negative ions respectively.

As shown in Tables (El-Hammamy, 2011), In case of methanol at 25 to 40°C: the values of å were higher than the sum of electrostatic radii ($R^+ + R^-$) obtained from Stokes' equation; which can be adequately explained by occurrence of ions solvation.

Thermodynamic studies of trimethylsulfonium halides (bromide and iodide) in methanol 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 salvation (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:

$$\Lambda o = A e^{-(\Delta Es / RT)} \quad \text{or} \quad \log \Lambda o = \log A - (\Delta Es /2.303RT) \tag{12}$$

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

$10^4 C$	$C^{1/2}$	$10^6 \varkappa$	Λ
Trimethylsulfonium Bromide at 25°C			
5.9508	0.0244	69.60	116.9587
5.3592	0.0231	62.89	117.3495
4.8798	0.0221	57.43	117.6889
4.4603	0.0211	52.63	117.9960
4.1128	0.0203	48.64	118.2626
3.8187	0.0195	45.25	118.4952
3.5744	0.0189	42.43	118.7048
3.3547	0.0183	39.88	118.8763
Trimethylsulfonium Bromide at 30°C			
5.8668	0.0242	73.84	125.8606
5.2714	0.0230	66.94	126.9848
4.6859	0.0216	60.04	128.1264
4.2650	0.0207	55.04	129.0480
3.9553	0.0199	51.34	129.7982
3.6682	0.0192	47.84	130.4167
3.4095	0.0185	44.68	131.0424
3.1871	0.0179	41.94	131.5925
Trimethylsulfonium Bromide at 35°C			
8.1300	0.0285	111.9	137.6377
7.1462	0.0267	99.0	138.5337
6.4316	0.0254	89.5	139.1545
5.9044	0.0243	82.5	139.7240
5.4028	0.0232	75.7	140.1123
4.9926	0.0223	70.2	140.6075
4.6420	0.0215	65.4	140.8868
4.3271	0.0208	61.1	141.2016
Trimethylsulfonium Bromide at 40°C			
12.6014	0.0355	174.69	138.6268
11.3455	0.0337	158.59	139.7821
10.2852	0.0321	144.69	140.6777
9.3452	0.0306	132.39	141.6657
8.6221	0.0294	122.69	142.2966
8.0048	0.0283	114.39	142.9005
7.4650	0.0273	107.19	143.5881
6.9746	0.0264	100.59	144.2221

* equiv L⁻¹   ** ohm⁻¹ equiv⁻¹ cm²

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

| $10^4 C$	$C^{1/2}$	$10^6 \varkappa$	Λ
Trimethylsulfonium Iodide at 25°C			
7.9363	0.0282	95.26	120.0298
7.0505	0.0266	85.13	120.7416
6.2898	0.0251	76.35	121.3851
5.6641	0.0238	69.08	121.9606
5.1758	0.0228	63.35	122.3957
4.7570	0.0218	58.43	122.8270
4.4088	0.0210	54.33	123.2298
4.0979	0.0202	50.63	123.5490
Trimethylsulfonium Iodide at 30°C			
1.7829	0.0134	25.60	143.5811
1.5983	0.0126	23.01	143.9628
1.4381	0.0120	20.75	144.2815
1.3167	0.0115	19.03	144.5217
1.2151	0.0110	17.59	144.7557
1.1199	0.0106	16.24	145.0045
1.0375	0.0102	15.07	145.2420
0.9748	0.0099	14.17	145.3600
Trimethylsulfonium Iodide at 35°C			
2.4297	0.0156	36.09	148.5341
2.1747	0.0147	32.43	149.1222
1.9711	0.0140	29.49	149.6100
1.7961	0.0134	26.95	150.0462
1.6513	0.0129	24.84	150.4212
1.5231	0.0123	22.97	150.8040
1.4127	0.0119	21.35	151.1218
1.3461	0.0116	20.37	151.3177
Trimethylsulfonium Iodide at 40°C			
1.8398	0.0136	28.38	154.2492
1.6591	0.0129	25.69	154.8351
1.5012	0.0123	23.32	155.3362
1.3744	0.0117	21.41	155.7715
1.2700	0.0113	19.84	156.2154
1.1848	0.0109	18.54	156.4782
1.1083	0.0105	17.38	156.8095
1.0384	0.0102	16.31	157.0685

