Electrical Conductance and Ion Pair Formation of S-Acetylthiocholine Halides in Methanol-Water Mixtures at 25 ºC

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Conductance of S-acetylthiocholine halides is measured at 25 ºC in methanol-water mixtures (35.1 < D < 73.7). The conductance parameters derived from the Fuoss-Onsager conductance theory indicate that the solvation of halides decreases with the decrease of the dielectric constants until a certain minimum and then increases again. The plot of log K_A *versus* 1/D is found to be non-linear indicating that the equation of association cannot be applied. The association constant is analyzed using the solvent separated-ion pair model.

Key Words: Electrical conductance, Ion pair formation.

INTRODUCTION

Ion-pair formation of S-acetylthiocholine halides in methanol solution was studied[1]. The conductometric measurements of these salts in methanol-water mixtures at 25 ºC are recorded and then analyzed in an attempt to illustrate the electrolyte-solvent interaction, using the Fuoss-Onsager equation[2]. The relation between K_A and size of anions in the above mentioned medium is discussed.

EXPERIMENTAL

Purification of S-acetylthiocholine halides are reported[1]. Methanol (BDH) was purified as reported[1]. Its specific conductance χ^o amounted to (2.72-7.08 × 10⁻⁷) ohm⁻¹ cm⁻¹.

Conductivity water was prepared as reported[3]. Its specific conductance χ^o amounts to (5-7 × 10⁻⁶) ohm⁻¹ cm⁻¹.

Properties of solvent mixtures: Densities (d) of the mixtures were determined using a 20 mL pyknometer at 25 ± 0.02 ºC. Viscosities (η) were measured using modified Ubeloehde suspended level viscometer with flow time at 25 ºC of 172.4 s for conductivity water. Dielectric constants (D) were obtained by interpolation from a large scale plot of data[4]. In the same way viscosities and densities of experimental solvent mixtures used were interpolated from large scale plots of their data. All solutions were weighted on microbalance with read ± 0.1 mg. Dilution was carried out successively into the cell by siphoning the solvent by means of a weighing pipette.

Conductivity bridge was model Crison Cl p 31 and the cell with bright platinum electrodes was used. The cell constant was 0.1 cm⁻¹ for dilute solution.

RESULTS AND DISCUSSION

Conductance data for S-acetylthiocholine halides in methanol-water mixtures at 25 ºC are obtained and represented in Fig. 1, where the equivalent conductance Λ (ohm⁻¹ equiv⁻¹ cm²) is given at several concentrations C is equiv/liter.
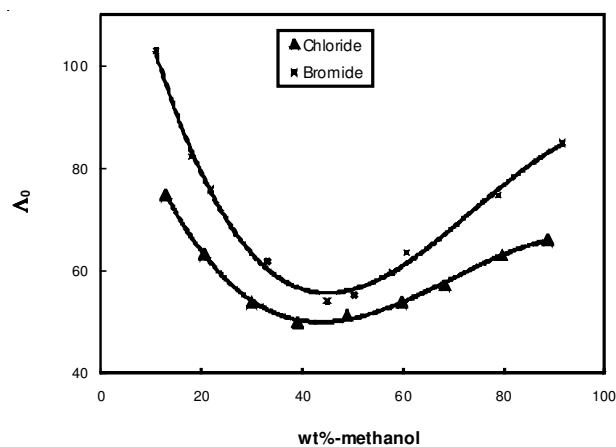

Fig. 1. Variation of Λ_o of S-acetylthiocholine salts with the composition of solvent mixtures

The data analyzed on an IBM-PC computer using the Fuoss-Onsager equation. In all computations the accuracies

required for the absolute values deviations are: ± 0.02 for $\Lambda_\circ$, 5 for $J < 200$, ± 10 for $J = 200 \rightarrow 1000$ and ± 15 for $J > 1000$. The results are depicted in Table-1.

It can be readily seen from Table-1 and Fig. 1 that $\Lambda_\circ$ for S-acetylthiocholine halides exhibit minima at 43 wt % methanol.

