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THE ELECTRICAL CONDUCTIVITY OF SOME ORGANIC SALTS IN METHANOL-NITROBENZENE MIXTURES AT 25 °C, 35 °C and 45 °C

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ABSTRACT :

Conductance measurements of S-n-butylisothiuronium bromide, -iodide and -picrate (S-n-Buis Br, S-n-Buis I and S-n-Buis Pi) in methanol-nitrobenzene mixtures at approximately 0.25, 0.5 and 0.75 mole fractions of methanol were studied at 25 °C, 35 °C and 45°C respectively. The data were analyzed using Fuoss' equation⁽¹⁾ (1980) to derive the molar conductance at infinitesimal concentration, Λ_0 , the association distance R and the association constant K_A corresponding to minimum standard deviation σ_A . The discussion was based on the variation of anionic size, the mole fraction of methanol and with varying temperature taking into account ionic solvation and viscosity effect. Thermodynamic parameters ΔG /(kJ/mole), ΔH /(kJ/mole) and ΔS /(J mol⁻¹ K⁻¹) were calculated and interpreted according to the variation of temperature and the mole fraction of methanol.

Key words: Electric conductivity, Ion-solvent interactions, Temperature dependence on the conductance, Thermodynamic parameters.

Introduction

Previous conductance studies of S-alkylisothiuronium salts⁽²⁻⁷⁾ $\left[\begin{array}{c} \text{NH}_2 \\ \diagup \\ \text{C-S-R} \\ \diagdown \\ \text{NH}_2 \end{array} \right] \text{X}$ show that they are considered as a good example of electrolytes with large solvophobic cations and can be used as an important source of information concerning the behaviour of ions in their solutions.

Binary solvent mixtures have a real behaviour upon ionization, dissociation or association and acid-base equilibria of some electrolytes that take place in a solution of two cosolvents. Recently, increasing attention was focused on non-

aqueous mixed solvents, especially those containing dipolar aprotic solvents due to their importance in several industries⁽⁸⁻¹¹⁾. Therefore, the knowledge of nature of binary mixtures provides an insight into the choice of the suitable solvents for different chemical and electrochemical studies.

Nitrobenzene is a versatile dipolar aprotic solvent having a moderately high dielectric constant of 34.82 at 25 °C and its mixtures with aliphatic alcohols of considerable interest from the viewpoint of the existence of specific interactions⁽¹²⁾ through hydrogen bond formation between the two components.

In this work, the conductance measurements of S-n-BuisBr, S-n-Buis I and S-n-BuisPi salts in methanol-nitrobenzene mixtures which are completely miscible at all proportions, show wide variation of there viscosities and are considered as an isodielectric mixture will be reported. The measurements are carried out at x_{MeOH} approximately 0.25, 0.5 and 0.75 and studied at 25 °C, 35 °C and 45°C respectively in order to derive the conductance parameters (Λ , R and K_A) related to minimum standard deviation σ_A . The discussion of these parameters is based on the variation of (a) anionic size, (b) mole fraction of methanol and (c) temperature.

Finally, thermodynamic parameters for the previous solutions can be calculated and interpreted according to the variation of both temperature and mole fraction.

Experimental

S-n-butyliothiuronium bromide⁽²⁾, -iodide⁽¹³⁾ and -picrate⁽³⁾ salts were previously prepared and purified in our laboratory.

The highest purity grade methanol MeOH (Merck) was purified as previously mentioned⁽¹⁴⁾; while the used nitrobenzene NB (BDH) grade was purified according to Mijangos' et al.,⁽¹⁵⁾ method; Nitrobenzene was repeatedly distilled before each measurement due to its hygroscopic nature and sensitivity to light and atmospheric oxygen. The specific conductances κ_o for pure MeOH and NB at 25 °C were found in the range from 7×10^{-8} to $8 \times 10^{-8} \text{ S cm}^{-1}$ and 0.85×10^{-10} to $10^{-10} \text{ S cm}^{-1}$ respectively.

The experimental techniques and apparatus used for measuring the electrical conductance⁽³⁾ (Λ), density(d), viscosity(η)^(7,14,16) and dielectric constant(D)⁽¹⁴⁾ have been mentioned elsewhere. The precision of 10^{-5} was obtained in calculating density at 25 °C and 3×10^{-5} at higher temperatures, (e.g. $0.78666 \pm 1 \times 10^{-5}$ and $0.77738 \pm 3 \times 10^{-5}$ at 25 °C and 35 °C respectively for pure methanol) while the precision was found 10^{-4} for viscosity at all temperatures used. The dielectric constant measurements of each mixture with frequency band from 10^2 - 10^4 kHz allowed a sensitivity of order 10^{-5} .

