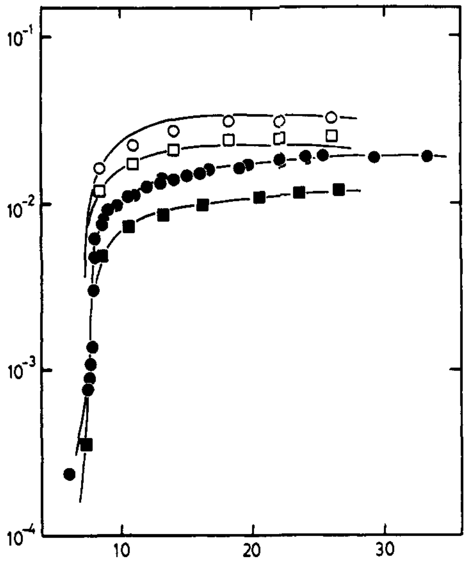

Figure 4. Solubility of naphthalene (2) and 2,5-xylenol (3) in supercritical carbon dioxide at 35 °C: (○), (□) experimental solubilities of naphthalene and 2,5-xylenol, respectively; (●) data of the supercritical carbon dioxide + naphthalene binary system from Tsekhanskaya et al. (7); (■) data of the supercritical carbon dioxide + 2,5-xylenol binary system from Iwai et al. (4); (—) calculated line.

mined from the experimental data of the ternary system. The values of interaction parameters determined are listed in Table IV. As shown in Figure 3, the experimental results for 3,4-xylenol are correlated within 5%. Experimental results for naphthalene + 2,5-xylenol were correlated within 8%, as illustrated in Figure 4.

Glossary

a,b,c	parameters of eq 2
k_{ij},l_{ij}	characteristic parameters between unlike molecules i and j
p	pressure
p_c	critical pressure
p^{satn}	saturation vapor pressure
R	gas constant
T	temperature
T_c	critical temperature
v	molar volume
v^S	solid-state molar volume
x	solid-phase mole fraction
y	solubility (gas-phase mole fraction)
ϕ^G	gas-phase fugacity coefficient
ω	Pitzer's acentric factor

Subscripts

i,j	components i and j
1	carbon dioxide
2,3	solutes 2 and 3

Registry No. CO_2, 124-38-9; 3,4-xylenol, 95-65-8; 2,5-xylenol, 95-87-4; naphthalene, 91-20-3.

Literature Cited

(1) Yoshitomi, S.; Nobe, Y.; Ukegawa, K. *Nenryo Kyokaishi* **1988**, *67*, 2.
(2) Arai, Y.; Iwai, Y.; Yamamoto, H. *Nenryo Kyokaishi* **1988**, *67*, 822.
(3) Iwai, Y.; Yamamoto, H.; Sohda, M.; Tanaka, Y.; Shimizu, T.; Arai, Y. *Mem. Fac. Eng., Kyushu Univ.* **1989**, *49*, 175.
(4) Iwai, Y.; Yamamoto, H.; Tanaka, Y.; Arai, Y. *J. Chem. Eng. Data* **1990**, *25*, 174.
(5) Yu, J.-M.; Lu, B. C.-Y. *Fluid Phase Equilib.* **1987**, *34*, 1.
(6) Yu, J.-M.; Lu, B. C.-Y.; Iwai, Y. *Fluid Phase Equilib.* **1987**, *37*, 207.
(7) Tsekhanskaya, Yu. V.; Iomtev, M. B.; Mushkina, E. V. *Russ. J. Phys. Chem.* **1964**, *38*, 1173.
(8) Iwai, Y.; Lu, B. C.-Y.; Yamamoto, H.; Arai, Y. *Kagaku Kogaku Ronbunshu* **1989**, *15*, 676.
(9) Arai, Y.; Iwai, Y.; Shimizu, T.; Fukuda, T. *Nenryo Kyokaishi* **1990**, *69*, 281.
(10) Simmrock, K. H.; Janowsky, R.; Ohnsorge, A. *Critical Data of Pure Substances*; Chemical Data Series; DECHEMA: Frankfurt/Main, FRG, 1986; Vol. II, Part 2, p 614.
(11) Boublik, T.; Fried, V.; Hala, E. *The Vapor Pressures of Pure Substances*; Physical Science Data 17; Elsevier: Amsterdam, 1984.
(12) Weast, R. C., Melvin, J. A., Eds. *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 1982.
(13) Andon, R. J. L.; Biddiscomebe, D. P.; Cox, J. D.; Handley, R.; Harrop, D.; Herrington, E. F. G.; Martin, J. F. *J. Chem. Soc.* **1960**, 5246.

Received for review October 7, 1991. Revised February 25, 1992. Accepted March 9, 1992. We gratefully acknowledge the financial support of a Grant-in-Aid for Energy Research of the Ministry of Education, Science and Culture (No. 60045085), the Kurata Research Grant (1985), General Sekiyu Research & Development Encouragement & Assistance Foundations (1985), and Japan Securities Scholarship Foundation (1987).

