Conductance of N-N´-Diphenyl-S-Alkylisothiouronium Bromides in Methanol-Water Mixtures at 25°C

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Summary: The conductance of N-N -Diphenyl-S-Alkylisothiouronium bromides is measured in methanol-water mixtures covering $32.63 < D < 66.36$ at 25°C. The data are analysed using the Fuoss-Onsager equation on a PDP 11/70 computer to get Λ_0, K_A, and $a°$. $\Lambda_0 \eta_0$ shows dependence on the solvent composition. The ion-size parameter, $a°$, decreases with decrease in dielectric constant up to $D = 57.14$ and increase thereafter. Log K_A vs. $1/D$ is not linear, indicating that solvent separated-ion pairs are found in systems characterized by strong hydrogen bonding.

Introduction

In recent studies on the conductivity of several alkyl-ammonium halides in methanol and ethanol, Kay and Co-workers [1] obtained values of the association constant, K_A, higher than those expected from the Bjerrum-Fuoss theory [2]. They explained this behaviour on the basis of the hypothesis that the ion-pair association process is affected by the particular structure of the alcohol.

Studies on various electrolytes in alcohol-dipolar aprotic solvent mixture such as methanol-acetonitrile [3], methanol-pyridine [4] and ethanol-acetone [5] gave surprising results for K_A values, which were explained by assuming that changes in alcohol structure affect K_A values much more than the changes in the dielectric constant.

Pistoia and Pecci [6] reached the same results in studying the ion-pair associations of Cs and tetraalkyl-ammonium perchlorates in ethanol-acetone mxitures at 25°C. They observed that (a) for none of the salts examined in these alcohol-dipolar aprotic solvent mixtures did log K_A linearly increase with $1/D$ as expected from the equation ($K_A = K_A° e^b$) and (b) the plot of log K_A vs mixture composition showed a minimum, whose position in a given mixture depended on the specific electrolyte. They concluded that the discontinuity of the solvents in the area near the ions produced anomalous K_A values when the structure of the solvent which more strongly affected these values was drastically changed by addition of another solvent of relatively high dielectric constant.

K.Miyoshi [7] measured the conductance of Bis(2,9-dimethyl 1,10 phenanthroline) copper I perchlorate in normal alcohols and ketones at 25°C. He found that in the plot log K_A vs. $1/D$ a curvature is observed

in this case. This behaviour was also found in dioxane-water mixtures [8]. It has been explained generally as being due to certain solute-solvent interactions.

In the present work N-N-Diphenyl-S-Alkylisothiouronium bromides are selected as electrolytes with large cation size. The effect of the cation size on the conductance of the salt can be discussed from variation of Λ_o, K_A and a° values. The conductance measurements in methanol-water mixtures can also be analysed using the Fuoss-Onsager equation and the derived constants may then illustrate the electrolyte-solvent interaction.

Experimental

Preparation of salts.

The general reaction between diphenylthiourea and alkylbromides was done by mixing equivalent amounts of both the reaatants in alcohol or acetone and refluxing for few hours on a steam bath. The rate of the addition reaction depends upon the solvent [9].

The alkyl halides used in this work were n-butyl-and n-octyl bromides. The addition reaction with diphenylthiourea was done in ethyl alcohol then' refluxing for 3-6 hours. The solution was evaporated to dryness and the resulting compound was doubly crystallized from absolute ethyl-alcohol. Then the compound was dried under vacuum using Abderhalden apparatus [10] and kept in brown bottles in a vacuum desiccator. Table (1) shows the melting points and analysis of salts.

Purification of materials.

Methanol (BDH) was kept in contact with molecular seives 4A(BDH) for about 24 hours with interval shaking, then distilled and refluxed with analar silver nitrate for 24 hours. After distillation it was refluxed again with analar magnesium turnings for 24 hours and then distilled. Again the distillate was kept in contact with activated alumina for 24 hours with interval shaking and then distilled. In all distillations a fractionating column was used and only the middle portion at 65.5°C/1 atm was taken. Its specific conductance ʕ amounts