The reported physical properties for pure solvents were found to be consistent with the literature data as shown in table (1). The physical properties of (MeOH-NB) mixtures (d, η and D) were measured and also reported in table (1) covering the whole miscibility range ($0 \leq x_{\text{MeOH}} \leq 1$) in the temperatures 25 °C, 30 °C, 35 °C, 40 °C and 45°C.

Table (1). Density d_{12} , Viscosity η_{12} and dielectric constant D_{12} of methanol-nitrobenzene mixtures at different mole fractions, x_{MeOH} and at 25 °C, 35 °C and 45 °C.

x_{MeOH}	25 °C			35 °C			45 °C		
	$d_{12}/(\text{g ml}^{-1})$	$\eta_{12}(\text{cP})$	D_{12}	$d_{12}/(\text{g ml}^{-1})$	$\eta_{12}(\text{cP})$	D_{12}	$d_{12}/(\text{g ml}^{-1})$	$\eta_{12}(\text{cP})$	D_{12}
0.000	1.19826	1.8078	34.82	1.1885	1.4938	33.08	1.17917	1.2501	31.41
	1.1983 ^(a)	1.800 ^(c)	34.82 ^(c)	1.1881 ^(b)	--	--	--	--	--
0.0995	1.1821	1.6650	33.86	1.1724	1.3810	32.25	1.1629	1.1581	30.67
0.2174	1.1601	1.5101	33.44	1.1502	1.2537	31.78	1.1406	1.0518	30.22
0.3308	1.1350	1.3520	32.99	1.1250	1.1264	31.39	1.1152	0.9452	29.81
0.3984	1.1178	1.2594	32.81	1.1075	1.0486	31.16	1.0977	0.8840	29.60
0.4652	1.0985	1.1692	32.64	1.0883	0.97380	30.97	1.0784	0.8204	29.39
0.5366	1.0752	1.0671	32.47	1.0649	0.89150	30.77	1.0549	0.7527	29.15
0.6037	1.0499	0.9912	32.36	1.0394	0.83120	30.62	1.0293	0.7045	29.04
0.6555	1.0280	0.9325	32.28	1.0175	0.76520	30.55	1.0074	0.6671	28.97
0.7049	1.0048	0.8770	32.19	0.99418	0.74090	30.47	0.98398	0.6314	28.89
0.8005	0.95155	0.7689	32.10	0.94093	0.65400	30.39	0.93066	0.5624	28.74
0.9005	0.88690	0.6561	32.22	0.87019	0.56430	30.46	0.86018	0.4903	28.77
1.000	0.78666	0.5439	32.60	0.77738	0.47530	30.77	0.76810	0.4181	28.98
	0.78664 ^(d)	0.5445 ^(f)	32.60 ^(e)	0.77729 ^(d)	0.4770 ^(b)	30.73 ^(e)	--	--	28.97 ^(e)

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Results

Table (2) contains the molar conductance $\Lambda/(\text{S cm}^2 \text{mol}^{-1})$ corresponding to the concentration $c/(\text{mol dm}^{-3})$ for S-n-butylisothiuronium salts in (MeOH-NB) mixtures (x_{MeOH} at approximately 0.25, 0.5 and 0.75) at 25 °C, 35 °C and 45 °C respectively. Figures (1-3) illustrate typical examples for the plot of Λ vs. $c^{1/2}$ for the used salts at different temperatures at x_{MeOH} approximately 0.25, 0.5 and 0.75 respectively.

Table (2). Conductance of S-n-butylisothiuronium bromide, -iodide and -picrate (S-n-Buis Br, S-n-Buis I and S-n-Buis Pi) in methanol-nitrobenzene mixtures at 25 °C, 35 °C, 45 °C.

