RESEARCH ARTICLE

ELECTROCHEMICAL STUDIES ON ION PAIRS FORMATION OF TRIMETHYLSULFONIUM HALIDES IN ACETONITRILE AT DIFFERENT TEMPERATURES

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ABSTRACT

The conductance data of trimethylsulfonium halides (bromide and iodide) in acetonitrile 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

Acetonitrile has increased with opens up broad possibilities for studying biological objects[1] and for analytical practice[2]. The selection of acetonitrile was caused by its high dissolving ability and weak solvation of cation in it. A quantitative description of trimethylsulfonium halides with participation of cation cannot be performed without taking into account ionic association between the cation and anion of salt under study. This is in part explained by the absence of reliable data on inter-ionic association constants for salts in non-aqueous solvents a wide temperature range. The purpose of this work was to study interionic association in solutions of trimethylsulfonium halides in acetonitrile at various temperatures. We also determined the acetonitrile of solvation effect to the energy characteristics of inter-ionic interactions. The conductometric method, allowed us to determine not only inter-ionic association constants but also the limiting conductivities of single ions[3,4], which gave additional information about the dynamics of ion-molecular interaction[5]. To study the influence of the nature of the anions on ionic association and solvation, we selected salts containing common cation and different anions but substantially different in electronic structures[6]. 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[7-10]. Furthermore, measuring conductivity was used to study the solute-solvent interaction of some electrolytic solutions and estimate the hydration free energy[11]. The aim of the present work is to determine trimethylsulfonium halides conductance values that measured in acetonitrile at various emperatures (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 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 (ΔE_s) were obtained.

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"**.**

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The specific conductance $\mathscr{B}_\circ$ for acetonitrile at different temperatures (25, 30, 35 and 40°C) was found to be (1.35- 2.12 x 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 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. The solvent constants used in all calculations were taken as reported [12-15], i.e., densities (d25°) = 0.7762 g cm^{-3}, (d30°) = 0.7712 g cm^{-3}, (d35°) = 0.7652 g cm^{-3}, (d40°) = 0.7492 g cm^{-3}, respectively, the viscosities (η25°) = 0.3412 ×10^{-2} P, (η30°) = 0.3270 ×10^{-2} P and (η35°) = 0.31309 ×10^{-2} P, (η40°) = 0.2995 ×10^{-2} P, respectively and the dielectric constants (D25°) = 36.61, (D30°) = 35.97, (D35°) = 35.36, (D40°) = 34.74, respectively.

RESULTS AND DISCUSSION

Conductance of trimethylsulfonium halides (bromide and iodide) in acetonitrile at different temperatures: The measured equivalent conductance data are shown in Tables (1-2). By plotting the extrapolation of against $C^{1/2}$, an approximate value of $_o$ was obtained. More precise values of $_o$ were resulted from the following Fuoss-Kraus-Shedlovsky (F.K.S) equation:

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

(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:

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

(2)

Where is the limiting tangent (Onsager slope). The plot of 1/ $S_{(z)}$ versus (C $S_{(z)}f^2$) gives 1/ $_o$ as the intercept and 1/K_D $_o^2$ as the slope. More accurate values of $_o$, $J_{(a)}$, a° and K_A were obtained from Fuoss-Onsager equation[16]. The starting $_o$ 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 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 was calculated using the equation[17]:

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

(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 acetonitrile 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[16]:

$$J = _1 + _2$$

(4)

Where $_1$ and $_2$ are the functions of J. The derived constants are represented in Tables (3-4) and it is observed that $_o$, K_A, a^o for trimethylsulfonium bromide and trimethylsulfonium iodide increase with increasing the temperatures. The values of $_o$ increase with increasing the size of the anion, in the order { $_o$ trimethylsulfonium iodide > $_o$ trimethylsulfonium bromide}, 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 trimethylsulfonium iodide > K_A trimethylsulfonium bromide}, according to the electrostatic theory.