Table-1: Analysis and M.P. of N-N-Diphenyl-S-Alkylisothiouronium Bromide

Name of Salt	M.P. Found	C% Calcd.	C% Found	H% Calcd.	H% Found	N% Calc.	N% Found	S% Calc.	S% Found	Br% Calc.	Br% Found
N-N-Diphenyl-S-n-Butyl-isothiouronium bromide (N-N-Diph-S-n-BuisBr)	135-136	55.91	56.20	5.75	5.50	7.67	7.20	8.78	8.90	21.88	22.0
N-N-Diphenyl-S-n-Octyl-isothiouronium bromide (N-N-Diph-S-n-OctisBr)	133-134	59.88	59.40	6.89	6.30	6.65	6.80	7.61	7.10	18.97	19.10

to $(9.5 \times 10^{-10}-1.09 \times 10^{-9})$ ohm^{-1} m^{-1}

Conductivity water was obtained by passing ordinary distilled water from a tin still over a 60 cm long Elgastat deioniser and guarded against contamination with atmospheric CO_2 by soda lime tubes. Its specific conductance ℓ_0 was (5.7×10^{-9}) ohm^{-1} m^{-1}.

Preparation of solvent mixture.

Densities (d) of the mixture were determined using a 20 ml pyknometer at $25 \pm 0.02°C$.

Viscosities (η) were measured using a modified Ubelonde suspended level viscometer with flow time at 25°C of 172.4s for conductivity water.

Dielectric constants were obtained by interpolation from a large scale plot of the data [11]. In the same way viscosities and densities of the experimental solvent mixtures used were interpolated from the large-scale plot of these data.

Conductance measurements

An Erlenmeyer cell with bright platinum electrodes was used. Its cell constant is $0.05443 \pm 0.43\%$ as calculated using the Lind, Zwolenik, and Fuoss [12] equation. A "Pye" conductance bridge, Model 11700, was used for measuring the resistance of the solutions.

Preparation of solutions

All solutions were prepared by weight reduced to vacuo. Salts were weighed by difference on microbalance

with reads to ± 0.1 mg. Dilution was carried out successively into the cell by siphoning the solvent by means of a dispenser.

Results and Discussion

Conductance data for N-N-Diphenyl-S-Alkylisothiouronium bromides in methanol-water mixtures at 25°C are summarized in Table (2), where the equivalent conductance Λ (ohm^{-1} equiv.$^{-1}$.cm^2) is given at several concentrations c in equiv./10^{-3} m^{-3}.

The data was analysed on a PDP 11/70 computer using the Fuoss-Onsager equation [13],

$$\Lambda = \Lambda_0 - s(c\ell)^{\frac{1}{2}} + Ec\ell \log c\ell + (J_{(a}{}^{\circ)} - B \Lambda_0)c\ell$$

$$- K_A C \quad (1)$$

where η_0 is the zero limiting equivalent conductance, S the Onsager slope, the degree of dissociation, E a function of η_0, J a function of the ion-size parameter, a°, K_A the association constant and f the activity coefficient.

$$- K_A C \Lambda \eta f^2 \quad (1)$$

The quantity, B, in equation (1), which corrects for the effect of added electrolyte, having large ions, on the viscosity the solvent [14], does not affect the limiting conductance or the association constant, but only changes slightly [15,16] the value of the contact distance a°. From this reason it can be set equal to zero.

In all computations the accuracies required for the absolute values deviations are: ± 0.02 for Λ_0 ; ± 2 for J < 200; ± 5 for J = 200 ------- 1000, and ± 10 for J > 1000. The results are depicted in Tables (3a and b).
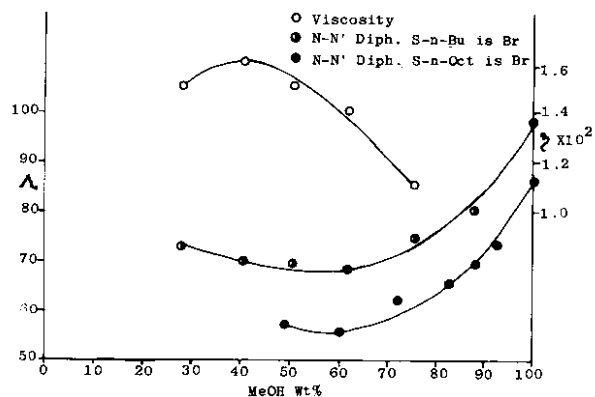
Fig.1: Variation of Viscosity of Solvent and Λ_o with composition of the solvent mixtures.
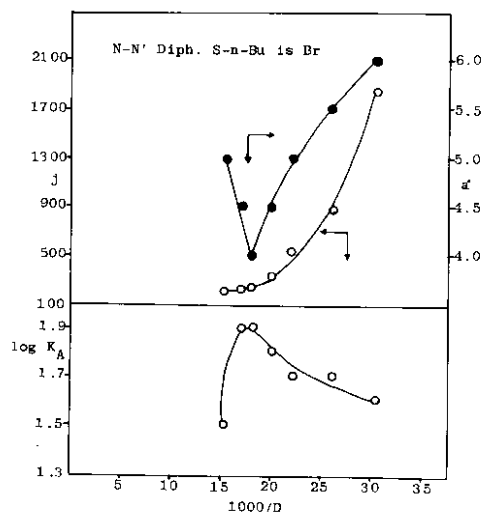