*equiv L⁻¹   ** ohm⁻¹ equiv⁻¹ cm²
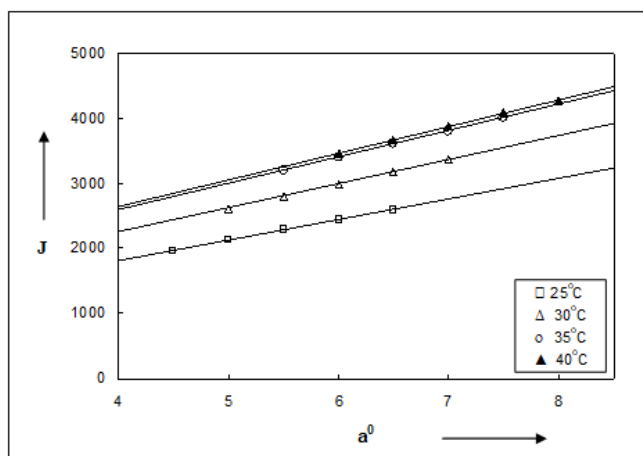
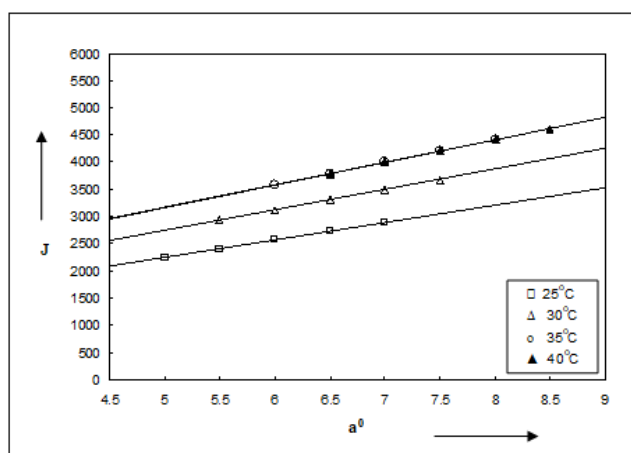**Figure 1. Variation of J and aᵒ of trimethylsulfonuim bromide in methanol at different temperatures**

Figure 2. Variation of J and aᵒ of trimethylsulfonuim iodide in methanol at different temperatures

Table 3. The characteristic parameters trimethylsulfonium bromide in methanol 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	124.30 ± 0.3366	2293.2	370.72	5.5	0.0044
30°C	143.30 ± 0.3196	3003.8	408.92	6.0	0.0361
35°C	149.87 ± 0.1001	3607.7	459.77	6.5	0.0608
40°C	157.96 ± 0.1340	3884.0	468.01	7.0	0.0744

Table 4. The characteristic parameters for trimethylsulfonium iodide in methanol 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	131.01 ± 0.1135	2571.6	376.97	6.0	0.0250
30°C	149.37 ± 0.1704	3313.8	419.19	6.5	0.0262
35°C	157.35 ± 0.1101	4004.1	473.01	7.0	0.0230
40°C	163.16 ± 0.1264	4217.8	484.65	7.5	0.0316

Table 5. Calculated values of K$_2$ and U for trimethylsulfonium bromide in methanol at 25, 30, 35 and 40°C:

Temperature	K$_A$	K$_1$	K$_2$	U
25°C	370.72	9.1434	39.5448	3.7024
30°C	408.92	9.9370	40.1510	3.7172
35°C	459.77	11.0728	40.5224	3.7262
40°C	468.01	10.9803	41.6223	3.7523

Table 6. Calculated values of K$_2$ and U for trimethylsulfonium iodide in methanol at 25, 30, 35 and 40°C:

Temperature	K$_A$	K$_1$	K$_2$	U
25°C	376.97	9.1818	40.0560	3.7149
30°C	419.19	10.1045	40.4852	3.7253
35°C	473.01	11.3450	40.6929	3.7303
40°C	484.65	11.4003	41.5120	3.7497

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

Temperature	$^{(1)}\Lambda_\circ$	$\lambda_\circ^- \eta_\circ$ $^{(2)}$	$\lambda_\circ^+ \eta_\circ$ $^{(2)}$	$\lambda_\circ^-$ $^{(1)}$	$\lambda_\circ^+$ $^{(1)}$	Av $\lambda_\circ^+$	R$^+$ (A°)	R$^-$ (A°)	R$^+$+R$^-$	a$^\circ$ (A°)
25°C	124.30	0.3065	0.3725	56.26	68.04	68.375	2.1996	2.6733	4.8730	5.5
30°C	143.30	0.3002	0.4211	59.7	83.60	83.735	1.9454	2.7286	4.6741	6.0
35°C	149.87	0.2919	0.4024	63.2	86.67	87.11	2.0360	2.8063	4.8423	6.5
40°C	157.96	0.2814	0.3808	66.7	91.26	90.26	2.1512	2.9111	5.0623	7.0