25°C						35°C						45°C					
$x_{\text{MeOH}} = 0.2486$ S-n-Buis Br		$x_{\text{MeOH}} = 0.2545$ S-n-Buis I		$x_{\text{MeOH}} = 0.2470$ S-n-Buis Pi		$x_{\text{MeOH}} = 0.4975$ S-n-Buis Br		$x_{\text{MeOH}} = 0.5106$ S-n-Buis I		$x_{\text{MeOH}} = 0.5090$ S-n-Buis Pi		$x_{\text{MeOH}} = 0.7547$ S-n-Buis Br		$x_{\text{MeOH}} = 0.7530$ S-n-Buis I		$x_{\text{MeOH}} = 0.7514$ S-n-Buis Pi	
$c/(\text{mol dm}^{-3})$	$\Lambda/(\text{S cm}^2 \text{mol}^{-1})$	$c/(\text{mol dm}^{-3})$	$\Lambda/(\text{S cm}^2 \text{mol}^{-1})$	$c/(\text{mol dm}^{-3})$	$\Lambda/(\text{S cm}^2 \text{mol}^{-1})$	$c/(\text{mol dm}^{-3})$	$\Lambda/(\text{S cm}^2 \text{mol}^{-1})$	$c/(\text{mol dm}^{-3})$	$\Lambda/(\text{S cm}^2 \text{mol}^{-1})$	$c/(\text{mol dm}^{-3})$	$\Lambda/(\text{S cm}^2 \text{mol}^{-1})$	$c/(\text{mol dm}^{-3})$	$\Lambda/(\text{S cm}^2 \text{mol}^{-1})$	$c/(\text{mol dm}^{-3})$	$\Lambda/(\text{S cm}^2 \text{mol}^{-1})$	$c/(\text{mol dm}^{-3})$	$\Lambda/(\text{S cm}^2 \text{mol}^{-1})$
14.180	29.455	13.346	34.014	14.900	23.836	21.103	41.289	22.737	43.980	21.07	35.196	17.289	56.198	24.444	39.803	22.731	45.765
19.701	31.040	11.122	34.835	11.694	23.148	17.274	43.284	18.061	44.458	16.724	36.390	13.323	57.475	19.435	41.041	17.604	47.036
7.3132	32.989	8.594	33.893	8.790	26.831	12.372	44.116	15.235	45.950	12.316	37.940	10.080	58.613	12.134	37.940	10.080	58.613
5.3171	34.503	6.4584	36.823	6.4531	28.303	8.993	45.899	11.215	47.151	8.610	39.500	7.656	59.574	11.003	40.561	10.371	48.308
3.9372	35.583	4.8778	37.787	4.9051	29.527	6.579	46.654	8.2799	48.233	6.2099	40.753	5.8723	60.470	10.542	41.835	9.8148	50.343
2.9989	36.529	3.7632	38.525	3.7609	30.631	5.1146	47.448	5.9895	49.178	5.1256	41.214	4.4262	61.250	9.4617	42.732	8.6462	51.250
2.3354	37.234	2.5897	39.253	2.5878	31.671	4.0977	48.070	4.4095	49.919	4.0823	42.553	3.4499	61.818	8.1719	43.620	7.3523	51.923

35°C						45°C											
$x_{\text{MeOH}} = 0.2486$ S-n-Buis Br		$x_{\text{MeOH}} = 0.2545$ S-n-Buis I		$x_{\text{MeOH}} = 0.2470$ S-n-Buis Pi		$x_{\text{MeOH}} = 0.4975$ S-n-Buis Br		$x_{\text{MeOH}} = 0.5106$ S-n-Buis I		$x_{\text{MeOH}} = 0.5090$ S-n-Buis Pi		$x_{\text{MeOH}} = 0.7547$ S-n-Buis Br		$x_{\text{MeOH}} = 0.7530$ S-n-Buis I		$x_{\text{MeOH}} = 0.7514$ S-n-Buis Pi	
$c/(\text{mol dm}^{-3})$	$\Lambda/(\text{S cm}^2 \text{mol}^{-1})$	$c/(\text{mol dm}^{-3})$	$\Lambda/(\text{S cm}^2 \text{mol}^{-1})$	$c/(\text{mol dm}^{-3})$	$\Lambda/(\text{S cm}^2 \text{mol}^{-1})$	$c/(\text{mol dm}^{-3})$	$\Lambda/(\text{S cm}^2 \text{mol}^{-1})$	$c/(\text{mol dm}^{-3})$	$\Lambda/(\text{S cm}^2 \text{mol}^{-1})$	$c/(\text{mol dm}^{-3})$	$\Lambda/(\text{S cm}^2 \text{mol}^{-1})$	$c/(\text{mol dm}^{-3})$	$\Lambda/(\text{S cm}^2 \text{mol}^{-1})$	$c/(\text{mol dm}^{-3})$	$\Lambda/(\text{S cm}^2 \text{mol}^{-1})$	$c/(\text{mol dm}^{-3})$	$\Lambda/(\text{S cm}^2 \text{mol}^{-1})$
14.180	29.455	13.346	34.014	14.900	23.836	21.103	41.289	22.737	43.980	21.07	35.196	17.289	56.198	24.444	39.803	22.731	45.765
19.701	31.040	11.122	34.835	11.694	23.148	17.274	43.284	18.061	44.458	16.724	36.390	13.323	57.475	19.435	41.041	17.604	47.036
7.3132	32.989	8.594	33.893	8.790	26.831	12.372	44.116	15.235	45.950	12.316	37.940	10.080	58.613	12.134	37.940	10.080	58.613
5.3171	34.503	6.4584	36.823	6.4531	28.303	8.993	45.899	11.215	47.151	8.610	39.500	7.656	59.574	11.003	40.561	10.371	48.308
3.9372	35.583	4.8778	37.787	4.9051	29.527	6.579	46.654	8.2799	48.233	6.2099	40.753	5.8723	60.470	10.542	41.835	9.8148	50.343
2.9989	36.529	3.7632	38.525	3.7609	30.631	5.1146	47.448	5.9895	49.178	5.1256	41.214	4.4262	61.250	9.4617	42.732	8.6462	51.250
2.3354	37.234	2.5897	39.253	2.5878	31.671	4.0977	48.070	4.4095	49.919	4.0823	42.553	3.4499	61.818	8.1719	43.620	7.3523	51.923