Fig.2: Variation of a, J and long K_A with dielectric constant.

Table-2: Conductance of N-N-Diphenyl-S-Alkylisothiouronium Bromides in Methanol-Water Mixtures at 25°C

$14^4C^{(a)}$	$\Lambda^{(b)}$	$10^4C^{(a)}$	$\Lambda^{(b)}$	$10^4C^{(a)}$	$\Lambda^{(b)}$
			N-N-Diph-S-n-BuisBr		
MeOH wt% = 28.09	(D = 66.36	MeOH wt% = 40.58	(D = 60.68)	MeOH wt% = 50.52	(D=56.04)
20.599	57.561	22.665	50.329	22.842	49.672
19.422	57.733	20.919	50.722	21.053	50.297
17.904	57.909	18.075	51.723	18.701	51.110
15.848	58.209	15.667	52.231	15.966	51.791
13.892	58.616	13.129	53.172	13.398	52.523
12.393	59.033	11.496	53.601	11.726	53.121
10.720	59.422	09.8459	54.373	09.4892	54.192
8.8666	59.823	08.3602	55.027	07.2617	55.118
MeOH wr% = 61.37	(D=51.04)	MeOH wt% = 75.28	(D=44.68)	MeOH wt% = 87.86	(D=38.88)
23.949	49.651	20.569	56.522	22.229	59.441
21.138	50.311	17.697	57.185	20.734	58.886
18.275	51.031	17.016	57.422	17.836	60.619
15.723	51.587	14.921	58.099	14.859	61.883
13.800	52.283	13.307	58.533	12.925	62.244
12.227	52.793	11.373	58.905	11.040	62.934
10.176	53.390	09.8344	59.742	08.6943	63.994
7.9843	54.210	08.1382	60.306	06.6826	64.969

Table-2: (continued)

$10^4 C$	Λ	$10^4 C$	Λ	$10^4 C$	Λ
		N-N-Diph-S-n-Octis Br			
MeOH wt % = 49.01	(D = 65.76)	MeOH wt% = 60.16	(D=51.60)	MeOH wt% = 72.14	(D=46.12)
29.323	52.672	29.709	49.248	28.592	52.662
27.159	53.073	27.139	49.597	25.242	53.395
24.806	53.398	24.164	49.950	22.585	53.881
21.973	53.802	19.592	50.755	18.586	55.122
18.718	54.327	16.680	51.235	15.730	55.690
15.014	55.188	14.873	51.375	13.484	56.155
12.661	55.556	12.021	51.984	11.415	57.048
09.8373	56.411	09.7833	52.524	09.1565	57.715
MeOH		MeOH			
wt = 82.58	(D = 41.36)	wt % = 91.87	(D = 36.92)		
30.173	55.112	29.563	60.342		
27.058	55.847	26.167	61.291		
22.557	56.705	23.165	61.878		
19.678	57.663	18.481	63.260		
16.460	58.117	16.203	64.075		
14.529	58.882	13.394	65.059		
12.040	59.502	11.395	65.678		
09.3784	60.407				

a - equiv./$10^{-3} m^3$ b - $Ohm^{-1} cm^2 equiv.^{-1}$.

It can be readily seen from Tables (3a and b) and Figure (1) that Λ_o for N-N-Diphenyl-S-alkylisothiouronium bromides exhibit minima at 55 wt% methanol, one can observe that the composition at which the minima occur do not coincide with the maximum in the viscosity - methanol wt % (maximum at 41 wt% methanol).

The occurrence of a minimum in the value of Λ_o is an unexpected behaviour, since on decreasing the dielectric constant, the ionic mobility are hindered and the chance for ion-pair formation is more prevailing; so Λ_o should decrease with decrease of dielectric constant.