The occurrence of a minimum in the value of $\Lambda_\circ$ is an unexpected behaviour. Since on decreasing the dielectric constant, the ionic mobilities are hindered and the chance for ion-pair formation is more prevailing, so $\Lambda_\circ$ should decrease with decrease of the dielectric constant. Figs. 2 and 3 show that a°, J and K_A pass through minimum values at certain dielectric constants.

The initial decreases in a° for s-acetylthiocholine halides can be explained on the basis that the strength of hydrogen bonds between ions and water are so high to be affected by adding small amounts of methanol. On increasing methanol content depolymerisation occurs and an increase of a° values is observed.

The minimum in log K_A *versus* 1/D plot may be explained on the basis that water is a highly associated solvent due to hydrogen bonds forming polymeric aggregates[5]. It is possible that pure water can stabilize the ion-pairs formed as a result of the molecular chains created by hydrogen bonding. On addition of methanol depolymerization occurs and less associated forms are produced, since it was seen from density and viscosity studies[6] that methanol-water is a strong hydrogen bonded system. On further increasing the methanol content the K_A values tend to increase regularly. In this region, it is assumed that over a certain methanol concentration, the water structure could affect the association process of the ions and would undergo less marked variation. The trend of a° shows that, on addition of methanol to water a° decreases (solvation decreases) till a minimum value and then increases for methanol-rich solution[7].

From the above picture of variation of both a° and K_A with dielectric constant, one can conclude that the sphere of
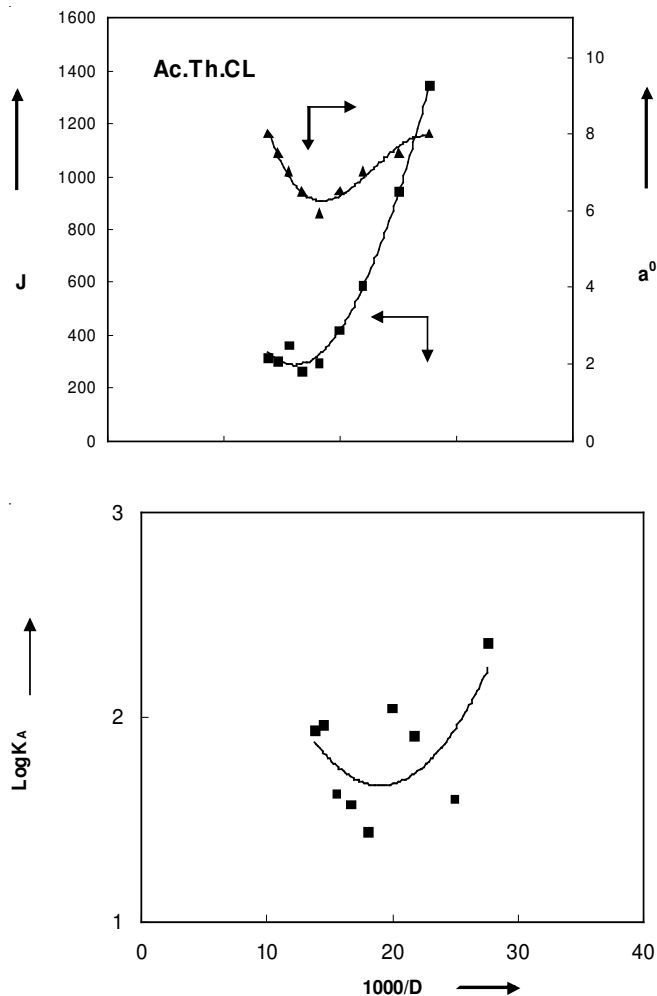

Fig. 2. Variation of J, a° and log K_A with dielectric constant of methanol-water mixtures

continuum model cannot be applied to these systems. Further evidence in support of this conclusion can be obtained by using the expression[8].