45°C						55°C											
$x_{\text{MeOH}} = 0.2486$ S-n-Buis Br		$x_{\text{MeOH}} = 0.2545$ S-n-Buis I		$x_{\text{MeOH}} = 0.2470$ S-n-Buis Pi		$x_{\text{MeOH}} = 0.4975$ S-n-Buis Br		$x_{\text{MeOH}} = 0.5106$ S-n-Buis I		$x_{\text{MeOH}} = 0.5090$ S-n-Buis Pi		$x_{\text{MeOH}} = 0.7547$ S-n-Buis Br		$x_{\text{MeOH}} = 0.7530$ S-n-Buis I		$x_{\text{MeOH}} = 0.7514$ S-n-Buis Pi	
$c/(\text{mol dm}^{-3})$	$\Lambda/(\text{S cm}^2 \text{mol}^{-1})$	$c/(\text{mol dm}^{-3})$	$\Lambda/(\text{S cm}^2 \text{mol}^{-1})$	$c/(\text{mol dm}^{-3})$	$\Lambda/(\text{S cm}^2 \text{mol}^{-1})$	$c/(\text{mol dm}^{-3})$	$\Lambda/(\text{S cm}^2 \text{mol}^{-1})$	$c/(\text{mol dm}^{-3})$	$\Lambda/(\text{S cm}^2 \text{mol}^{-1})$	$c/(\text{mol dm}^{-3})$	$\Lambda/(\text{S cm}^2 \text{mol}^{-1})$	$c/(\text{mol dm}^{-3})$	$\Lambda/(\text{S cm}^2 \text{mol}^{-1})$	$c/(\text{mol dm}^{-3})$	$\Lambda/(\text{S cm}^2 \text{mol}^{-1})$	$c/(\text{mol dm}^{-3})$	$\Lambda/(\text{S cm}^2 \text{mol}^{-1})$
14.180	29.455	13.346	34.014	14.900	23.836	21.103	41.289	22.737	43.980	21.07	35.196	17.289	56.198	24.444	39.803	22.731	45.765
19.701	31.040	11.122	34.835	11.694	23.148	17.274	43.284	18.061	44.458	16.724	36.390	13.323	57.475	19.435	41.041	17.604	47.036
7.3132	32.989	8.594	33.893	8.790	26.831	12.372	44.116	15.235	45.950	12.316	37.940	10.080	58.613	12.134	37.940	10.080	58.613
5.3171	34.503	6.4584	36.823	6.4531	28.303	8.993	45.899	11.215	47.151	8.610	39.500	7.656	59.574	11.003	40.561	10.371	48.308
3.9372	35.583	4.8778	37.787	4.9051	29.527	6.579	46.654	8.2799	48.233	6.2099	40.753	5.8723	60.470	10.542	41.835	9.8148	50.343
2.9989	36.529	3.7632	38.525	3.7609	30.631	5.1146	47.448	5.9895	49.178	5.1256	41.214	4.4262	61.250	9.4617	42.732	8.6462	51.250
2.3354	37.234	2.5897	39.253	2.5878	31.671	4.0977	48.070	4.4095	49.919	4.0823	42.553	3.4499	61.818	8.1719	43.620	7.3523	51.923

A preliminary Λ_0 value was taken from the freehand extrapolation to zero concentration of the above plot. The obtained value was introduced as input in Fuoss-Kraus-Shedlovsky (FKS)

equation⁽¹⁷⁾ to give the best straight line to obtain more accurate Λ_0 value; hence

the latter was used as input in the Fuoss⁽¹⁸⁾ (F-80) equation^(1c) to calculate the three adjustable parameters Λ_0 , R and K_A that minimize the standard deviation σ_A . For this purpose a scan computer program

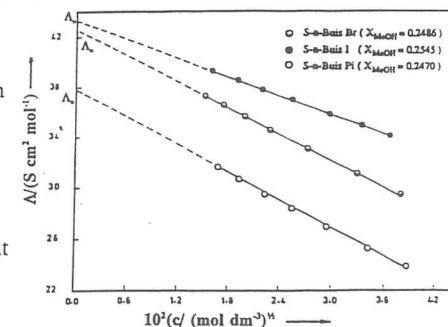


Fig-1: Variation of Λ with $c^{1/2}$ for S-n-butylisothiuronium bromide, -iodide and -picrate in methanol-nitrobenzene mixtures ($x_{\text{MeOH}} = 0.25$) at 25 °C.

