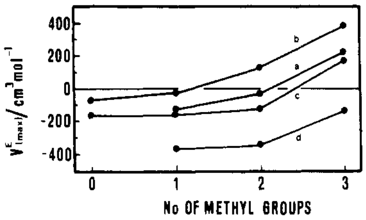

Figure 4. Values of V^E(max) plotted against the number of methyl groups in the methyl-substituted benzene compounds. The same letters are used as in Figure 3. No values of V^E(max) for benzene + 1,3-dioxolane and benzene + oxolane have been found in the literature.

of naphthalene plays a less steric effect on ether than methylbenzene.

It is noteworthy that also V^E curves show a trend similar to the H^E curves, as can be seen from Figures 2 and 4.

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Conductance Behavior of Some Potassium and Tetraalkylammonium Salts in Sulfolane + Water

Ashwini K. Srivastava* and Archana R. Desai

Department of Chemistry, University of Bombay, Vidyanagari, Santacruz (E), Bombay 400 098, India

The conductance behavior of potassium picrate, salicylate, bromide, and iodide as well as tetraethylammonium bromide and tetrabutylammonium tetraphenylboride and iodide has been studied at x = 0.20, 0.40, 0.60, and 0.80 (at 25 °C) and 1.0 (at 30 °C) for mixtures of x sulfolane + (1 - x) water. The conductance data are organized and treated on the basis of the Fuoss (1978) equation using the Fuoss computer program. Values of the limiting molar conductance (Λ_0), association constant (K_A), and cosphere diameter (R) are obtained as a result of the treatment. The limiting ionic mobilities of the individual ions have been reported on the basis of tetrabutylammonium tetraphenylboride reference electrolyte. The Walden product for each system interestingly showed maxima and minima at different mole fractions of sulfolane studied.

Introduction

Sulfolane (tetramethylene sulfone) is of intermediate dielectric constant (43.3 at 30 °C) and belongs to the family of protophobic aprotic solvents. The value of pK_a(S) of sulfolane as a Bronsted acid is estimated to be greater than 31 (*1*), and in addition, sulfolane is known to behave as a very weak base (pK_a(SH$^+$) = -12.9) (*2*). Thus, the solvent is expected to cover an acidity range of over 40 pH units, and therefore, it is a good solvent for a variety of organic and inorganic materials. Ion-dipole-type solute-solvent interactions are expectedly much favored in sulfolane owing to its high dipole moment (4.7). Furthermore, selective solvation of ions in binary solvent mixtures involving a protic and a dipolar aprotic solvent is of considerable importance, both from a fundamental (*3*) and from a technological point of view (*4*).

Although the behavior of electrolytes in sulfolane has been the subject of several conductance investigations, there have been a few conductance studies in sulfolane + water mixtures (*5-7*). The purpose of the present work is to study the behavior of some potassium and tetraalkylammonium salts for x = 0.2, 0.4, 0.6, 0.8, and 1.0 for x sulfolane + (1 - x) water through conductivity measurements. The limiting ionic mobilities of individual ions have been determined on the basis of the limiting molar conductance of the reference electrolyte tetrabutylammonium tetraphenylboride in the above sulfolane + water mixtures.

Experimental Section

Solvent. Commercially available sulfolane (99% pure; Fluka) was first heated with solid NaOH at 100-180 °C, for 24 h, for complete thermal decomposition of 3-sulfolene and elimination of SO_2 and other volatile impurities (if present). This product was distilled twice under reduced pressure in the presence of NaOH. Finally, a third distillation was carried out without any additive under reduced pressure. The fraction boiling at approximately 80 °C at ~133 Pa was used in the present investigation. The specific conductance of the purified solvent ranged between 4 × 10^{-8} and 5 × 10^{-8} S cm^{-1} at 30 °C. Infrared measurements of sulfolane purified in this manner did not reveal any extraneous peaks.

Demineralized water, distilled twice from a Corning glass still was used to prepare sulfolane + water mixtures. The specific conductivity of water varied between 7 × 10^{-7} and 9 × 10^{-7} S cm^{-1}.

Weighed amounts of sulfolane and water were mixed together to obtain the desired compositions.