This unexpected behaviour is ascribed to changes in dielectric constant, which for the most part varies directly with the methanol additions which leads to modifications in the water structure. These modifications may therefore, result in a varying influence of the solvent on the ion-pair formation.

Table-3a: The characteristic Parameters derived from the
Fuoss-Onsagar Equation for N-N-Diphenyl-S-n-Butylisothiouronium bromide
in Methanol-Water Mixture at 25°C.

Methanol wt%	D	1000/D	Λ_o (a)	J	$a°$ (b)	K_A	log K_A	U
28.09	66.36	15.069	62.82	204.48	5.04	30.38	1.48259	2.869
40.58	60.68	16.480	59.66	212.49	4.53	77.77	1.89081	3.766
50.52	56.04	17.844	59.61	226.62	4.01	83.74	1.92293	3.751
61.37	51.04	19.592	58.47	313.65	4.53	60.44	1.78132	3.129
75.28	44.68	22.381	65.15	530.01	5.01	53.86	1.73127	2.632
87.86	38.88	25.720	70.36	885.19	5.53	52.23	1.71792	2.202
100	32.63	30.647	88.09	1844.2	6.04	38.43	1.584670	1.394

a - Ohm^{-1} cm^2 equiv.$^{-1}$ b - 10^{-10}m

Table-3b: The characteristic Parameters derived from the Fuoss-Onsager Equation
for N-N-Diphenyl-S-n-Octyl-isothiouronium bromide in
Methanol-Water Mixtures at 25°C

Methanol wt %	D	1000/D	Λ_o (a)	J	$a°$ (b)	K_A	log K_A	U
49.01	56.76	17.618	57.48	150.78	2.73	1.33	0.12385	-0.360
60.17	51.60	19.380	55.81	136.38	2.06	23.96	1.37949	1.722
72.14	46.12	21.683	62.66	252.48	2.54	45.97	1.66247	2.233
82.58	41.36	24.178	65.84	421.80	3.03	39.30	1.59439	1.859
91.87	36.92	27.086	73.47	732.25	3.49	37.00	1.56820	1.497
100	32.63	30.647	86.52	1335.30	4.03	20.94	1.32098	0.584

a - Ohm^{-1} cm^2 equiv.$^{-1}$ b - 10^{-10}m

Forster and Amis [17] obtained similar behaviour for Λ_o in case of tetra ethylammonium picrate in methanol-water and ethanol-water mixtures [18] and for KCl in methanol-water systesm [9].

Hamer (20) obtained similar behaviour for Λ_o in the cases of HCl, CH_3COOH, NaCl, and CH_3COONa in methanol-water systems at 25°C. It is interesting to note that, while the slat curves show flat minima which are in the trend of the solvent viscosity changes, the acid curves fail to pass through a minimum until a composition of over 90% methanol has been reached, and therefore, they rise sharply. Looking at these acid curves from the alcohol end of the graph, the sharp drop can be explained in the following manner. On the addition of traces of water, protons bound to H_2O molecules will not tend to jump to CH_3OH molecules of lower dipole moment. Thus a corresponding decrease in conductance will take place. When sufficient water has been added, however, proton jumps from H_2O to H_2O become progressively more probable and the conductance begins to rise.

Sadek et al. [21] obtained similar behaviour for Λ_o in the case of S-alkylisothiouronium iodides in methanol-water at 25°C. They also deduced that the minimum in the conductance curves coincide with the maximum in the viscosity curve.

Lal Bahadur et al. [22] obtained similar behaviour for Λ_o in case of tetra-alkylammonium bromides in N-N-Dimethylacetamide-water systems at 35°C. However minimum values of Λ_o for the same salts are obtained at 30 mole % DMA.

Singh et al. [23] obtained similar behaviour for Λ_o in case of Na salts (NaCl, $NaNO_2$, and CH_3COONa) in N-N-Dimethyl formamide-water mixtures at 35°C.

The existance of a maximum in viscosity of the solvent mixtures can lead to a minimum in Λ_o. However, these two do not correspond to the same composition of the solvent mixtures (η_{max}: 25 mole %, and Λ_o min.: 40 mole % DMF). This indicates the simultaneous effect of other factors along with the hydrodynamic viscous force. The shift in Λ_o min. from the expected composition (25 mole % DMF) is attributed to the larger solvated ion in the DMF-rich region.