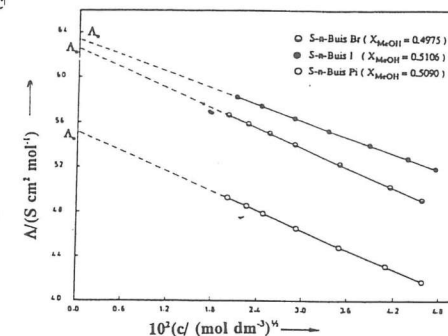


Fig-2: Variation of Λ with $c^{1/2}$ for S-n-butylisothiuronium bromide, -iodide and -picrate in methanol-nitrobenzene mixtures ($x_{\text{MeOH}} = 0.5$) at 35 °C.

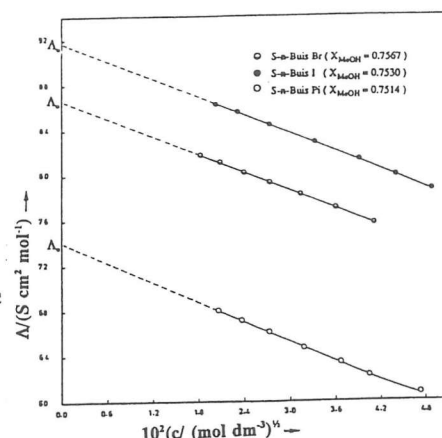


Fig-3: Variation of Λ with $c^{1/2}$ for S-n-butylisothiuronium bromide, -iodide and -picrate in methanol-nitrobenzene mixtures ($X_{\text{MeOH}} = 0.75$) at 45 °C.

provided by Prof. Fuoss was used to analyze the data. In this program a fairly wide range of R values were made to locate the minimum in σ_A vs. β/R curve ($\beta = e^2/DkT$ where k is the Boltzmann's constant) and then a fine

scan around the minimum was made to obtain the accurate value of R that minimize the standard deviation σ_A ; hence the corresponding Λ_0 and K_A are taken.

Table (3) collects the derived Λ_0 and K_A values corresponding to accurate R value for the three used salts at different solvent compositions and at 25 °C, 35°C and 45 °C.

Thermodynamic parameters ΔG , ΔH and ΔS for the solutions of the salts under investigation were calculated according to Barthel *et al.*,⁽¹⁸⁾ relationships:

$$\Delta G = -RT \ln K_A = A_0 + A_1(T-298.15) + A_2[(T-298.15)^2] \quad (1)$$

$$\Delta H = A_0 + 298.15 A_1 + A_2[T^2(298.15)^2] \quad (2)$$

$$\Delta S = A_1 + 2A_2(T - 298.15) \quad (3)$$

in which $A_0 = \Delta G_{298}^\circ$, $A_1 = \Delta S_{298}^\circ$ and $K_A^{(m)}$ in molal scale is related to the association constant $K_A^{(c)}$ which expressed in molar scale by the following relation⁽¹⁹⁾:

$$K_A^{(m)} = d \cdot K_A^{(c)} \quad (5)$$

where d is the density of pure solvent at temperature T. The calculated data are listed in table (4).

Discussion

Table (3) shows that Λ_0 values derived for the salts with common cation (S-n-Buis⁺) at x_{MeOH} approximately 0.25, 0.5 and 0.75 and at any temperature obey the trend $\lambda_{\text{I}}^\circ - > \lambda_{\text{Br}}^\circ - > \lambda_{\text{Pi}}^\circ -$. This trend is consistent with the behaviour of these ions in the dipolar protic solvent MeOH⁽¹⁴⁾ but differ from it for the dipolar aprotic one⁽²⁰⁾.

Table (3): Molar conductance at infinitesimal concentration Λ_0 , the association distance R, the association constant K_A corresponding to minimum standard deviation σ_A for S-n-butylisothiuronium bromide, -iodide and -picrate in (MeOH-NB)⁺ mixtures at 25 °C, 35 °C and 45 °C using Fuoss' Equation (1980).