Chemicals. Potassium picrate was prepared by neutralizing recrystallized picric acid solution with potassium hydroxide solution. The product obtained was recrystallized three times from water and then finally with distilled alcohol. It was dried at 100 °C.

Potassium salicylate was prepared by adding potassium hydroxide to a solution of salicylic acid. The product obtained was recrystallized twice with aqueous alcohol.

Tetra-*n*-butylammonium tetraphenylboride was prepared by the addition of equimolar quantities of tetra-*n*-butylammonium

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Table I. Dielectric Constant ϵ, Density ρ, and Viscosity η for x Sulfolane + $(1 - x)$ Water at 25 °C

x	ϵ	ρ/(g cm^{-3})	$10^2\eta$/P
0.00	78.30	0.9971	0.8903
0.20	61.0	1.155	2.47[a]
0.40	53.7	1.210	3.91[a]
0.60	49.6	1.238	5.49[a]
0.80	47.0	1.255	7.48[a]
1.00	43.32[b]	1.2615[b]	10.30[a,b]

[a] Present work. [b] At 30 °C.

iodide in aqueous solution to an aqueous solution of sodium tetraphenylboride. The precipitate which formed was filtered and recrystallized from a 3:1 mixture of acetone and water. After being dried under vacuum, the product had a melting point of 234 °C.

Potassium bromide (SD, India) was recrystallized three times with alcohol. Tetraethylammonium bromide (SISCO, India) was dried under vacuum for 12 h before use. Potassium iodide (SISCO, India), tetra-*n*-butylammonium iodide (SISCO, India), and sodium tetraphenylboride (Merck) were high-purity materials and were used without further purification.

Conductance Measurements. All conductances were measured, either at 25 or 30 ± 0.05 °C, using a dip-type cell (cell constant 0.9200 at 25 °C) with lightly platinized electrodes. The working solutions were prepared by adding aliquots of stock solutions to a known volume of the solvent using a microliter syringe buret. A Toshniwal conductivity meter, type CL01.07A, was used in the measurements. The reported conductances refer to a frequency of 3 kHz. All equivalent conductances were calculated after correcting for the solvent conductance.

Viscosity Measurements. A Brookfield LVT DVII viscometer with a UL adapter was used to measure the viscosity of the required mole fraction of sulfolane + water mixtures.

Results and Discussion

The physical properties density (ρ), dielectric constant (D), and viscosity (η) of sulfolane + water mixtures (*5*) are given in Table I. The molar conductance values (Λ (S cm^2 mol^{-1})) as a function of concentration (c (mol dm^{-3})) in sulfolane at 30 °C and in four compositions of sulfolane + water mixtures at 25 °C are shown in Tables II and III, respectively. The conductance data are analyzed by the Fuoss (1978) conductance–concentration equation (*8*), following the method of calculations suggested by Fuoss (*9*). For a given set of conductance data (c_j, Λ_j, j = 1, ..., N) preferably spanning a concentration range of at least a decade, the three adjustable parameters limiting molar conductance (Λ_0), association constant (K_A), and cosphere diameter (R) are derived from the following three equations:

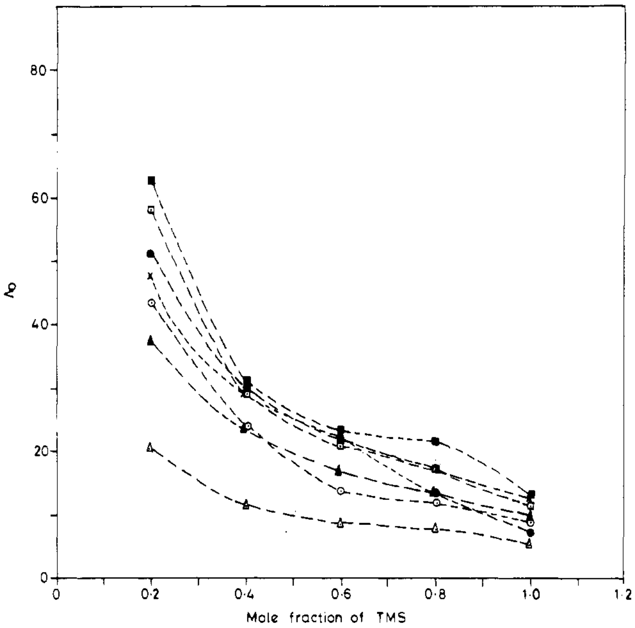

Figure 1. Variation of Λ_0 (S cm^2 mol^{-1}) with x: KBr (■); KI (⊡); potassium salicylate (●); Et$_4$NBr (×); potassium picrate (⊙); Bu$_4$NI (▲); Bu$_4$NBPh$_4$ (△).