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

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

Temperature	$^{(1)}\Lambda_\circ$	$\lambda_\circ^- \eta_\circ$ $^{(2)}$	$\lambda_\circ^+ \eta_\circ$ $^{(2)}$	$\lambda_\circ^-$ $^{(1)}$	$\lambda_\circ^+$ $^{(1)}$	Av $\lambda_\circ^+$	R$^+$ (A°)	R$^-$ (A°)	R$^+$+R$^-$	a$^\circ$ (A°)
25°C	131.01	0.3394	0.3725	62.3	68.71	68.375	2.1996	2.4141	4.6138	6.0
30°C	149.37	0.3294	0.4211	65.5	83.87	83.735	1.9454	2.4870	4.4325	6.5
35°C	157.35	0.3224	0.4024	69.8	87.55	87.11	2.0360	2.5409	4.5770	7.0
40°C	163.16	0.3118	0.3808	73.9	89.26	90.26	2.1512	2.6274	4.7787	7.5

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

Table 9. Thermodynamic parameters of trimethylsulfonium bromide in methanol 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	124.30	370.72			-14.66	91.81
303	143.30	408.92	11.89	12.70	-15.15	91.92
308	149.87	459.77			-15.70	92.22
313	157.96	468.01			-16.00	91.71

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

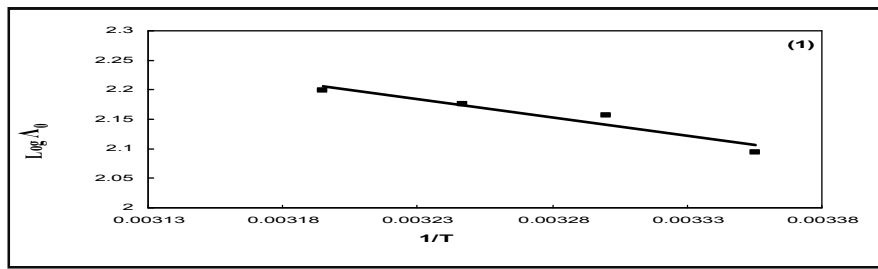| T (°K)	$\Lambda_\circ$ (ohm^{-1} equiv $^{-1}$ cm^2)	K$_A$	ΔE_s° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔG° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K^{-1})
298	131.01	376.97			-14.70	94.99
303	149.37	419.19	11.07	13.60	-15.21	95.11
308	157.35	473.01			-15.77	95.39
313	163.16	484.65			-16.09	94.89

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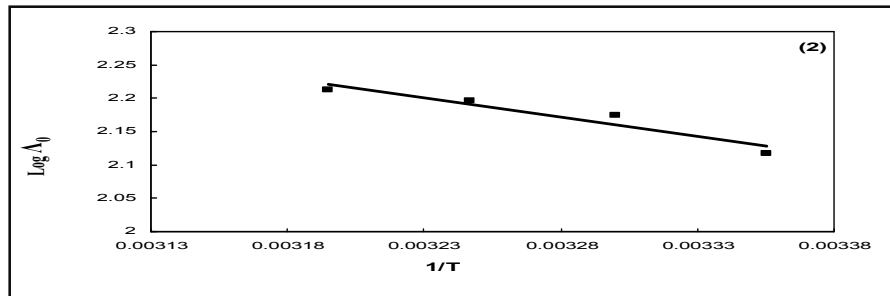

Figure 4. The variation of log Λ_0 vs. 1/T for trimethylsulfonium iodide in methanol at different temperatures
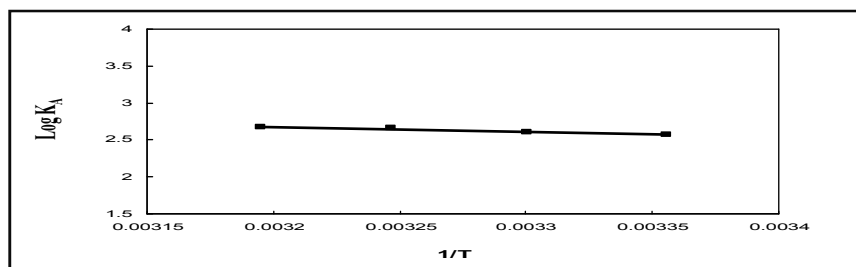