Salt	X_{MeOH}	X_{NB}	$\Lambda / (\text{S cm}^2 \text{ mol}^{-1})$			$R / (\text{\AA})$			$K_A / (\text{l mol}^{-1})$			$10^3 \sigma_A$		
			25°C	35°C	45°C	25°C	35°C	45°C	25°C	35°C	45°C	25°C	35°C	45°C
S-n-Buis I	0.000 ⁺	0.0000	31.05±0.11	35.34±0.06	41.54±0.15	8.05 [*]	8.20 [*]	8.36 [*]	4467±48	3504±20	2998±37	13.20	9.70	26.1
S-n-Buis Pi		0.0000	26.26±0.75	30.53±0.22	36.61±0.07	8.05 [*]	8.20 [*]	8.36 [*]	28468±1934	22302±383	18837±92	17.46	6.45	2.59
S-n-Buis Br		0.2486	41.20±0.04	47.95±0.001	55.62±0.01	12.2	13.5	13.9	369.65±0.27	33.20±0.07	311.2±0.54	2.76	0.76	8.45
S-n-Buis I	= 0.25	0.2545	42.28±0.03	49.30±0.005	56.43±0.002	14.2	15.4	16.1	189.60±0.18	165.64±0.26	152.2±0.08	2.58	4.65	1.59
S-n-Buis Pi		0.2470	36.85±0.01	43.20±0.002	49.76±0.003	9.1	10.1	10.4	544.82±0.96	502.79±0.12	489.7±0.12	5.73	0.92	1.04
S-n-Buis Br	= 0.5	0.4975	52.26±0.03	61.26±0.002	70.33±0.03	15.2	16.2	17.4	135.2±0.11	121.79±0.04	111.7±0.68	2.97	0.68	27.1
S-n-Buis I		0.5106	53.75±0.03	62.41±0.004	71.01±0.004	15.5	16.5	17.0	93.46±0.08	81.52±0.08	72.83±0.08	2.58	0.85	3.55
S-n-Buis Pi		0.5090	46.37±0.04	53.97±0.009	62.12±0.002	10.3	10.4	10.7	163.80±0.17	143.29±0.25	133.2±0.06	3.45	6.44	1.9
S-n-Buis Br	= 0.75	0.7567	65.67±0.06	75.60±0.002	86.40±0.02	16.7	18.6	21.1	75.86±0.15	65.66±0.04	57.42±0.42	5.67	1.17	22.4
S-n-Buis I		0.7530	70.49±0.02	80.95±0.001	91.42±0.03	16.2	17.2	18.2	57.22±0.21	51.75±0.02	47.58±0.40	12.62	0.23	31.8
S-n-Buis Pi		0.7514	56.13±0.11	64.44±0.001	73.4±0.003	10.3	10.3	10.5	77.68±0.27	69.90±0.03	63.73±0.05	9.30	1.08	1.9
S-n-Buis Br	1.000 ⁺	1.0000	96.90±0.193	111.7±0.003	123.98±0.002	23.2	23.8	24.0	69.71±2.68	56.07±0.31	46.34±0.08	162.7	7.46	3.87
S-n-Buis I		1.0000	104.10±0.02	118.0±0.001	131.87±0.001	22.6	22.8	22.7	33.36±0.41	27.84±0.07	21.82±0.07	20.01	4.46	3.7
S-n-Buis Pi		1.0000	89.08±0.00	101.3±0.005	113.73±0.007	9.2	9.8	10.4	57.53±0.01	46.91±0.09	42.08±0.12	0.38	4.94	6.86

* This value is equal to $\beta/2$ where $\beta = e^2/DkT$ and k is the Boltzmann's constant.
+ MeOH-NB= methanol-nitrobenzene

Evans *et al.*⁽²¹⁾, observed the same behaviour for tetraalkylammonium chloride, bromide and iodide salts in n-propanol-acetone mixtures at 25 °C. Up to 80% acetone, they found that $\lambda_{\text{I}}^\circ - > \lambda_{\text{Br}}^\circ - > \lambda_{\text{Cl}}^\circ -$ whereas at 100% acetone the

trend becomes $\lambda_{Cl^-}^o > \lambda_{Br^-}^o > \lambda_{I^-}^o$. The authors attributed the previous picture to the change of anionic solvation by adding one solvent to the other.

Variation of R and K_A with anionic size (Table 3) were found to obey the following trends at the same temperature

For R at	$x_{MeOH} \approx 0.25$	$I^- > Br^- > Pi^-$
"	$x_{MeOH} \approx 0.50$	$I^- \approx Br^- > Pi^-$
"	$x_{MeOH} \approx 0.75$	$Br^- > I^- > Pi^-$

Meanwhile K_A at the three mole fractions studied has the trend $Pi^- > Br^- > I^-$.