Excess Molar Enthalpies and Excess Molar Volumes of 1,2,4-Trimethylbenzene + Cyclic Ethers at 298.15 K

Fabio Comelli

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

Romolo Francesconi*

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

Excess molar enthalpies and excess molar volumes of the binary systems 1,2,4-trimethylbenzene + oxane, + 1,4-dioxane, + oxolane, or + 1,3-dioxolane have been measured with an LKB microcalorimeter and an Anton Paar density meter, respectively. Results were correlated by polynomial equations of the type $X^E = x_1x_2\sum_{k\geqslant0}a_k(x_1 - x_2)^k$. The results are interpreted in terms of molecular interactions.

Introduction

The present paper forms the final part of the program to measure excess properties for several binary mixtures containing some methyl-substituted benzene compounds as a common component + some cyclic ethers. The binary mixtures studied in the present work include 1,2,4-trimethylbenzene + four cyclic ethers, oxane, 1,4-dioxane, oxolane, or 1,3-dioxolane.

0021-9568/92/1737-0319$03.00/0 © 1992 American Chemical Society

Table I. Specification of Materials and Experimental Values of Densities, ρ

material	supplier	purity/%	$\rho/(\mathrm{g/cm^3})$ exptl	$\rho/(\mathrm{g/cm^3})$ lit.
1,2,4-trimethylbenzene	Kodak	99	0.8719	0.8718[a]
oxane	Fluka	99	0.8791	0.8792[b]
1,4-dioxane	Aldrich	99.8	1.0279	1.0279[b]
oxolane	Aldrich	99.9	0.8822	0.8827[b]
1,3-dioxolane	Aldrich	99.5	1.0588	1.0587[b]

[a] Dreisbach (*6*). [b] Inglese et al. (*7*), rounded values.

A comparison of these results with those obtained previously (*1*–*3*) and those reported in the literature (*4*, *5*) is made. A literature survey has shown that the excess properties for the systems studied have not been reported with the exception of the 1,2,4-trimethylbenzene + 1,3-dioxolane system (*1*).

Experimental Section

Materials. 1,2,4-Trimethylbenzene (TMB) and cyclic ethers are the same as used in refs 1 and 2. Before use, all liquids were stored over molecular sieves (Union Carbide Type 4A, $^1/_{16}$-in. pellets) to remove trace amounts of water and put in dark bottles. Estimated purities of components are reported in Table I.

Apparatus and Procedure. Densities ρ were determined to check the purity of components and are compared with literature values (*6*, *7*) in Table I.

Binary mixtures were prepared by mass, using a Mettler balance to give mole fractions with an accuracy of 0.0001. Flasks of 25 cm^3 volume were used, and the vapor space in the flask was always less than 2 cm^3.

Because of the small vapor space and the reproducibility of the measurements, no correction was applied for evaporation of components. Instead, all weighings were corrected for buoyancy since mole fractions were affected by this error about the same amount as that due to weighing uncertainties.

The excess volumes have been determined at 298.15 K by using an Anton Paar digital density meter, model DMA 60/602 (Graz, Austria) (*8*). Measurements were made with a sensitivity up to 0.000 001 g/cm^3 and a selected period of 10 000 oscillation cycles. The estimated precision of the temperature is less than 0.01 K, determined with a digital thermometer (DT 100-25, Anton Paar, Graz, Austria) and a bath circulator was used with a temperature uniformity of ±0.005 K.

Excess enthalpies were measured at 298.15 ± 0.01 K by an isothermal flow microcalorimeter (LKB-2107, LKB-Produkter AB, Bromma, Sweden) (*9*). The performance of the apparatus was checked using cyclohexane + hexane at 298.15 K, the agreement with the results of ref 10 being better than 0.5% over the central range of concentrations. Full automatic burets (ABU, Radiometer, Copenhagen, Denmark) were used to pump the pure liquids into the flow-mixing cell: details of calibration and analytical measurements are given in ref 11.

Discussion of Results

The experimental results for the binary mixtures TMB + cyclic ethers are reported in Tables II and III and were fitted by the least-squares method with a polynomial function of the form

$$X^{\mathrm{E}}(\mathrm{J\ mol^{-1}\ or\ cm^3\ mol^{-1}}) = x_1 x_2 \sum_{k \geq 0} a_k (x_1 - x_2)^k \qquad (1)$$

with unit statistical weight assigned to each point.