On the other hand Figures (2-3) show that a° and J pass through minimum values at certain dielectric constant (D = 57.14); while K_A passes through a maximum value at (D 57.14) for N-N-Diph-S-n-BuisBr but in case of N-N-Diph-S-n-OctisBr the maximum of K_A is slightly shifted from this composition.

The trend of variation of a° can be explained using the Frank and Wen [24] picture for an ion in water as well as in pure methanol, as illustrated in the following scheme;
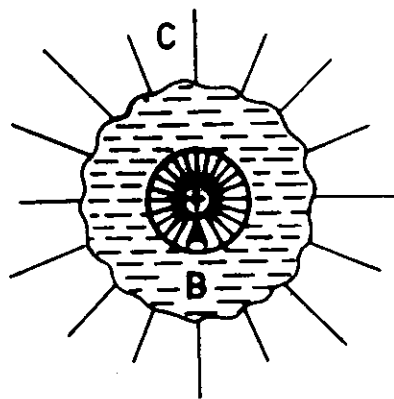
They postulated that the solvent around an ion can be divided into three regions of different structures. The region nearest the ion (A) is one of dielectric saturation, because the ionic field is of the order of hundreds of mega volts/cm. The thrid region (C) is the solvent at relatively large distance from the ion, where the solvent can be described by its macroscopic properties. The second region (B) is a rather vaguely defined region of transition between completely oriented or hydrogen bonded molecules and completely free solvent molecules [24].

The change in the structure of water or methanol around the ion on addition of one of them to the other can be exaplained in terms of the findings of Franks and Ives [25] and other Workers [26]. They found that small additions of methanol to water are responsible for the desctruction of the chain and cyclic polymeric structure of methanol and formation of hydrogen bonds with water. So contraction in volume occurs [27].

The initial decreases in a° for N-N-Diphenyl-S-alkylisothiouronium bromides can be explained on the basis that the strength of hydrogen bonds between ions and water are too high to be affected by adding small amounts of methanol. On increasing methanol-content depolymerisation occurs and increasing of a° values is observed. According to Namiot [28] methanol interacts through its hydroxyl groups not with all water molecules but mainly with existing aggregates. (Ice bergs in region C), and is dissolved at their surface. As the methanol concentration increases the size of icebergs falls but their number rises, i.e., a° increases.

The maximum in log K_A vs. I/D plot can be explained on the basis that on decreasing the dielectric constant, the ionic mobilities are hindered and the chance for ion-pair formation is more prevailing. It was found that Λ should decrease with decrease of dielectric constant until a minimum value at D 52.63 as shown in Figure (1) and increase again with increasing the wt% of methanol. Accordingly K_A must increase in the same direction until a maximum value at D 57.14 is reached as shown in Figures (2-3), there decreasing again with increasing wt% of methanol. The initial increase in K_A for N-N-Diphenyl-S-alkyliso-thiouronium bromides can be explained on the basis that the strength of hydrogen bonds between these salts and water are so high to be affected by adding small amounts of the organic solvent, so K_A goes in the
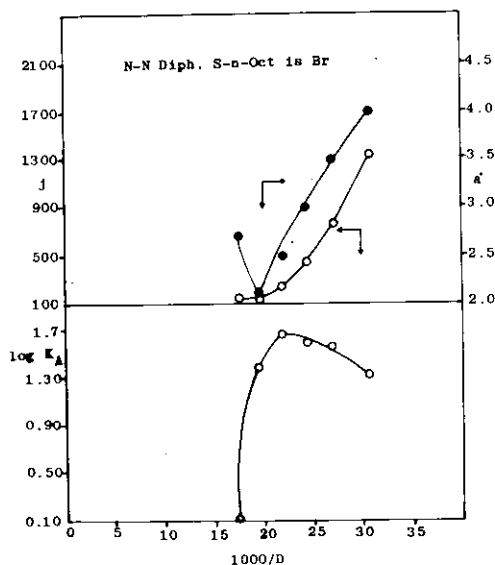

Fig.3: Variation of a°, J and log K_A with dielectric constant.

normal trend. On increasing methanol-content depolymerisation occurs and less associated forms are produced, i.e., the ion-pair formation decrease with increasing the wt% of Methanol. Also the trend of a° shows that, on addition of methanol to water a° decrease (solvation decreases) till a minimum value and then increases for the methanol-rich solutions as discussed before. From electrostatic point of view K_A must pass through a maximum value.