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

(5)

where, $U = S / k - E_s / kT$

(6)

S/k is the entropy Boltzman constant ratio which illustrates the probability of the orientation of solvent molecules around the free ions, and Es/kT is an energy relationship which includes the energy of the solvent molecules with respect to both free ions (i.e. ion-dipole interaction) and ion-pairs. In case of acetonitrile in Tables (5-6), the U term increases with increasing the temperatures for the two salts, i.e. the entropy term is more predominant than the ion–dipole term for the two salts.

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

$10^4 C$	$C^{1/2}$	$10^6 \kappa$	
Trimethylsulfonium Bromide at 25°C			
1.6758	0.0129	30.71	183.2452
1.5055	0.0123	27.74	184.2490
1.3705	0.0117	25.37	185.1075
1.2526	0.0112	23.29	185.9227
1.1579	0.0108	21.61	186.6164
1.0770	0.0104	20.17	187.2625
1.0064	0.0100	18.90	187.7977
0.9427	0.0097	17.75	188.2792
Trimethylsulfonium Bromide at 30°C			
7.0446	0.0265	137.04	194.5303
6.3222	0.0251	123.41	195.1990
5.7809	0.0240	113.15	195.7304
5.3127	0.0230	104.23	196.1895
4.9128	0.0222	96.59	196.6063
4.5666	0.0214	89.95	196.9696
4.2624	0.0206	84.10	197.3024
3.9836	0.0200	78.73	197.6344
Trimethylsulfonium Bromide at 35°C			
6.9220	0.0263	139.49	201.5157
6.2367	0.0250	126.07	202.1420
5.6418	0.0238	114.38	202.7360
5.1839	0.0228	105.35	203.2229
4.7942	0.0219	97.63	203.6381
4.4272	0.0210	90.33	204.0313
4.1125	0.0203	84.06	204.4001
3.8559	0.0196	78.93	204.6987
Trimethylsulfonium Bromide at 40°C			
5.0818	0.0225	104.38	205.3958
4.5617	0.0214	94.28	206.6742
4.1648	0.0204	86.48	207.6416
3.8071	0.0195	79.38	208.5012
3.5454	0.0188	74.18	209.2262
3.2924	0.0181	69.08	209.8157
3.0787	0.0175	64.78	210.4080
2.8955	0.0170	61.08	210.9477

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

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

$10^4 C$	$C^{1/2}$	$10^6 \kappa$	
Trimethylsulfonium Iodide at 25°C			
1.2616	0.0112	23.20	183.8816
1.1255	0.0106	20.84	185.1565
1.0052	0.0100	18.73	186.3250
0.9159	0.0096	17.14	187.1287
0.8434	0.0092	15.85	187.9238
0.7804	0.0088	14.71	188.4746
0.7260	0.0085	13.73	189.1149
0.6780	0.0082	12.86	189.6542
Trimethylsulfonium Iodide at 30°C			
3.2891	0.0181	65.32	198.5923
2.9507	0.0172	58.77	199.1699
2.6763	0.0164	53.43	199.6359
2.4258	0.0156	48.54	200.0954
2.2471	0.0150	45.04	200.4286
2.0876	0.0144	41.91	200.7537
1.9453	0.0139	39.11	201.0430
1.8160	0.0135	36.56	201.3146
Trimethylsulfonium Iodide at 35°C			
1.0019	0.0100	20.73	206.8981
0.9127	0.0096	18.95	207.6170
0.8332	0.0091	17.35	208.2087
0.7697	0.0088	16.07	208.7705
0.7138	0.0084	14.94	209.2791
0.6665	0.0082	13.98	209.7455
0.6256	0.0079	13.14	210.0326
0.5941	0.0077	12.50	210.3812
Trimethylsulfonium Iodide at 40°C			
2.2316	0.0149	49.25	220.6846
2.0493	0.0143	45.30	221.0439
1.8689	0.0137	41.37	221.3507
1.7263	0.0131	38.27	221.6760
1.6110	0.0127	35.75	221.9043
1.5077	0.0123	33.49	222.1247
1.4188	0.0119	31.54	222.2955
1.3353	0.0116	29.71	222.4938