TABLE-1
CHARATERISTIC PARAMETERS FOR S-ACETYLTHIOCHOLINE SALTS IN METHANOL-WATER MIXTURES AT 25 ºC

| Wt (%)	D	1000/D	$\Lambda_\circ$	J	a°	K_A	log K_A	σ_A
			S-Acetylthiocholine chloride					
12.96	72.5	13.7931	74.699	314.45	7.988	85.604	1.9325	0.021
20.61	68.8	14.5349	63.222	300.48	7.513	90.689	1.9576	0.011
29.99	64.4	15.5280	53.930	363.15	7.000	42.386	1.6272	0.007
38.97	60.0	16.6667	49.755	263.13	6.488	37.566	1.5748	0.017
49.01	55.3	18.0832	51.297	296.24	5.938	27.245	1.4353	0.160
59.64	50.2	19.9203	53.962	419.07	6.500	110.87	2.0448	0.014
68.26	45.8	21.8341	57.238	585.27	7.000	80.170	1.9040	0.015
79.77	40.0	25.0000	63.078	943.10	7.500	39.591	1.5976	0.008
88.68	36.2	27.6243	66.030	1344.0	8.000	108.75	2.3643	0.014
			S-Acetylthiocholine bromide					
10.87	73.7	13.5685	103.04	367.18	7.500	113.09	2.0524	0.035
17.87	70.2	14.2450	82.318	316.83	7.125	113.44	2.0548	0.070
21.70	68.3	14.6413	75.884	289.60	6.600	193.20	2.2860	0.020
33.04	62.9	15.8983	61.952	264.01	6.025	76.019	1.8809	0.023
44.91	57.3	17.4521	53.987	265.04	5.489	84.691	1.9278	0.014
50.31	54.8	18.2482	55.311	297.51	5.013	88.152	1.9451	0.016
57.80	51.1	19.5695	59.721	375.83	5.494	73.837	1.8683	0.011
60.75	49.6	20.1613	63.485	426.52	5.500	43.691	1.6404	0.014
78.94	40.7	24.5700	74.904	915.26	6.338	89.401	1.9513	0.158
91.76	35.1	28.4900	84.974	1159.1	7.013	55.376	1.7433	0.013

Ac.Th.Br
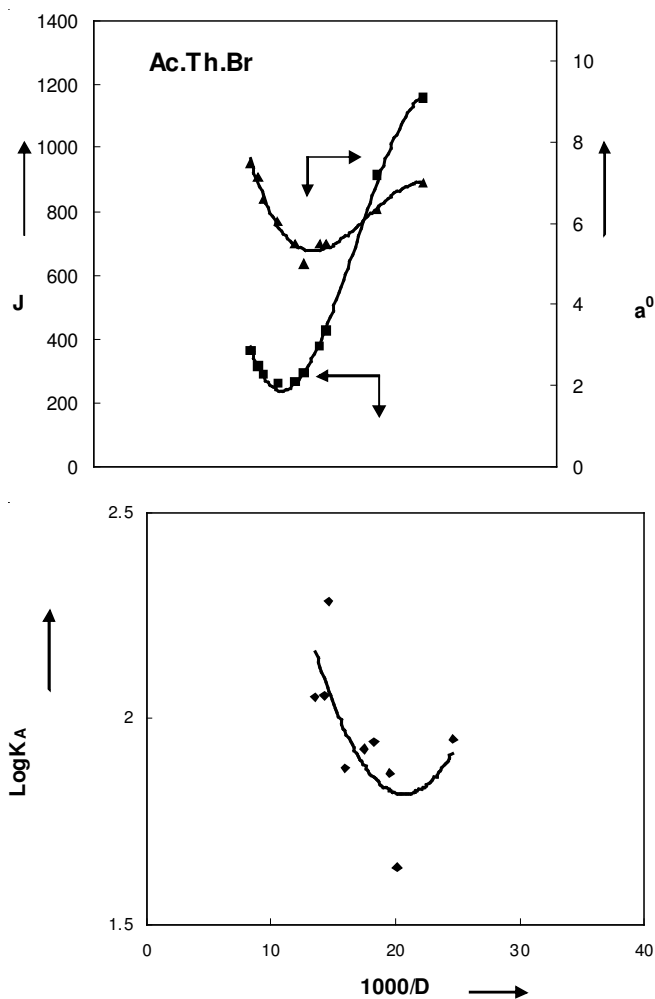
Fig. 3.　Variation of J, $a°$ and log K_A with dielectric constant of methanol-water mixtures
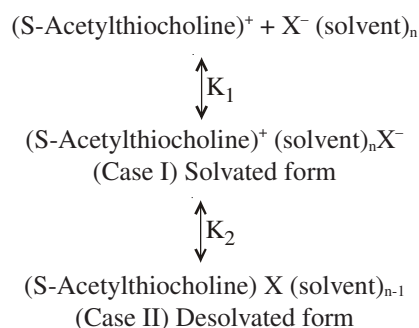
$$\ln K_A = \ln\left(\frac{4\pi Na^{03}}{3000}\right) + \frac{e^2}{a° DkT} + U$$

where $U = \dfrac{\Delta S}{k} - \dfrac{Es}{kT}$.