From the above picture of variation of both a° and K_A with dielectric constant, one can conclude that the sphere in continuum model cannot be applied to these systems. The curvature in the plot of log K_A vs I/D in simple and mixed solvents [6-8] has been attributed to certain solute-solvent interactions, and a two step association mechanism involving solvent-separated and contact ion-pairs has been proposed [16,29-34].

D'Aprano and Co-Workers [35,36] explained the minimum in the plot of log K_A vs. I/D for $KClO_3$ sulpholane -water and ethylene carbonate-water mixtures as being due to the increase of ionic solvation as the sulpholane depolymerises the water structure.

Sadek and Hafez [21,37] related the occurance of this minimum for S-alkylisothiouronium iodides and bromides in mixed solvents to the structure modifications produced on the water structure on addition of the organic solvent.

Thus, the sphere in continuum model can not be applied to the case of N-N-Diphenyl-S-alkylisothiouronium bromides in methanol-water

mixtures. Further evidence in support of this conclusion can be abtained when the expression [38]

$$ln\ K_A = In(4\pi Na°^3/3000) + e^2/a°DKT$$

$$+ U \text{ is considered where}$$

$$U = \Delta S/K - E_s/KT$$

The factor E_s/KT was introduced by Gilkerson [39] 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 [38] to account for the change of entropy due to different arrangements of solvent molecules around free ions and ion-pairs.

The last column in Tables (3a and b) shows that U increases as methanol wt% increase at certain value. This gives the proof that the $\Delta S/K$ (entropy/Boltzmann constant
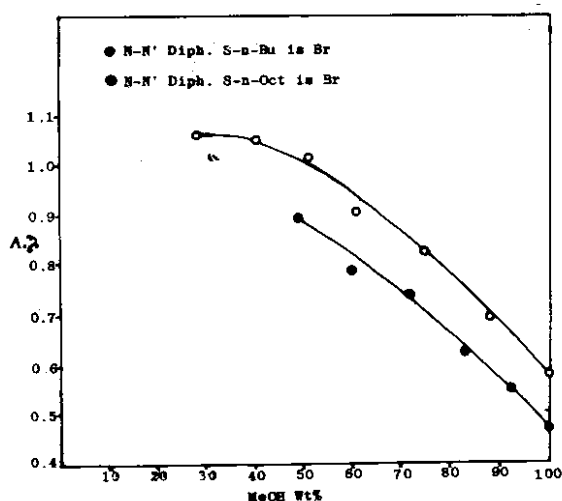

Fig.4: Variation of Walden Product with Composition of the Solvent Mixture.

Table-4a: Estimation of K_2 for

N-N-Diphy-S-n-BuisBr in

Methanol-Water Mixtures at 25°C

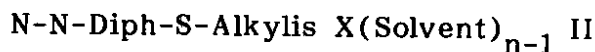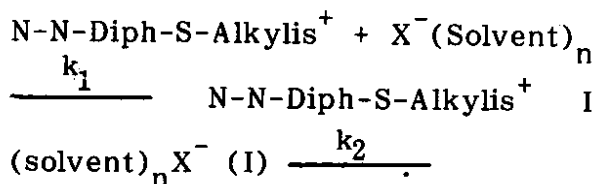| Methanol wt %	K_A	K_1	K_2
28.09	30.38	1.72	16.62
40.58	77.77	1.80	42.22
50.52	83.74	1.97	41.58
61.37	60.44	2.64	21.86
75.28	53.86	3.87	12.91
87.86	52.23	5.77	08.05
100	38.43	9.53	03.03

Table-4b: Estimation of K_2 for

N-N-Diph-S-n-OctisBr in

Methanol-Water Mixtures at 25°C.

Methanol wt %	K_A	K_1	K_2
49.10	1.33	1.91	0.30
60.17	23.96	4.28	4.60
72.14	45.97	4.39	8.33
82.58	39.30	6.12	5.42
91.67	37.00	8.28	3.43
100	20.91	9.53	3.03

this may be attributed to modification of the structure of mixed solvent and interaction between solute and solvent. On further addition of methanol, the U term decreases as the dielectric constant of medium decreases, i.e., U decreases when the methanol content increases. This means that $\Delta S/k$ ratio decreases, while the ion-dipole interaction terms increases, i.e, the disturbance due to orientation of solvent molecules around the ion decreases as the dielectric constant decreases.