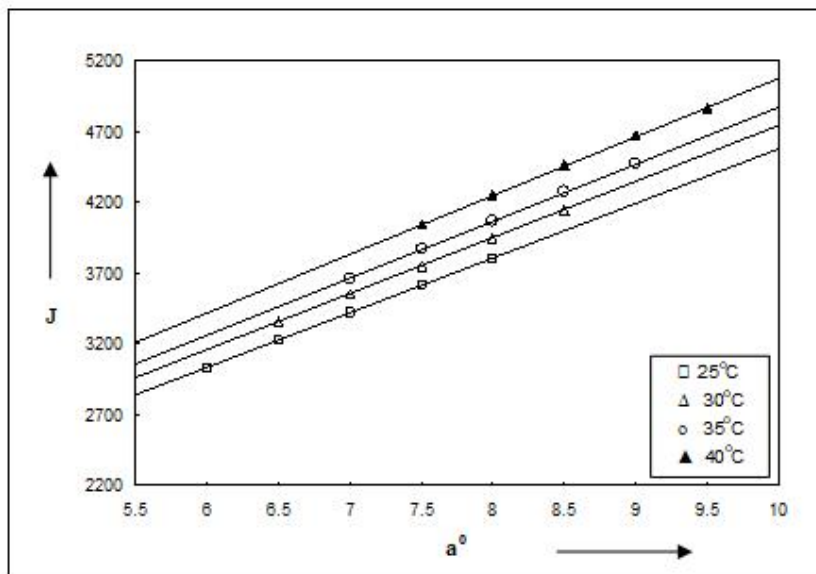* equiv L^{-1} ** $ohm^{-1}\ equiv^{-1}\ cm^2$

Figure 1. Variation of J and a^o of trimethylsulfonuim bromide in acetonitrile at different temperatures.
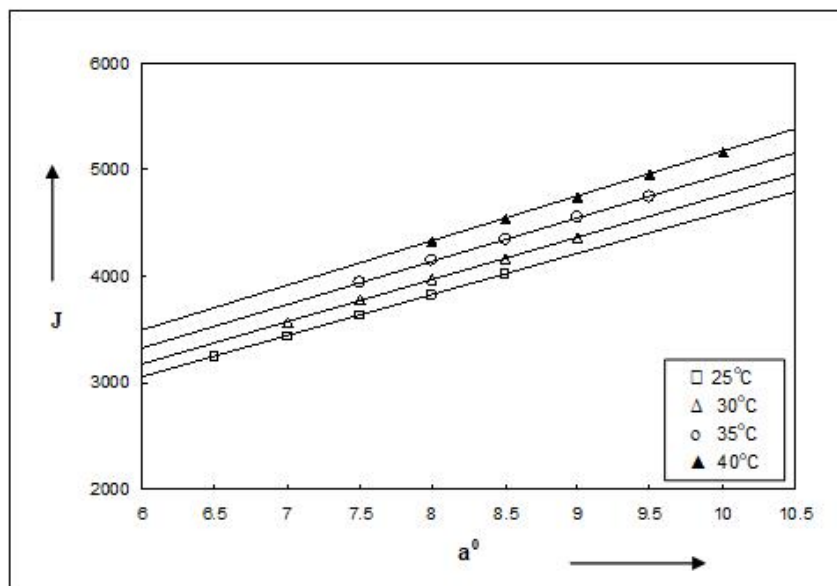

Figure 2. Variation of J and a^o of trimethylsulfonuim iodide in acetonitrile at different temperatures

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

Temperature	(ohm^{-1} equiv^{-1} cm^2)	J	K_A	a ( )	
25°C	197.83 ± 0.1981	3445.5	676.66	7.0	0.0687
30°C	206.49 ± 0.7208	3753.5	814.49	7.5	0.0124
35°C	213.67 ± 0.7199	4072.5	874.09	8.0	0.0116
40°C	223.53 ± 0.2807	4457.4	949.37	8.5	0.0392