The factor Es/kT was introduced by Gilkerson[9] to account for the energy of ion-dipole interaction, which should be different from that when ion-pairs are considered. The entropy term $\Delta S/k$ was included[8] to account for the change of entropy due to different arrangements of solvent molecules around free ions and ion-pairs.

The last column in Table-2 shows that U term decreased slightly as methanol wt % increases. This may be due to the fact that the entropy/Boltzman ratio $\Delta S/k$ decreases as the dielectric constant of medium decreases. This means that the ion-dipole interaction term increases as a result of modification of structure of the mixed solvent and interaction between solute and solvent.

Finally, the solvent separated ion pairs model[10] is applied as follows:

(S-Acetylthiocholine)$^+$ + X$^-$ (solvent)$_n$

$\updownarrow$ K$_1$

(S-Acetylthiocholine)$^+$ (solvent)$_n$X$^-$
(Case I) Solvated form

$\updownarrow$ K$_2$

(S-Acetylthiocholine) X (solvent)$_{n-1}$
(Case II) Desolvated form

The association constant is given by expression:

$$K_A = K\Sigma = \frac{[C_{(Ion\text{-}pairs)}]}{[C_{(s\text{-}acetylthiocholine)^+}][C_{X\text{-}(solvent)_n}]}$$

$$= K_1(1 + K_2)$$

where $K\Sigma = K_A$ is obtained from conductance measurements $K_1 = 4\pi Na^{03}e^b/3000$ then K_2 can be calculated $b = e^2/a° DkT$.

TABLE-2
CALCULATED VALUES OF K$_2$ AND U FOR S-ACETYLTHIOCHLINE SALTS IN METHANOL-WATER AT 25 ºC

Methanol (Wt %)	K$_A$	K$_1$	K$_2$	U
S-Acetylthiocholine chloride				
12.96	85.604	3.38339	24.30124	3.23085
20.61	90.689	3.16258	27.67564	3.35605
29.99	42.386	2.99833	13.13654	2.64868
38.97	37.566	2.90521	11.93056	2.55959
49.01	27.245	2.90837	8.367790	2.23728
59.64	110.87	3.85630	27.75036	3.35865
68.26	80.170	4.96565	15.14492	2.78156
79.77	39.591	6.88583	4.749630	1.74914
88.68	108.75	8.93625	11.16953	2.49894
S-Acetylthiocholine bromide				
10.87	113.09	2.93267	37.56213	3.65227
17.87	113.44	2.79694	39.55861	3.70275
21.70	193.20	2.51328	75.87155	4.34214
33.04	76.019	2.41941	30.42047	3.44746
44.91	84.691	2.47644	33.19869	3.52189
50.31	88.152	2.44168	35.10301	3.58637
57.80	73.837	3.06741	23.00103	3.17810
60.75	43.691	3.27108	12.35675	2.59202
78.94	89.401	5.63325	14.87023	2.76444
91.76	55.376	8.46859	5.539900	1.87778

From Table-2 it is evident that K_2 decrease as the dielectric constant decrease. This means that as the dielectric constant decrease as the ion-pair prefers the more solvated form (Case I), *i.e.*, the disturbance due to orientation of solvent molecules around the ion and ion pair decreases by decreasing dielectric constant. This is in good agreement with result of U and K_A.