$$\Lambda = p[\Lambda_0(1 + \Delta x/x) + \Delta\Lambda_e] \qquad (1)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \qquad (2)$$

$$\ln f = -\beta\kappa/2(1 + \kappa R) \qquad (3)$$

Table II. Molar Conductance Λ at Concentration c of Various Salts in Sulfolane at 30 °C

10^4c/(mol dm^{-3})	Λ/(S cm^2 mol^{-1})	10^4c/(mol dm^{-3})	Λ/(S cm^2 mol^{-1})	10^4c/(mol dm^{-3})	Λ/(S cm^2 mol^{-1})
Potassium Picrate		Potassium Salicylate		KI	
214.6	7.16	201.1	4.12	202.4	10.32
156.0	7.49	153.9	4.53	101.2	10.67
124.6	7.63	126.9	4.83	80.1	10.71
100.0	7.71	108.4	5.02	61.2	10.78
81.0	8.22	81.0	5.32	42.9	10.89
60.6	8.26	60.5	5.75	21.1	11.02
41.0	8.19	41.1	6.02	15.4	11.05
20.0	8.54	16.5	6.65	11.9	11.08
15.1	8.62	13.8	6.70	9.6	11.09
12.6	8.76	11.1	6.80	7.2	11.17
10.1	8.89	8.3	6.90	4.8	11.23
7.6	8.98				
Bu$_4$NBPh$_4$		Bu$_4$NI		Et$_4$NBr	
93.6	4.94	155.6	9.33	205.2	10.39
80.0	4.97	106.5	9.46	150.7	10.64
63.7	5.05	83.4	9.57	126.3	10.87
48.3	5.13	63.6	9.58	105.9	10.98
23.2	5.28	40.3	9.69	80.8	11.25
20.5	5.30	20.3	9.70	63.0	11.41
15.5	5.35	15.0	9.83	40.5	11.67
12.5	5.38	12.6	9.85	21.9	11.70
10.1	5.39	10.2	9.86	15.9	11.93
8.4	5.40	8.3	9.87	12.8	11.94
6.6	5.43	6.4	9.90	10.7	11.95
4.5	5.45			8.6	12.09
				6.5	12.12
				4.3	12.24