Similar to the case of S-Alkylisothiouronium iodides in methanol-water mixtures [21] the solvent separated-ion pairs model [29] is applied as follows :

$$N-N-Diph-S-Alkylis^+ + X^-(Solvent)_n$$

$$\xrightarrow{k_1} N-N-Diph-S-Alkylis^+ \quad I$$

$$(solvent)_n X^- (I) \xrightarrow{k_2}$$

$$N-N-Diph-S-Alkylis \ X(Solvent)_{n-1} \quad II$$

The association constant is given by:

$$K_A = K\Sigma = \frac{C_{(ion-pairs)}}{[C_{(N-N-Diph-S-Alkylis^+,)}][C_{(x^- solvent)_n}]}$$

$$= K_1 \ (1 = K_2)$$

where, $K\Sigma = K_A$ obtained from conductance measurements,

$$K_1 = 4\pi Na°^3/3000 \ e^b.$$

It can be readily seen from Tables (4a,b) that K_2 increases by increasing methanol wt% at a certain value, and then decreases on further addition of methanol content.

This means that, the rate of desolvation K_2 increases at certain value

ratio) increases as the dielectric constant of medium is decreased at a certain value. This indicates that the addition of methanol to water causes the entropy change due to solvent molecules arrangement around ions and pairs to be greater than the ion-dipole interaction term, and

as the dielectric constant decreases, i.e.,the formed ion pair prefers the more desolvated form (case II) to the completely solvated one (case I). Then it can be concluded that the orientation of solvent molecules surround the ion rapidly in case of ions when increasing the methanol wt% at a certain value. But when the rate of desolvation decreases on increasing the methanol wt% or decreasing the dielectric constant of medium. This means that as the methanol wt% increases or dielectric constant decreases the ion pair prefers the more solvated form (case I) to the desolvated form (case II), i.e., the disturbance due to orientation of solvent molecules around the ion decreases by decreasing dielectric constant. This is in good agreement with the result of U and K_A.

Radius of the ion

The Walden product $\Lambda_o \eta_o$ is considered as a function of the solvent composition. Figure (4) shows that the Walden product $\Lambda_o \eta_o$ for N-N-Diphenyl-S-alkylisothiouronium bromides in methanol-water mixtures at 25°C varies in the usual manner. Since it decreases with decreasing dielectric constant, the same behaviour is found in case of $KClO_3$ in dioxan-water mixtures, where the Walden product decreases as the viscosity of solvent increases [40].

The Walden constant $\Lambda_o \eta_o$ for $NaNO_3$ in dioxan-water mixtures [41] at 25°C, shows a miximum at a composition 20% dioxan and then decreases monotonically with decrease in dielectric constant to a magnitude for less than that for water. This is in agreement with general findings on the several small size (uni-univalent

Table-5a: Ionic Equivalent conductances for N-N-Diphenyl-S-n-Butylisothiouronium Bromide in Methanol-Water Mixtures at 25°C ($Ohm^{-1} cm^2 equiv^{-1}$)

Methanol wt %	Λ_o	λ_o^-	λ_o^+
28.09	62.82	40.63	22.19
40.38	59.66	38.58	21.08
50.52	59.61	38.55	21.06
61.37	58.47	37.81	20.66
75.28	65.15	42.13	23.02
87.86	70.36	45.50	24.86
100	88.09	56.97	31.12

Table-5b: Ionic Equivalent Conductances for N-N-Diphenyl-S-n-Octylisothiouronium Bromide in Methanol-Water Mixtures at 25°C. ($Ohm^{-1} cm^2 equiv^{-1}$)

Methanol wt %	Λ_o	λ_o^-	λ_o^+
49.01	57.48	37.84	19.64
60.17	55.81	36.74	19.07
72.14	62.66	41.25	21.41
82.58	65.84	43.35	22.49
91.87	73.47	48.37	25.10
100	86.53	56.97	29.56

[42,43] and bi-bivalent [44] systems and can be attributed to ion-solvent relaxation drag [45,46].

Table-6a: Calculation of the Radius of Ions of N-N-Diphenyl-S-n-Butylisothiouronium Bromide in Methanol-Water Mixture at 25°C.