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

Temperature	(ohm^{-1} equiv^{-1} cm^2)	J	K_A	a ˙ ( )	
25°C	199.12 ± 0.1428	3630.2	713.15	7.5	0.0459
30°C	207.93 ± 0.3685	3973.9	821.13	8.0	0.0067
35°C	217.70 ± 0.1471	4354.4	887.15	8.5	0.0433
40°C	228.12 ± 0.3130	4750.7	964.31	9.0	0.0176

Table 5: Calculated values of K₂ and U for trimethylsulfonium bromide in acetonitrile at 25, 30, 35 and 40°C:

Temperature	K_A	K_1	K_2	U
25°C	676.66	7.6950	86.9343	4.4765
30°C	814.49	8.1976	98.3567	4.5987
35°C	874.09	8.7689	98.6801	4.6019
40°C	949.37	9.4237	99.7422	4.6125

Table 6: Calculated values of K₂ and U for trimethylsulfonium iodide in acetonitrile at 25, 30, 35 and 40°C:

Temperature	K_A	K_1	K_2	U
25°C	713.15	8.1809	86.1718	4.4678
30°C	821.13	8.7565	92.7729	4.5408
35°C	887.15	9.3968	93.4096	4.5476
40°C	964.31	10.1183	94.3027	4.5570

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

Temperature	$\lambda^{(1)}$	$\lambda_-^{(2)}$	$\lambda_+^{(2)}$	$\lambda_-^{(1)}$	$\lambda_+^{(1)}$	Av. λ_+	R^+ (A°)	R^- (A°)	$R^+ + R^-$	a° (A°)
25°C	197.83	0.3432	0.3304	100.70	97.13	96.925	2.4798	2.3869	4.8668	7.0
30°C	206.49	0.3490	0.3261	106.74	99.75	99.75	2.5120	2.3475	4.8596	7.5
35°C	213.67	0.3368	0.3324	107.59	106.08	106.195	2.4643	2.4324	4.8968	8.0
40°C	223.53	0.3484	0.3264	116.35	107.18	109.0	2.5099	2.3514	4.8614	8.5

(1) ohm⁻¹equiv⁻¹cm²   (2) ohm⁻¹equiv⁻¹cm² p

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

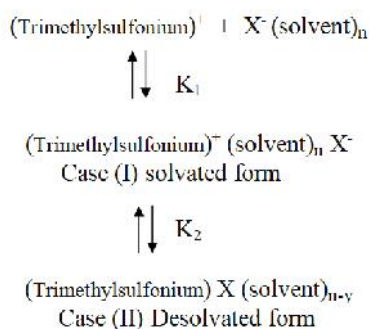| Temperature	$\lambda^{(1)}$	$\lambda_-^{(2)}$	$\lambda_+^{(2)}$	$\lambda_-^{(1)}$	$\lambda_+^{(1)}$	Av. λ_+	R^+ (A°)	R^- (A°)	$R^+ + R^-$	a° (A°)
25°C	199.12	0.3490	0.3304	102.40	96.72	96.925	2.4798	2.3473	4.8271	7.5
30°C	207.93	0.3537	0.3261	108.18	99.75	99.75	2.5120	2.3163	4.8284	8.0
35°C	217.70	0.3487	0.3324	111.39	106.31	106.195	2.4643	2.3494	4.8138	8.5
40°C	228.12	0.3513	0.3264	117.30	110.82	109.0	2.5099	2.3323	4.8423	9.0

(1) ohm⁻¹equiv-1cm²   (2) ohm⁻¹equiv-1cm² p

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

T (K)	(ohm⁻¹ equiv⁻¹ cm²)	K_A	E_s (kJ mol⁻¹)	H (kJ mol⁻¹)	G (kJ mol⁻¹)	S (kJ mol⁻¹ K⁻¹)
298	197.83	676.66			-16.15	110.92
303	206.49	814.49	6.21	16.90	-16.89	111.52
308	213.67	874.09			-17.35	111.25
313	223.53	949.37			-17.84	111.02