Table III. Conductance Data for x Sulfolane + $(1 - x)$ Water at 25 °C

x = 0.20		x = 0.40		x = 0.60		x = 0.80	
10^4c/ (mol dm^{-3})	Λ/ (S cm^2 mol^{-1})	10^4c/ (mol dm^{-3})	Λ/ (S cm^2 mol^{-1})	10^4c/ (mol dm^{-3})	Λ/ (S cm^2 mol^{-1})	10^4c/ (mol dm^{-3})	Λ/ (S cm^2 mol^{-1})
Potassium Picrate							
203.2	38.13	127.3	22.50	188.2	12.94	201.7	9.49
128.2	38.72	106.8	22.79	121.0	13.18	151.5	9.87
100.2	39.01	81.1	23.00	102.6	13.43	123.6	10.07
81.8	39.30	60.9	23.19	81.9	13.70	102.1	10.03
62.3	39.95	40.9	23.41	61.5	13.73	84.2	10.15
40.2	40.65	20.2	23.59	42.0	13.84	64.4	10.32
20.7	41.44	15.0	23.69	20.2	13.88	42.5	10.48
16.7	41.55	12.9	23.75	16.3	13.91	20.5	10.52
13.9	41.60	10.8	23.77	12.3	13.94	15.4	10.65
11.2	41.76	8.7	23.84	10.7	13.96	12.7	10.70
8.4	41.99	6.5	23.85	8.3	14.01	10.1	10.75
5.6	42.20	4.4	23.96	6.7	14.03	8.3	10.79
2.8	42.58	2.2	23.97	4.2	14.06		
				2.5	14.11		
Potassium Salicylate							
153.6	45.04	156.2	26.78	235.1	16.39	191.3	10.33
126.6	45.69	128.7	27.11	137.1	18.00	137.0	10.85
100.6	46.78	103.7	27.62	107.3	18.24	104.4	11.19
82.9	47.16	81.0	27.80	81.5	18.71	83.6	11.48
60.7	47.60	62.5	28.11	63.8	19.12	64.1	11.79
40.3	48.43	40.4	29.03	40.7	20.06	43.1	12.18
20.2	49.15	20.8	29.27	20.9	20.44	20.6	12.65
15.1	49.42	16.7	29.38	16.1	20.65	12.3	12.80
12.5	49.58	14.0	29.44	13.0	20.89	9.7	12.85
10.8	49.73	11.2	29.59	9.8	21.10	7.4	12.96
		8.5	29.63	6.5	21.24	5.0	13.12
		5.7	29.83			2.5	13.23
KI							
149.7	55.73	201.2	26.21	212.3	19.22	161.2	15.04
126.6	55.93	106.4	27.68	161.8	19.47	126.0	15.13
108.3	56.00	80.1	27.82	116.8	19.72	108.6	15.34
88.9	56.13	60.1	27.83	81.4	19.99	80.4	15.62
68.5	56.50	40.8	28.03	60.7	20.09	61.2	16.11
47.0	56.66	20.8	28.08	41.9	20.26	40.8	16.39
19.5	57.02	15.0	28.12	21.8	20.35	20.3	16.50
16.3	57.15	13.1	28.14	15.4	20.42	17.7	16.63
13.1	57.16	10.1	28.17	11.1	20.44	13.7	16.75
9.8	57.32	8.1	28.36	8.9	20.48	11.0	16.79
6.6	57.42	6.1	28.38	6.7	20.52	8.3	16.92
3.3	57.53	4.1	28.53	4.5	20.55		
		2.1	28.63	2.3	20.79		
KBr							
220.3	54.06	201.0	26.27	108.0	18.52	211.0	16.57
156.0	55.49	153.2	27.06	82.6	19.12	158.3	17.54
125.9	56.27	103.8	27.82	60.3	19.78	125.7	17.88
103.7	56.82	80.2	28.19	42.3	20.42	103.9	18.36
80.1	57.65	60.8	28.77	23.0	21.23	85.6	18.76
61.5	58.31	40.6	29.10	15.2	21.75	65.5	19.03
42.0	59.18	20.6	29.80	12.9	22.00	43.2	19.84
21.5	60.27	15.6	29.90	10.6	22.28	20.0	20.26
15.9	60.60	10.5	30.36	7.1	22.31	15.6	20.34
11.6	61.07	8.4	30.54	4.8	22.70	12.9	20.45
8.7	61.38	6.4	30.55			10.2	20.69
5.8	61.59					8.4	20.78
						6.6	20.82
						4.7	20.95
						2.8	21.18
Bu_4NBPh_4							
12.2	17.89	32.3	10.71	63.0	8.26	55.9	6.74
7.1	18.56	21.5	10.86	41.7	8.39	50.4	6.84
6.6	18.64	15.0	10.95	42.3	8.51	41.9	7.04
6.1	18.69	12.1	11.02	15.2	8.56	33.3	7.10
5.4	18.81	10.2	11.10	12.5	8.60	21.0	7.31
4.6	19.01	8.7	11.17	10.3	8.62	14.3	7.45
3.5	19.26	6.8	11.24	8.0	8.63	12.5	7.51
2.0	19.61	4.9	11.29	6.2	8.64	10.6	7.62
		3.9	11.35	4.5	8.66	8.6	7.81
		2.8	11.38	3.4	8.73	6.6	7.71
		1.8	11.41	1.7	8.79	4.1	7.82
						2.3	7.91
						1.6	8.01