Methanol wt %	$\Lambda_0\eta_0$ (a)	$\lambda_0^-\eta_0$ (a)	$\lambda_0^+\eta_0$ (a)	R^+ (b)	R^- (b)	R^++R^- (b)	a° (b)
28.09	0.9593	0.6204	0.3388	2.42	1.32	3.74	5.04
40.38	0.9474	0.6127	0.3348	2.45	1.34	3.79	4.53
50.52	0.9162	0.5925	0.3237	2.53	1.38	3.91	4.01
61.37	0.8075	0.5222	0.2853	2.87	1.57	4.44	4.53
75.28	0.7258	0.4693	0.2564	3.20	1.75	4.95	5.01
87.86	0.5896	0.3813	0.2083	3.93	2.15	6.08	5.53
100	0.4796	0.3102	0.1694	4.84	2.64	7.48	6.04

a - Ohm^{-1} cm^2 equiv^{-1} poise

b - 10^{-10} m.

Table-6b: Calculation of the Radius of Ions of N-N-Diphenyl-S-n-Octylisothiouronium Bromide in Methanol-Water Mixtures at 25°C.

Methanol wt %	$\Lambda_0\eta_0$ (a)	$\lambda_0^-\eta_0$ (a)	$\lambda_0^+\eta_0$ (a)	R^+ (b)	R^- (b)	R^++R^- (b)	a° (b)
49.01	0.8921	0.5873	0.3048	2.69	1.40	4.09	2.73
60.17	0.7819	0.5147	0.2672	3.07	1.59	4.66	2.06
72.14	0.7388	0.4863	0.2524	3.25	1.68	4.93	2.54
82.58	0.6268	0.4127	0.2141	3.83	1.99	5.82	3.03
91.87	0.5496	0.3618	0.1878	4.36	2.26	6.62	3.49
100	0.4711	0.3102	0.1610	5.09	2.64	7.73	4.01

a - Ohm^{-1} cm^2 equiv^{-1} poise b - 10^{-10} m

The electrostatic radii R^+ and R^- can be determined by using the Stokes' equation in the following form:

$$R^+ = 0.8194 \times 10^{-8} / \lambda_o \ \eta_o \text{ and } R^- = 0.8194 \times 10^{-8} / \lambda_o \ \eta_o$$

It is clear that application of Stokes' equation needs the determination of the true values of ionic conductance. According to the Fuoss assumption [47] that the transport number is independent of the solvent composition, the ionic equivalent conductances for cations and anions in methanol-water mixture can be caluculated. These values are summarized in Tables (5a, b).

Ionic equivalent conductances λ_o^- and η_o^+ in mixed solvent were used in application of Stoke's equation and the results are contained in Tables (6a, b).

It can be readily seen from Tables (6a,b) that the values of R^+ and R^- increase on decreasing dielectric constant. This can be explained on the basis that addition of water to an alcoholic electrolyte solution diminshes the ionic radii [48].

Kortum and Weller [40] found that the radius of the solvated Li^+ ion in ethanol-water mixtures increases from water to ethanol, i.e., the radius of the solvated ion increases as the amount of the solvent composition with the larger molar volume (ethanol)

increases. This is illustrated in the following Table.

Hughes and Hartley [50] observed the same trend on Stokes' radius for Li^+, Na^+, K^+, $N(C_2H_5)_4^+$, Cl^-, Br^-, I^-, ClO_4^-, and picrate ions in alcohol-water and acetone-water mixtures.

El-Hammamy [27] found that the same trend in Stokes' radii for S-Alkylisothiouronium iodides, in methanol-water mixtures at 25°C. On comparing the summation of electrostatic radii $(R^+ + R^-)$ with closest distance of approach a° which was previously derived using the Fuoss-Onsager equation [13], one can observe that a° is always greater except in case of pure methanol. This behaviour can be explained using Nightingale's [51] conclusion that for water and mixed solvents of high dielectric constant, and high viscosity, Stokes' equation gives appropriate small values due to uncontinuity of the medium.

In the present work, it was found that a° is greater than Stokes' radii $(R^+ + R^-)$ for N-N-Diph-S-n-BuisBr in mixed solvent except in methanol but in case of N-N-Diph-S-n-OctisBr, a° is less than $(R^+ + R^-)$ in mixed solvent and methanol. This behaviour can be considered as due to ion association as proposed by Kay [52]. The summation $(R^+ + R^-)$ increases with decreasing the dielectric constant of medium which may be due to cosolvent structure.

EtOH mole %	0	10	20	30	40	60	80	100
$r^+_{Li^+}(10^{-10}m)$	3.18	3.30	3.47	3.72	3.89	4.30	4.68	5.13

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