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

T (K)	(ohm⁻¹ equiv⁻¹ cm²)	K_A	E_s (kJ mol⁻¹)	H (kJ mol⁻¹)	G (kJ mol⁻¹)	S (kJ mol⁻¹ K⁻¹)
298	199.12	713.15			-16.28	105.86
303	207.93	821.13	7.04	15.27	-16.91	106.19
308	217.70	887.15			-17.38	106.02
313	228.12	964.31			-17.88	105.92

Finally, the solvent separated ion-pair model can be applied [19]. In this model a multiple-step association was suggested, i.e. solvent separated and contact ion-pair can be illustrated in the following scheme:

(Trimethylsulfonium)⁺ + X⁻ (solvent)ₙ

⇅ K₁

(Trimethylsulfonium)⁺ (solvent)ₙ X⁻
Case (I) solvated form

⇅ K₂

(Trimethylsulfonium) X (solvent)ₙ₋ᵧ
Case (II) Desolvated form

Where y = number of escaping solvent molecules from solvation.

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

$$K_A = K \; \Sigma \; \frac{\left[C_{(Ion\ pairs)} \right]}{\left[C_{(Trimethylsulfonium)}^+ \right] \left[C_{X^-\ (solvent)n} \right]} = K_1(1 + K_2) \tag{7}$$

where $K_A = K$ is obtained from the conductance measurements and since $K_1 = 4 \quad N \, a^{o\,3} \, e^b / 3000$ then K_2 can be calculated and $b = e^2 / a^o DTk$

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

Radii of ions

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

$$R^{\pm} = 0.8194 \times 10^{-8} / \quad^{\pm} \quad , \tag{8}$$

where $\quad_o$ is the viscosity of pure solvent and $\quad_o^-$ is obtained from the intercept of the straight line, resulting from the plots of Walden product $\quad_o \quad_o$ versus the reciprocal of the molecular weight as previously discussed [20].

From the data in Tables (7-8), it could be noticed that; in case of acetonitrile 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 acetonitrile 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), o values increase upon the increase in temperature in an indication of higher mobility of the ions or lower solvation [21]. 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 [22]. Svante Arrhenius [23] combined the activation energy concepts and the Boltzmann distribution law into one equation:

$$o = Ae^{-(\ Es / RT)} \quad or \quad \log \quad o = \log A - (\ Es / 2.303 RT) \tag{9}$$

Where R is the ideal gas constant, A is the Arrhenius, pre-exponential, collision or frequency factor, E_S is the Arrhenius activation energy (J/mol) and T is the temperature (absolute, Kelvin). By plotting a graph between log o and 1/T, as displayed in Figures (3, 4), straight lines are obtained with slope (- $E_S/2.303R$) from which E_S value is computed and recorded as seen in Tables (9,10). As shown, the activation energy (E_s) has a positive value which points to the high mobility of ions in the solution and thus high o values.

The change in Gibbs free energy G^o upon the process of association is obtained from equation[24]:

$$G^o = -RT \ln K_A \tag{10}$$

As observed in Tables (9,10), values of G^o are negative for trimethylsulfonium halides (bromide and iodide) in acetonitrile 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 G^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[1].