Fig. 4 shows that the Walden product $\Lambda_\circ\eta_\circ$, a function of solvent composition, for S-acetylthicholine halides in methanol-water mixtures at 25 ºC varies in the usual manner, *i.e.*, it decreases with decreasing dielectric constant. This is in agreement with general findings on several small size (uni-univalent)[11,12] and (bi-bivalent)[13] systems and can be attributed to ion-solvent relaxation drag[14,15].
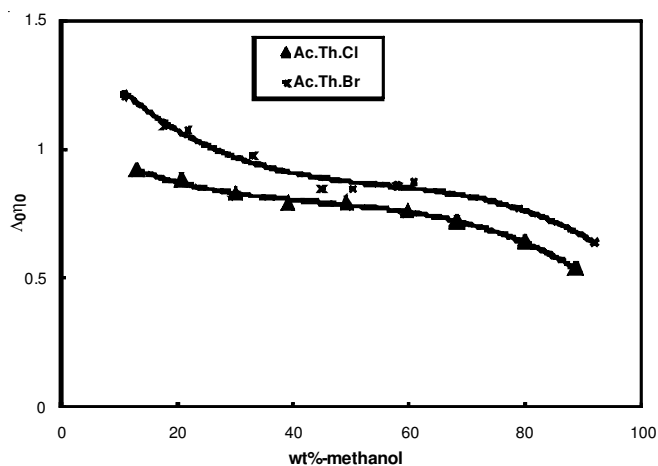

Fig. 4. Variation of Walden product with composition of solvent mixtures

The electrostatic radii R^+ and R^- can be determined by using the Stokes equation in the following form: $R\pm = 0.8194 \times 10^{-8}/\lambda_\circ\eta_\circ$. It is clear that application of Stokes equation needs the determination of the true values of ionic conductance. According to the Fuoss assumption[16] that the transport number is independent of the solvent composition, the ionic equivalent conductance for cations and anions in methanol-water mixtures

are calculated and introduced in the Stokes equation. The results are contained in Table-3.

It can be readily seen from Table-4 that the values of R^+ and R^- increase on decreasing the dielectric constant. This can be explained on the basis that the addition of water to an alcoholic electrolyte solution diminishes the ionic radii[17]. On comparing the summation of electrostatic radii $(R^+ + R^-)$ with the closest distance of approach aº which was previously derived using Fuoss-Onsager equation, one can observe that aº is always greater except in case of rich methanol content. The behaviour can be explained on the basis of Nightingale'[18] conclusions. The summation $(R^+ + R^-)$ increases with decreasing the dielectric constant of the medium which may be due to cosolvent structure[19].

TABLE-3
IONIC EQUIVALENT CONDUCTANCE FOR
S-ACETYLTHIOCHOLINE SALTS IN METHANOL-
WATER MIXTURES AT 25 ºC

Methanol (wt %)	$\Lambda_\circ$	$\lambda_\circ^-$	$\lambda_\circ^+$
S-Acetylthiocholine chloride			
12.96	74.699	61.13142	13.56758
20.61	63.222	51.73899	11.48301
29.99	53.930	44.13469	9.795310
38.97	49.755	40.71800	9.037600
49.01	51.297	41.97993	9.317070
59.64	53.962	44.16088	9.801120
68.26	57.238	46.84186	10.39614
79.77	63.078	51.62114	11.45686
88.68	66.030	54.03697	11.99303
S-Acetylthiocholine bromide			
10.87	103.04	84.28363	18.75637
17.87	82.318	67.33365	14.98435
21.70	75.884	62.07084	13.81316
33.04	61.952	50.67487	11.27713
44.91	53.987	44.15975	9.827250
50.31	55.311	45.24274	10.06826
57.80	59.721	48.84999	10.87101
60.75	63.485	51.92883	11.55617
78.94	74.904	61.26922	13.63478
91.76	84.974	69.50618	15.46782