Table III (Continued)

x = 0.20		x = 0.40		x = 0.60		x = 0.80	
10^4c/ (mol dm^{-3})	Λ/ (S cm^2 mol^{-1})	10^4c/ (mol dm^{-3})	Λ/ (S cm^2 mol^{-1})	10^4c/ (mol dm^{-3})	Λ/ (S cm^2 mol^{-1})	10^4c/ (mol dm^{-3})	Λ/ (S cm^2 mol^{-1})
Bu_4NI							
204.5	34.10	202.5	21.77	201.7	15.89	217.0	11.28
100.7	34.88	102.4	22.32	103.2	16.21	150.3	11.90
83.0	35.33	80.0	22.46	82.4	16.30	126.0	11.96
60.0	35.59	61.2	22.69	60.0	16.43	100.3	12.04
40.3	35.82	40.3	22.88	40.1	16.51	81.0	12.29
21.1	36.17	20.3	22.94	20.3	16.65	64.5	12.51
16.0	36.31	14.6	23.00	15.6	16.67	42.6	12.85
13.4	36.37	12.9	23.07	12.4	16.69	20.2	13.00
10.8	36.46	10.4	23.09	10.8	16.76	15.3	13.06
8.1	36.47	8.7	23.16	8.4	16.77	12.8	13.11
6.4	36.51	6.1	23.26	6.7	16.82	10.3	13.20
4.6	36.66	4.4	23.38	4.2	17.05	7.7	13.26
2.7	36.73	2.6	23.79			5.2	13.58
						2.6	13.62
Et_4NBr							
223.0	43.60	145.5	23.75	222.3	19.27	209.1	14.09
150.2	44.33	123.4	24.22	162.5	19.72	152.9	14.63
126.0	44.79	105.1	24.56	128.1	19.97	126.1	14.88
100.4	44.90	80.6	25.11	108.1	20.18	108.9	15.03
81.4	45.21	60.2	25.71	97.9	20.21	97.0	15.18
61.5	45.42	40.3	26.39	81.7	20.29	79.6	15.30
40.7	45.83	20.5	27.21	62.2	20.85	61.2	15.72
22.6	46.40	15.8	27.46	41.5	21.40	41.9	16.04
18.9	46.47	11.9	27.76	22.9	21.46	21.5	16.37
15.2	46.52	10.0	27.94	19.7	21.48	18.5	16.59
11.5	46.61	8.0	28.06	16.5	21.54	15.5	16.60
7.7	46.83	6.0	28.33	13.2	21.67	12.4	16.73
				10.0	21.82	9.4	16.67
				6.7	21.86	6.3	16.77
						3.1	17.04

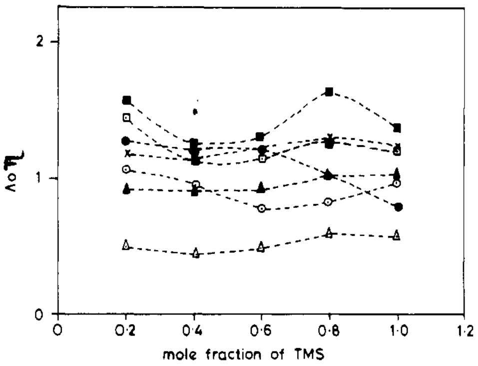

Figure 2. Variation of salt Walden product ($\Lambda_0\eta$ (S cm^2 mol^{-1} P)) with x: KBr (■); KI (⊡); potassium salicylate (●); Et_4NBr (×); potassium picrate (⊙); Bu_4NI (▲); Bu_4NBPh_4 (△).

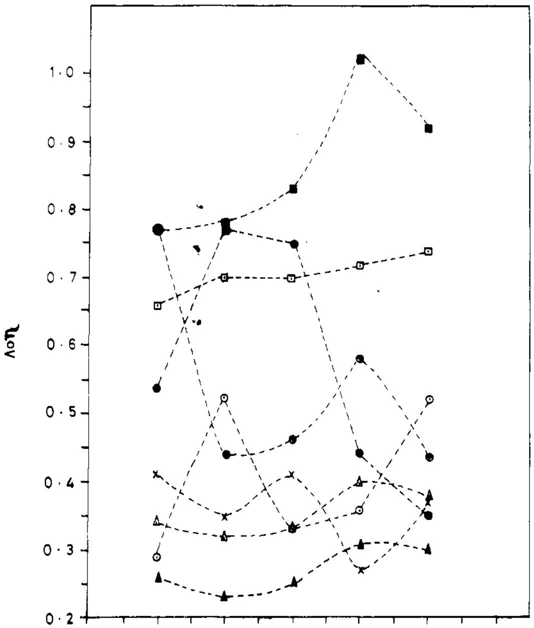

Figure 3. Variation of ionic Walden product ($\lambda_0\eta$ (S cm^2 mol^{-1} P)) with x: Br^- (■); salicylate(−) (O); I^- (⊡); K^+ (⊕); Et_4N^+ (×); Ph_4B^- (△); picrate(−) (⊙); Bu_4N^+ (▲).