Referring to Fuoss⁽¹¹⁾ opinion that small R values indicate contact distance, moderate R values indicate closest approach distance between solvated ions and large R values indicate Fuoss cosphere diameter that contains more than one non-conducting pair. The previous trends indicate that R represents the closest approach distance. At x_{MeOH} approximately 0.25, I^- is more solvated than Br^- in dipolar aprotic solvent rich composition. Accordingly, K_A for bromide salts must be larger than iodide one. At approximately x_{MeOH} 0.5, R has $I^- \approx Br^-$ may be due to the equal radii of solvated Br^- and I^- . Hence the increase of K_A of Br^- than I^- may be attributed to the role of the solvent in stabilizing the formed ion-pair specially for ion with the higher charge density. At approximately $x_{MeOH} = 0.75$ where R for $Br^- > I^-$, the ionic charge density governs anion solvation, so, R in rich MeOH mixture obeys solvation trend.

The large K_A value of Br salt than that of iodide one may be due to the role of MeOH in stabilizing the formed ion - pair through hydrogen bond formation⁽²²⁾.

The lower R value of picrate salt than those of halides in the above three mole fractions and at all temperatures is only acceptable in both x_{MeOH} at approximately 0.5 and 0.75; Since Pi^- is less solvated than halide ions due to its low charge density in these solvents rich with the dipolar component. The higher K_A value of picrate salt than halides can be explained on the basis of ionic solvation and the role of the solvent in stabilizing the formed ion-pair.

In case of R and K_A for picrate salts, it will be discussed later.

Variation of the three adjustable parameters Λ_o , K_A and R with x_{MeOH}

Inspection of Table (3) indicates that Λ_o value for S-n-BuisBr at 25°C varies from 41.2 to 96.9 giving the ratio 2.35 when going from x_{MeOH} at approximately 0.25 to unity. This ratio was found to be 3.35 and 3.39 for S-n-Buis I and S-n-BuisPi salts respectively when going from pure NB to pure MeOH at 25 °C. This change is due to viscosity effect on ionic mobility; since viscosity varied from 1.8078 cP (NB) to 0.5439 cP (MeOH) at 25 °C. Another reason that may cause the increase of Λ_o with the increase of MeOH content is the preferential solvation of the anions by MeOH as suggested by Sadek and Fuoss⁽¹²⁾.

A glance at Table (3) indicates that R for halide salts increases by increasing MeOH content, whereas that of picrate salts is approximately constant. On the other hand, K_A decreases as MeOH content increases for the three salts under investigation and at all temperatures.

The results of the association distance, R, indicate that bromide and iodide ions are preferentially solvated by MeOH which is a protic solvent while S-n-Buis⁺

cation is preferentially solvated by NB. In other words, these two electrolytes possess heteroselective preferential solvation in MeOH-NB mixtures. The apparent constancy of R values of picrate salt with the mole fraction of MeOH supports the above conclusion; since it is poorly solvated by MeOH due to its low charge density. The heteroselective preferential solvation was also observed for many electrolytes in protic - dipolar aprotic solvents^(23,24).

Table (3) shows that K_A is suddenly decreased from 4467 and 28468 in pure dipolar aprotic solvent nitrobenzene to 189.6 and 544.8 at approximately $x_{\text{MeOH}} = 0.25$ for iodide and picrate salts at 25 °C respectively. In other words, in the region in which ions are predominantly solvated by NB, K_A decreases by a factor 23.6 for iodide salt and 52.3 for picrate one. In the range of x_{MeOH} approximately 0.25 to unity, K_A decreases by factors 5.3, 5.7 and 9.5 for Br, I and Pi salts respectively. This behaviour supports preferential solvation of anions with MeOH, hence electrostatic attraction between opposite charged ions is decreased. The above picture supports the ionic selective solvation.

Studies on various electrolytes in alcohol - dipolar aprotic solvent mixtures such as MeOH-acetonitril,^(24,25) MeOH-NB⁽¹²⁾, ethanol-acetone⁽²⁶⁾ and n-propanol-acetone⁽²¹⁾, in alcohol - apolar aprotic such as MeOH-carbon tetrachloride and MeOH-pyridine⁽²⁷⁾ as well as dipolar aprotic-apolar aprotic such as acetonitril-toluene⁽²⁸⁾ gave surprising results for K_A values which were also explained by assuming that change of solvent structure around ions is more effective than the change of dielectric constant.