Figure 5. The variation of log K_A vs. 1/T for trimethylsulfonium bromide in methanol at different temperatures
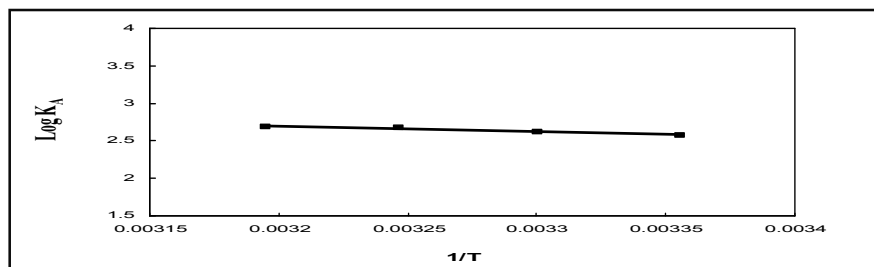

Figure 6. The variation of log K_A vs. 1/T for trimethylsulfonium iodide in methanol at different temperatures

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 Λ_o and 1/T, as displayed in Figures (3, 4), straight lines are obtained with slope ($-\Delta E_S/2.303R$) from which ΔE_S value is computed and recorded as seen in Tables (9,10). As shown, the activation energy (ΔE_s) 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, 1889):

$$\Delta G^o = -RT \ln K_A \qquad\qquad (13)$$

As observed in Tables (9,10), values of ΔG^o are negative for trimethylsulfonium halides (bromide and iodide) in methanol 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 K_A versus 1/T as shown in Figures (5, 6). By applying the Van't Hoff's isochore expression:

$$d \ln K_A/dT = \Delta H^o/RT^2 \qquad (14)$$

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

or $\quad \log K_A = -(\Delta H^o/2.303 R)(1/T) + \Delta S^o/2.303 R \qquad (15)$

ΔH^o positive values for trimethylsulfonium halides (bromide and iodide) in methanol 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:

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (16)$$

For trimethylsulfonium halides (bromide and iodide) in methanol, 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). The main factors which govern the standard entropy of ion association of electrolytes are (i) the size and shape of ions, (ii) charge density on ions, (iii) electrostriction of the solvent molecules around the ions and (iv) the penetration of the solvent molecules inside the space of ions (Victor, 1999). Bag et al. (2001) have measured the conductance of Co (III) salt monochloride in MeOH-H$_2$O mixtures at different temperatures (25, 30, 35 and 40 ^{o}C). It was found that, at a particular temperature ΔG^o becomes more negative with increase in temperature. This indicates that ion-pair association is favored with lowering of dielectric constant of medium. A positive entropy change is explained on the assumption that iceberg structure around the cation is broken when association takes place leading to an increase in the degree of disorderness (De, 1975). Dash et al. (2006) have measured the conductance of Co (III) salt of chloride and bromide in different composition of H$_2$O-MeOH, H$_2$O-EtOH and H$_2$O-n-PrOH at different temperatures. It was found that, the association constant K_A values of Co (III) salts of chloride and bromide increase with increase in temperature. It is evident that the activation energy E_S is positive for both K_A in all solvents and free energy change ΔG^o values are negative for both association constants in solvent with increase the temperature. This indicates that the association process is favored over dissociation process in all solvent systems. The positive values of ΔH^o for both salts show that the association processes are endothermic in nature. The positive value of ΔS^o indicates the randomness of ions in solvent system studied (Dash, 2006). S. Pura (2007), has measured the conductance of ferric chloride (FeCl$_3$) in primary alcohols at different temperatures. It was found that, at particular temperature ΔG^o values decrease with increase in temperature.