Here $\Delta x/x$ and $\Delta\Lambda_e$ are the relaxation and electrophoretic terms, respectively, and expressions used for these terms are the same as those used by Fuoss (*8*). The program SCAN ON RHO is used to compute the conductance parameters. Various parameters thus derived from the conductance data are assembled in Table IV; σ (%) is the standard deviation calculated as a percentage of the limiting molar conductance (i.e., $\sigma \times 100/\Lambda_0$). The last column gives the corresponding Walden product ($\Lambda_0\eta$) values.

According to the assumptions of Fuoss et al. (*10*, *11*), the limiting transference number for the Bu_4N^+ ion in Bu_4NBPh_4 is 0.519 and independent of the kind of solvent used, so the ionic limiting conductivity was calculated on the basis of the following relation:

$$\Lambda_0(Bu_4N^+) = 0.519\Lambda_0(Bu_4NBPh_4)$$

The limiting ionic conductances ($\lambda^\circ_\pm$) and the Walden products of ions ($\lambda^\circ\eta$) are presented in Table V. The limiting ionic conductances 2.95, 4.26, 7.22, and 5.03 for Bu_4N^+, K^+, I^-, and picrate(−) ions, respectively, in sulfolane at 30 °C obtained in the present work are in agreement with the values 2.80, 4.05, 7.22, and 5.28, respectively, reported in the literature (*12*).

The limiting molar conductance variations with mole fraction of sulfolane are shown in Figure 1. A decrease in Λ_0 for each electrolyte with a corresponding increase in the viscosity of the

Table IV. Derived Conductance Parameters for Salts in Sulfolane + Water Mixtures at 25 °C and in Sulfolane at 30 °C

x	$\Lambda_0 \pm \Delta\Lambda_0$/(S cm^2 mol^{-1})	K_A	K_R	K_S	R/Å	σ/%	$\Lambda_0\eta$/(S cm^2 mol^{-1} P)
			Potassium Picrate				
0.20	43.30 ± 0.06	78.76	63.14	0.25	26	0.27	1.069
0.40	24.49 ± 0.04	42.93	38.40	0.12	21	0.39	0.957
0.60	14.47 ± 0.06	75.03	68.48	0.10	26	0.90	0.794
0.80	11.21 ± 0.48	30.15	21.77	0.38	16	0.81	0.838
1.00	9.29 ± 0.07	27.08	9.00	2.01	10	1.32	0.953
			Potassium Salicylate				
0.20	51.33 ± 0.12	10.27	4.07	1.52	8	0.40	1.260
0.40	30.65 ± 0.07	16.57	8.67	0.91	11	0.46	1.198
0.60	22.06 ± 0.08	24.02	4.35	4.53	7	0.64	1.211
0.80	13.58 ± 0.04	25.99	5.73	3.53	8	0.55	1.015
1.00	7.64 ± 0.08	80.55	4.00	19.14	5	1.38	0.784
			KI				
0.20	58.37 ± 0.05	72.42	69.79	0.04	27	0.16	1.444
0.40	29.08 ± 0.12	47.52	43.17	0.10	22	0.98	1.136
0.60	21.07 ± 0.05	61.31	55.85	0.10	24	0.50	1.156
0.80	17.51 ± 0.06	21.09	9.93	1.12	11	0.65	1.310
1.00	11.48 ± 0.02	61.33	53.37	0.15	23	0.28	1.189
			KBr				
0.20	62.87 ± 0.02	9.81	3.21	2.05	7	0.08	1.552
0.40	31.43 ± 0.05	13.98	4.76	1.94	8	0.32	1.228
0.60	23.45 ± 0.05	59.34	20.94	1.83	16	0.33	1.287
0.80	21.60 ± 0.07	24.45	5.73	3.26	8	0.74	1.615
			Bu_4NBPh_4				
0.20	20.52 ± 0.02	411.83	248.37	0.66	43	0.09	0.506
0.40	11.73 ± 0.01	117.83	6.46	0.22	30	0.20	0.458
0.60	8.90 ± 0.02	33.64	31.75	0.06	21	0.54	0.488
0.80	8.18 ± 0.03	48.29	13.87	2.48	13	0.69	0.611
1.00	5.68 ± 0.01	42.31	29.83	0.42	18	0.30	0.583
			Bu_4NI				
0.20	37.47 ± 0.06	31.73	28.06	0.13	19	0.38	0.925
0.40	23.90 ± 0.05	47.71	43.17	0.10	22	0.54	0.934
0.60	17.28 ± 0.03	125.52	117.68	0.07	32	0.32	0.948
0.80	13.84 ± 0.05	21.41	9.93	1.16	11	0.76	1.035
1.00	10.17 ± 0.02	113.12	104.10	0.09	30	0.33	1.044
			Et_4NBr				
0.20	47.99 ± 0.06	16.36	13.34	0.23	14	0.24	1.185
0.40	29.17 ± 0.02	42.89	19.84	1.16	16	0.16	1.140
0.60	22.58 ± 0.06	20.05	11.18	0.79	12	0.58	1.239
0.80	17.43 ± 0.04	22.47	8.31	1.70	10	0.47	1.304
1.00	12.54 ± 0.03	25.36	12.59	1.01	12	0.53	1.287