As resulted in Tables (9,10), the enthalpy change or heat of association (H^o) has been calculated where (– $H^o/2.303R$) 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:

$$d \ln K_A/dT = \quad H^o/RT^2 \tag{11}$$

Then,

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

or

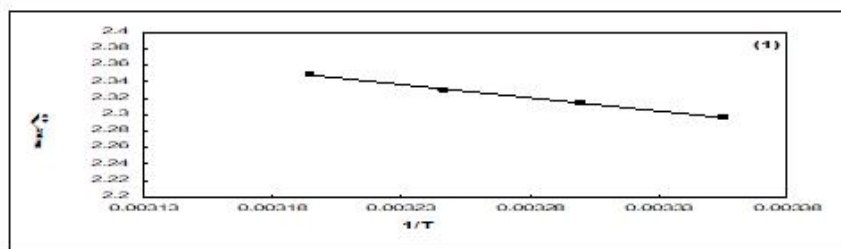$$\log K_A = -(\ H^o/2.303\ R)(1/T\ ) + \quad S^o/2.303\ R \tag{12}$$

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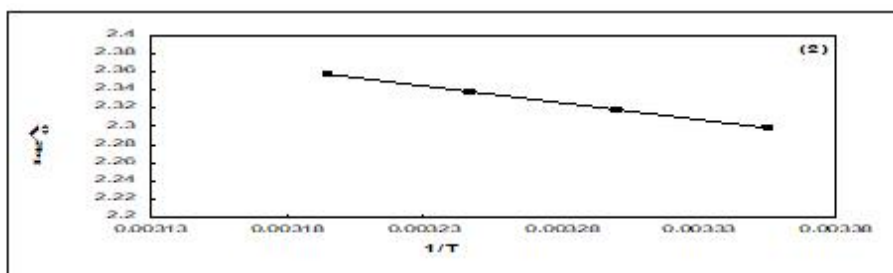

Figure 4: The variation of log Λ_0 vs. 1/T for trimethylsulfonium iodide in acetonitrile at different temperatures
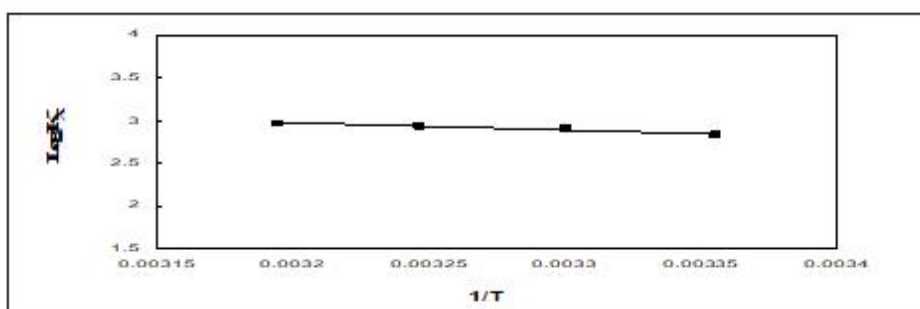

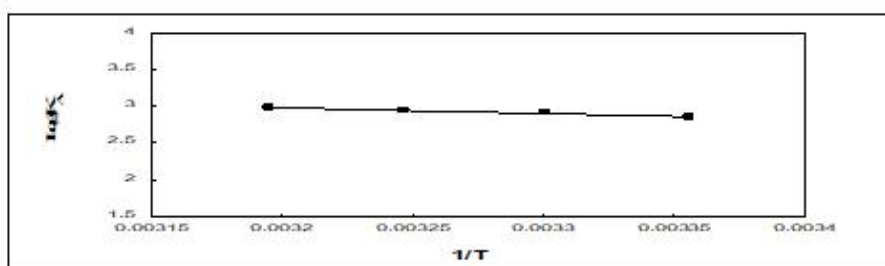**Figure 5: The variation of log K_A vs. 1/T for trimethylsulfonium bromide in acetonitrile at different temperatures.**

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

ΔH^o positive values for trimethylsulfonium halides (bromide and iodide) in acetonitrile refer to endothermic (endergonic) association process because the enthalpy of the products is higher than the enthalpy of the reactants of the system[25]. Gibbs-Helmholtz equation was applied to estimate ΔS^o values (The change of entropy) where:

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{13}$$

For trimethylsulfonium halides (bromide and iodide) in acetonitrile, 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[26-28]. El-Hammamy et al. [29], 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 [16], 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 λ_0 versus 1/T for acetylthiocholine halides and perchlorate in acetonitrile solutions at different temperatures, positive values of E_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.