Variation of the three adjustable parameters Λ_o , R and K with temperature

A glance at Table (3) shows that Λ_o values for any specific electrolyte at different mole fractions increase by raising temperature. This is an expected behaviour due to the increase of ionic mobility and decrease of viscosity.

In case of the two pure solvents, the association distance R also is shown to increase by the increase of temperature whereas K_A decreases at all MeOH properties. This behaviour is in quite agreement with the rules of electrostatic interactions; since the ionic mobility increases and the electrostatic attraction between ions is weakened. Furthermore, the orientation of solvent molecules around the ions and also around the ion-pair is changed.

Thermodynamic parameters.

Table (4): Thermodynamic parameters (ΔG , ΔH and ΔS) for S-n-butylisothiuronium bromide, -iodide and -picrate in methanol-nitrobenzene mixtures at 25 °C, 35 °C and 45 °C.

Salt	x_{MeOH}	x_{NB}	$-\Delta G/(\text{kJ/mol})$			$-\Delta H/(\text{kJ/mol})$			$\Delta S/(\text{J mol}^{-1} \text{K}^{-1})$		
			25°C	35°C	45°C	25°C	35°C	45°C	25°C	35°C	45°C
S-n-Buis I	0.000 ¹⁴	0.0000	26.48±0.01	26.72±0.01	27.15±0.01	21.99±0.03	16.27±0.06	10.37±0.02	15.1	33.9	52.8
S-n-Buis Pi		0.0000	31.07±0.07	31.46±0.07	32.02±0.02	21.58±0.05	16.84±0.04	11.94±0.03	31.8	47.5	63.1
S-n-Buis Br		0.2486	20.71±0.07	21.11±0.21	21.59±0.17	9.77±0.11	7.45±0.12	5.06±0.08	36.7	44.3	52.0
S-n-Buis I	= 0.25	0.2545	19.06±0.09	19.33±0.16	19.71±0.05	12.64±0.09	9.29±0.09	5.82±0.01	21.5	32.6	43.7
S-n-Buis Pi		0.2470	21.67±0.17	22.16±0.02	22.79±0.06	8.67±0.07	4.87±0.05	0.94±0.07	43.6	56.1	68.7
S-n-Buis Br	= 0.5	0.4975	18.70±0.08	19.04±0.03	19.40±0.60	9.14±0.05	8.27±0.04	7.37±0.05	32.1	34.5	37.8
S-n-Buis I		0.5106	17.82±0.08	18.04±0.09	18.30±0.11	11.81±0.06	10.63±0.05	9.41±0.04	20.2	24.1	28.0
S-n-Buis Pi		0.5090	19.20±0.10	19.48±0.17	19.89±0.05	13.09±0.08	8.84±0.03	4.46±0.06	20.5	34.5	48.5
S-n-Buis Br	= 0.75	0.7567	17.90±0.20	18.10±0.06	18.31±0.73	11.89±0.12	11.79±0.16	11.69±0.03	20.2	20.5	20.8
S-n-Buis I		0.7530	17.19±0.34	17.48±0.04	17.80±0.85	8.88±0.20	8.07±0.18	7.24±0.04	27.9	30.5	33.2
S-n-Buis Pi		0.7514	17.95±0.35	18.25±0.04	18.57±0.08	9.13±0.11	8.59±0.07	8.03±0.06	29.6	31.4	33.1
S-n-Buis Br	1.000 ¹⁴	1.0000	18.46±0.38	18.49±0.55	18.55±0.18	18.16±0.15	17.03±0.13	15.87±0.09	1.00	4.71	8.42
S-n-Buis I			16.63±0.27	16.69±0.26	16.56±0.31	11.83±0.11	5.69±0.11	1.04±0.07	16.1	35.7	55.3
S-n-Buis Pi			17.98±0.01	18.03±0.20	18.30±0.27	16.21±0.20	9.48±0.08	2.54±0.11	5.94	27.7	49.5

Table (4) shows that the free energy change $\Delta G/(\text{kJ/mole})$ for all salts have negative values at all temperatures and their negativity increases by raising temperature. Moreover, the negativity of ΔH decreases with raising temperature whereas ΔS increases with temperature. This behaviour was previously observed and explained in case of pure solvents⁽¹⁴⁾.

Table (4) also shows the decrease of the negativity of ΔG with the increase of MeOH content. On the other hand, ΔH and ΔS shows fluctuating results with trend of decreasing values by increasing MeOH content. Hence the entropy term ($-T \Delta S$) is playing major role in these solvent mixtures. In other words the contribution of ΔH which represents the work done in separating contact pair to infinity is unfavorable to ion-ion association while the value of $(-T\Delta S)$ illustrating the work done to associate the pair is favourable at the used temperatures.

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