Table V. Limiting Ionic Conductances λ_0 and Ionic Walden Products $\lambda_0\eta$ in Sulfolane at 30 °C and in Sulfolane + Water Mixtures at 25 °C

x	Bu_4N^+	Et_4N^+	K^+	I^-	Br^-	salicylate(−)	picrate(−)	Ph_4B^-
				λ_0/(S cm^2 mol^{-1})				
0.20	10.65	16.67	31.55	26.82	31.32	19.78	11.75	9.87
0.40	6.09	9.01	11.27	17.81	20.16	19.38	13.22	5.64
0.60	4.62	7.54	8.41	12.66	15.04	13.65	6.06	4.28
0.80	4.24	3.74	7.91	9.60	13.69	5.67	3.30	3.94
1.00	2.95	3.62	4.26	7.22	8.92[a]	3.38	5.03	2.73
				$\lambda_0\eta$/(S cm^2 mol^{-1} ρ)				
0.20	0.263	0.412	0.779	0.663	0.774	0.489	0.290	0.244
0.40	0.238	0.352	0.441	0.696	0.788	0.758	0.517	0.221
0.60	0.254	0.414	0.462	0.695	0.826	0.749	0.333	0.235
0.80	0.317	0.280	0.592	0.718	1.024	0.424	0.247	0.295
1.00	0.304	0.373	0.439	0.744	0.919	0.348	0.518	0.281

[a] From ref 12.

solvent mixtures has been observed.

The variations of salt and ionic Walden products for each system with mole fraction of sulfolane are presented in Figures 2 and 3, respectively. It is observed from Figure 2 that tetraalkylammonium salts nearly obey the Walden rule while potassium salts show deviation from the rule.

The association constant or conductimetric pairing constant (K_A) for all the systems is found to be generally appreciable (>10) which reflects significant association in sulfolane and its water mixtures. This association constant is the product of two terms (*8*), one (K_R) of which depends explicitly on the dielectric constant of the solvent while the other (K_S) is system specific depending on short-range ion–ion and ion–solvent interactions. The relationship is given as

$$K_A = K_R(1 + K_S) \tag{4}$$

As is evident from Table IV, K_A values for the three potassium salts in sulfolane were found to be in the order potassium