The decrease in ΔG^o values for FeCl$_3$ to more negative values at increasing temperature favor the transfer of the released solvent molecules into the bulk solvent and lead to a smaller ΔG^o values. The experimental values of ΔG^o for FeCl$_3$ varied in the order: MeOH > EtOH > 1-PrOH > 1- BuOH. At the temperature range studied, It was observed that the ΔH^o values of FeCl$_3$ in alcoholic organic solvents decrease in the order of MeOH > EtOH > n-PrOH > n- BuOH. The values of ΔH^o were found to be positive in all alcohols. Positive and high ΔH^o can be attributed to the interaction between ions. The ΔS^o values of FeCl$_3$ in primary alcohols were found to decrease in the order MeOH < EtOH < n-PrOH < n- BuOH, indicating a weakening in the ion solvation due to the formation of ion pairs. The values of ΔS^o for all alcohols used in the study were positive because of the decrease in solvation of the ion pairs compared to that of the free ions. The positive ΔS^o values for FeCl$_3$ in all alcohols may be attributed to the increase in the degree of freedom upon association mainly due to the release of solvent molecules. In other words, the solvation of ions became weaker as soon as the ion pair formation occurs. The radii of solvent molecules and the degree of solvation decreases with of the length of hydrocarbon (–CH$_2$–) groups of primary alcohols. For that reason, higher increase in entropy was observed, and the changes of entropy became more positive values from MeOH to n- BuOH. Positive values of ΔH^o and ΔS^o values for FeCl$_3$ can be attributed to the counter balance entropy change resulting from both short- and long- term desolvation of ions. Positive (ΔS^o) values attributed to desolvation of ions are also supported by the positive enthalpy values indicating a lack of the covalent bonds (Pura, 2001). El-Hammamy et al. (EI-Hammamy, 1951), have measured the conductance of cobalt (III) salt, chloropentammine chloride, in water at different temperatures 40 → 60°C. The results were analyzed using Fuoss-Edelson equation (Fuoss and Edelson, 1951), 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 Λ_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^o, ΔG^o, ΔS^o for the salt.
It was found that, ΔH^o and ΔS^o are positive at a particular temperature but ΔG^o 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^o is constant but ΔG^o decreases in the negative value with increasing the temperature. El-Hammamy et al., have measured the conductance of 1:1 s-acetylthiocholine salts (Cl$^-$, Br$^-$, I$^-$ and ClO$_4^-$) in water at different temperatures (25,30,35^{o}C). The results were analyzed using Fuoss-Onsager equation (Fuoss, 1959), 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 process (EI-Hammamy, 2009). The negative values of different thermodynamic parameters ΔH^o, ΔG^o, ΔS^o, for all salts studied in the used solvent, indicated that exothermic association process was less energy-consuming and more stabilized (Dash, 1997).

El-Hammamy et al., (2013) have measured the conductance of 1:1 s-acetylthiocholine salts (Br^-, I^- and ClO_4^-) in acetonitrile 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$^{\circ}$ (solvation) were obtained. It was found that, Λ_0 and K_A increase with increasing the temperature. Thus, from the plot of log Λ_0 versus $1/T$ for acetylthiocholine halides and perchlorate in acetonitrile solutions at different temperatures, positive values of ΔE_S have been evaluated, also ΔH^o, ΔG^o and ΔS^o for all salts. It was found that, ΔH^o and ΔS^o have positive values at a particular temperatures but ΔG^o has negative value. This is due to lower solvation processes but association of ion increase with thermodynamic parameters. Endothermic solvation process needs energy to break the bond around free ion and ion-pairs, i.e. this process was less energy-consuming and more stabilized. El-Hammamy et al., have measured the conductance of 1:1 s-acetylthiocholine salts (Br^-, I^- and ClO_4^-) in methanol at different temperatures (25,30,35,40^{o}C). The results were also analyzed using Fuoss-Onsager equation (Fuoss, 1959), from which the values of Λ_0, K_A and a$^{\circ}$ (solvation) were obtained. It was found that Λ_0 and K_A increase with increasing the temperature. Thus from the plot of log Λ_0 versus $1/T$, for acetylthiocholine chloride, bromide and perchlorate in methanol at different temperatures, ΔE_S values have been evaluated; also ΔH^o, ΔG^o, ΔS^o for all salts. It was found that values of ΔG^o are negative for three K_A constants in solvent with increase the temperature. This indicates that ion association process is favored over dissociation process in all solvent systems. The positive values of ΔH^o are endothermic in nature for the three salts. ΔS^o positive values are due to the randomness of ions in solvent system studied. El-Hammamy et al. (El-Hammamy, 2016; El-Hammamy, 2017), have measured the conductance of sodium diethyldithiocarbamate in methanol (El-Hammamy, 2016) and water (El-Hammamy, 2017) at different temperatures (25, 30, 35 and 40°C). The results were also 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 logΛ_0 versus $1/T$, in methanol and water 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 both 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. ΔS^o positive values are due to the randomness of ions in the solvent system studied.

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