TABLE-4
CALCULATION OF RADII OF THE IONS FOR S-ACETYLTHIOCHOLINE SALTS IN METHANOL-WATER MIXTURES AT 25 ºC

Methanol (Wt %)	$\Lambda_\circ\eta_\circ$	$\lambda_\circ^-\eta_\circ$	$\lambda_\circ^+\eta_\circ$	R^-	R^+	$R^+ + R^-$	aº
S-Acetylthiocholine chloride							
12.96	0.91611	0.74972	0.16639	1.093	4.925	6.018	7.988
20.61	0.87910	0.71943	0.15967	1.139	5.132	6.271	7.513
29.99	0.83101	0.68007	0.15094	1.205	5.429	6.634	7.000
38.97	0.79071	0.64709	0.14362	1.266	5.705	6.971	6.488
49.01	0.79454	0.65023	0.14431	1.260	5.678	6.938	5.938
59.64	0.75887	0.62103	0.13783	1.319	5.945	7.264	6.500
68.26	0.71885	0.58829	0.13257	1.393	6.276	7.669	7.000
79.77	0.64125	0.52478	0.11647	1.561	7.035	8.596	7.500
88.68	0.53808	0.44034	0.09773	1.860	8.384	10.244	8.000
S-Acetylthiocholine bromide							
10.87	1.21072	0.99033	0.22039	0.827	3.718	4.545	7.500
17.87	1.09129	0.89352	0.19884	0.917	4.121	5.038	7.125
21.70	1.07535	0.87812	0.19541	0.933	4.193	5.126	6.600
33.04	0.97457	0.79712	0.17739	1.028	4.619	5.647	6.025
44.91	0.84781	0.69348	0.15433	1.182	5.309	6.491	5.489
50.31	0.84930	0.69470	0.15460	1.180	5.300	6.480	5.012
57.80	0.85933	0.70290	0.15642	1.166	5.238	6.404	5.494
60.75	0.87400	0.71490	0.15909	1.146	5.151	6.297	5.500
78.94	0.77353	0.63273	0.14081	1.295	5.819	7.114	6.338
91.76	0.63510	0.51949	0.11561	1.577	7.088	8.665	7.013

REFERENCES

1. N.H. El-Hammamy, A.I. Kawana, S.A. El-Shazly and H.M. Moharem, *J. Alex. Pharm. Sci.*, **24**, 97 (2010).
2. R.M. Fuoss and L. Onsager, *J. Phys. Chem.*, **61**, 668 (1957); R.M. Fuoss and L. Onsager, *J. Am. Chem. Soc.*, **81**, 2659 (1959).
3. N.H. El-Hammamy, A.I. Kawana, M.F. Amira and N.S. El-Sisy, *Int. J. Pharm. Biol. Sci.*, **1**, 1 (2010).
4. A.R. Gupta, *J. Phys. Chem.*, **83**, 23 (1979).
5. M. Ageno, *Proc. Nat. Acad. Sci.*, **57**, 856 (1967).
6. N.H. El-Hammamy, H. Sadek, A.M. Hafez and G.A. Ibrahim, *J. Alex. Pharm. Sci.*, **23**, 20 (2009).
7. N.H. El-Hammamy, S.A. Shazly, A.I. Kawana and F.M. Abd El-Halim, *J. Chem. Soc. Pak.*, **13**, 236 (1991).
8. Accasina, A.D. Aprano and R. Triolo, *J. Phys. Chem.*, **71**, 3474 (1967).
9. W.R. Gilkerson, *J. Chem. Phys.*, **25**, 1199 (1956).
10. D.F. Evans and P. Gardam, *J. Phys. Chem.*, **73**, 158 (1969).
11. J.E. Lind and R.M. Fuoss, *J. Phys. Chem.*, **65**, 1001 (1961).
12. R.W. Kunze and R.M. Fuoss, *J. Phys. Chem.*, **67**, 911 (1963).
13. G. Atkinsen and S. Petrucci, *J. Am. Chem. Soc.*, **86**, 7 (1964).
14. R.M. Fuoss, *Proc. Nat. Acad. Sci. USA*, **45**, 807 (1959).
15. R. Zwanzig, *J. Chem. Phys.*, **38**, 1603 (1963).
16. H. Sadek and R.M. Fuoss, *J. Am. Chem. Sci.*, **81**, 4507 (1959).
17. J.T. Denison and J.B. Ramsay, *J. Am. Chem. Soc.*, **77**, 2615 (1955).
18. E.R. Nightingale, *J. Phys. Chem.*, **62**, 1381 (1959).
19. N.H. El-Hammamy, A.A. Hasanien, H.A. Mahmoud and F.M. Abd El-Hlem, *J. Chem. Soc. Pak.*, **8**, 125 (1986).