REFERENCES

1) O.N. Kalugin, V.N. Agieienko, N.A. OtroshKo and V.V. Moroz, Russian J. Phys. Chem. A, 83, 231 (2009).
2) A.D. Roshal, A.V. Grigorovich and A.O. Doroshenko, J. Phys. Chem., 102, 5907 (1998).
3) A. Feofanov, A. Ianoul and S. Gromov, J. Phys. Chem., 101, 4077 (1997).
4) A. Nezhadali, M. Hakimi and A. Naem, Asian J. Chem., 20, 1451 (2008).
5) W. Libus and H. Strzelecki, J. Electrochim. Acta, 15, 703 (1970).
6) W. Libus and H. Strzelecki, J. Electrochim. Acta, 16, 1749 (1971).
7) G. H. Zimmerman and R. H. Wood, J. Solution Chem., 31,995(2003).
8) A. V. Sharygin, R. H. Wood, G. H. Zimmerman and V. N. Balashov, J. Phys. Chem., 106,7121(2002).
9) A. V. Sharygin, I. M. C. Xiao and R. H. Wood, J. Phys. Chem., 105, 229(2001).
10) C. Ho. Patience, D. A. Palmer and R. H. Wood, J. Phys. Chem., 104, 12084 (2000).
11) W. Liu, R. H. Wood and D. J. Doren, J. Chem. Phys., 118, 2837(2003).
12) N.H. El-Hammamy, A.I. Kawana and H.M. Moharem, Alex. J. Pharm. Sci., 25, 34 (2011).
13) N.H. El-Hammamy, A.I. Kawana, M.N. El-Hammamy and H.M. Moharem, J. Chem. Sci. Res., 2, 292 (2011).
14) N.H. El-Hammamy, M.N. El-Kholy, A.I. Kawana and H.M. Moharem, J. Indian Chem. Soc., 89, 1677 (2012).
15) N.H. El-Hammamy, A.I. Kawana, M.N. El-Hammamy and H.M. Moharem, J. Chem. Pharm. Res., 3, 959 (2011).
16) R.M. Fuoss and L. Onsager, J. Phys. Chem., 61, 668 (1957); R.M. Fuoss, J. Am. Chem. Soc., 81, 2659 (1959).
17) G. W. Brown, Am. J. Dis. Child., 136, 937(1982).
18) F. Accascina, A. D'Aprano and R. Triolo, J. Phys. Chem., 71,3469 (1967).
19) D. F. Evans and P. Gardam, J. Phys. Chem., 73, 158(1969).
20) N. H. El-Hammamy, M. F. Amira, S. A. Abou El-Enein and F. M. Abd El-Halim, Indian J. Chem., 23, 43(1984).
21) U. N. Dash, J. R. Mohatra and B. Lal, J. Molecular Liquids, 124, 13 (2006).
22) J. F. Coetzee and C. D. Ritchie, "Solute-Solvent Interaction", Marcel-Dekker, New York, vol. 2 (1976).
23) S. A. Arrhenius, Z. Phys. Chem., 4, 96(1889).
24) S. Glasstone, in: An Introduction to Electrochemistry, Affiliated East-West Press, 4th Ed., New Delhi (1974).
25) R. H Petrucci, W. S. Harwood, F. G. Herring and J. D. Madura, General Chemistry: Principles and Modern Applications. 9th Ed. Pearson Prentice Hall Inc., New Jersey, (2007).
26) S. Pura, J. Molecular Liquids, 136, 64 (2007).
27) H. Yokoyama and H. Kon, J. Phys. Chem., 95, 8956 (1991).
28) S. Pura and G. Atun, J. Solution Chem., 32, 341 (2003).
29) N. H. EI-Hammamy, M. N. EI-Hammamy, N. M. EI-Mallah, A. I. Kawana and H. M. Moharem, Asian J. Chem., 25 (13), 7225 (2013).

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