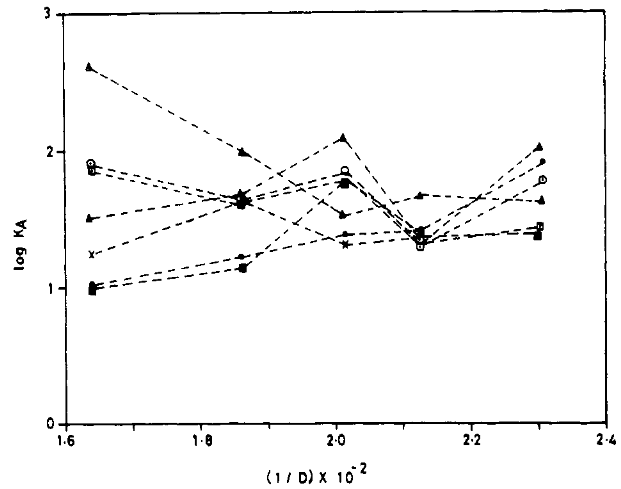

Figure 4. log K_A vs $(1/D) \times 10^{-2}$ for salts: Bu_4NBPh_4 (△); potassium picrate (⊙); KI (⊡); Bu_4NI (▲); Et_4NBr (×); potassium salicylate (●); KBr (■).

picrate < KI < potassium salicylate, indicating that the ion–solvent electrostatic interaction is greater in the case of picrate ion as compared to salicylate ion (cation being common). This order is reversed in sulfolane + water mixtures.

The conventional log K_A vs $1/D$ graph given in Figure 4 never showed any linear variation for all the salts studied. This indicates that ion association may not be solely dependent on the dielectric constant of the medium; however, the other factors like shape, size, dipole moment, polarizability, and possibly other details of solvent molecules could also be taken into account for the rationalization of association constant values obtained in the present work.

The cosphere diameter (R) values for all the salts under study in sulfolane and sulfolane + water mixtures are also portrayed in Tables IV and V, respectively. The R values were found to have a somewhat irregular trend in the solvents studied. As R is the measure of the extent of influence of ionic charge in the solvent and consequently the ionic association, R and K_A values are expected to increase with the decrease of the dielectric constant of the solvents, but no systematic trend in R values for all the salts studied has been observed in the given solvent mixture (sulfolane + water). Since the best fit conductance parameters are reproduced equally well over a wide range of arbitrarily chosen R values, a comprehensive correlation of the cosphere diameter of the respective system could not be made in the present instance.

Registry No. KI, 7681-11-0; $Bu_4N^+Ph_4B^-$, 15522-59-5; $Bu_4N^+I^-$, 311-28-4; $Et_4N^+Br^-$, 71-91-0; KBr, 7758-02-3; potassium picrate, 573-83-1; potassium, 578-36-9; sulfolane, 128-33-0.

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Excess Molar Volumes of 1-Chloronaphthalene and 1-Methylnaphthalene + Five Methyl *n*-Alkyl Ketones at 298.15 K

Fabio Comelli

Centro di Studio per la Fisica delle Macromolecole del CNR, via Selmi 2, 40126 Bologna, Italy

Romolo Francesconi*

Dipartimento di Chimica "G. Ciamician", Universita' degli Studi, via Selmi 2, 40126 Bologna, Italy

Excess molar volumes V^E of 1-chloronaphthalene and 1-methylnaphthalene + five methyl *n*-alkyl ketones have been determined from density measurements at 298.15 K and atmospheric pressure by means of an Anton Paar digital densimeter. Values of V^E are all negative ($-0.9 \leqslant V^E_{min}/(cm^3\ mol^{-1}) \leqslant -0.7$). The variation of V^E with molecular size is discussed.

Introduction

In previous publications (*1, 2*), the excess molar enthalpies H^E of 1-chloronaphthalene and 1-methylnaphthalene + five methyl *n*-alkyl ketones were reported. This paper reports the excess molar volumes V^E of the same systems. These results provide more information about the thermodynamic properties of these mixtures.

Table I. Densities ρ of Pure Components at 298.15 K and Comparison with Literature Data

component	$\rho/(g\ cm^{-3})$	
	this paper	lit.
1-chloronaphthalene	1.188 093	1.188 11 (*3*)
1-methylnaphthalene	1.015 430	1.016 76 (*1*)
2-propanone	0.785 005	0.784 7 (*4*)
2-butanone	0.799 905	0.799 45 (2)
2-pentanone	0.801 400	0.801 5 (*1*)
2-octanone	0.814 359	0.814 3 (*1*)
2-undecanone	0.821 704	no lit. data at 298.15 K

Experimental Section

Reagents. 1-Chloronaphthalene and 1-methylnaphthalene, a Kodak and an Aldrich product, analytical grade 99% and 98%, respectively, were purified by two fractional distillations through a 120 theoretical plate column at the rate of 30 mL/h.