Table II. Excess Molar Enthalpies H^{E} at 298.15 K for Binary Mixtures of 1,2,4-Trimethylbenzene + Cyclic Ethers

x_1	$H^{\mathrm{E}}/(\mathrm{J\ mol^{-1}})$	x_1	$H^{\mathrm{E}}/(\mathrm{J\ mol^{-1}})$	x_1	$H^{\mathrm{E}}/(\mathrm{J\ mol^{-1}})$
1,2,4-Trimethylbenzene (1) + Oxane (2)					
0.0559	−11.4	0.3215	3.3	0.7398	20.9
0.1059	−14.6	0.4618	17.1	0.8108	18.1
0.1509	−13.9	0.5160	20.4	0.8951	11.8
0.2070	−9.6	0.5871	22.6	0.9446	6.7
0.2622	−3.7	0.6808	22.4		
1,2,4-Trimethylbenzene (1) + 1,4-Dioxane (2)					
0.0493	85.9	0.2931	422.3	0.7133	356.8
0.0939	175.7	0.3834	479.2	0.7886	277.5
0.1170	214.8	0.4826	488.0	0.8326	216.5
0.1717	294.1	0.5543	470.7	0.8818	155.1
0.2372	373.4	0.6510	411.4	0.9372	84.6
1,2,4-Trimethylbenzene (1) + Oxolane (2)					
0.0470	−35.7	0.3717	−203.6	0.7802	−265.5
0.0897	−65.9	0.4702	−241.7	0.8256	−241.6
0.1647	−115.7	0.5419	−260.3	0.8765	−199.2
0.2283	−149.1	0.6396	−282.1	0.9342	−124.3
0.2828	−171.7	0.7029	−280.1	0.9551	−91.5

Table III. Excess Molar Volumes V^{E} at 298.15 K for Binary Mixtures of 1,2,4-Trimethylbenzene + Cyclic Ethers

x_1	$V^{\mathrm{E}}/(\mathrm{cm^3\ mol^{-1}})$	x_1	$V^{\mathrm{E}}/(\mathrm{cm^3\ mol^{-1}})$	x_1	$V^{\mathrm{E}}/(\mathrm{cm^3\ mol^{-1}})$
1,2,4-Trimethylbenzene (1) + Oxane (2)					
0.0259	0.0222	0.4156	0.1728	0.7391	0.1095
0.0660	0.0558	0.4330	0.1724	0.8225	0.0766
0.1231	0.0938	0.5088	0.1650	0.8366	0.0714
0.2286	0.1412	0.5460	0.1595	0.8835	0.0501
0.3061	0.1610	0.5833	0.1517	0.9549	0.0198
0.3681	0.1690	0.6459	0.1372	0.9880	0.0031
0.3772	0.1710	0.7031	0.1205		
1,2,4-Trimethylbenzene (1) + 1,4-Dioxane (2)					
0.0056	0.0116	0.2763	0.3312	0.6368	0.3457
0.0365	0.0647	0.3214	0.3553	0.6695	0.3290
0.0570	0.0992	0.3445	0.3640	0.7814	0.2501
0.1099	0.1762	0.3917	0.3769	0.8484	0.1908
0.1624	0.2384	0.4262	0.3846	0.9076	0.1231
0.2077	0.2810	0.5031	0.3839	0.9783	0.0291
0.2338	0.3023	0.5497	0.3770		
1,2,4-Trimethylbenzene (1) + Oxolane (2)					
0.0084	−0.0050	0.2729	−0.1159	0.4817	−0.1324
0.0568	−0.0333	0.2940	−0.1196	0.6177	−0.1186
0.0816	−0.0503	0.3214	−0.1206	0.8030	−0.0747
0.1122	−0.0584	0.3411	−0.1240	0.9133	−0.0390
0.1441	−0.0785	0.3760	−0.1275	0.9763	−0.0152
0.1990	−0.0970	0.4079	−0.1299		
0.2304	−0.1057	0.4255	−0.1330		
1,2,4-Trimethylbenzene (1) + 1,3-Dioxolane (2)					
0.0043	0.0046	0.2953	0.1937	0.5523	0.2193
0.0550	0.0500	0.3327	0.2015	0.6301	0.2042
0.0788	0.0708	0.3619	0.2104	0.6940	0.1850
0.1238	0.1043	0.3814	0.2143	0.8246	0.1246
0.1951	0.1481	0.4266	0.2186	0.8975	0.0796
0.2361	0.1682	0.4603	0.2214	0.9740	0.0192
0.2686	0.1807	0.5027	0.2271		

The values of the coefficients a_k obtained from the analysis are listed in Table IV along with the standard deviation $\sigma(H^{\mathrm{E}}, V^{\mathrm{E}})$ defined as

$$\sigma(H^{\mathrm{E}}, V^{\mathrm{E}}) = |\phi_{\mathrm{m}}/(N - n)|^{0.5} \qquad (2)$$

where ϕ_{m} is the minimum of the objective function, N is the number of experimental points, and n is the number of parameters. In Figures 1 and 2, the continuous curves have been calculated for each mixture by using eq 1 and the a_k of Table IV.

Table IV. Constants of the Polynomial Function, Equation 1, for the Binary Liquid Mixtures of 1,2,4-Trimethylbenzene + Cyclic Ethers at 298.15 K

system	function	a_0	a_1	a_2	a_3	σ
1,2,4-trimethylbenzene + oxane	H^E	78.471	110.14	−150.10	106.46	0.19
	V^E	0.6688	−0.2327			0.0013
1,2,4-trimethylbenzene + 1,4-dioxane	H^E	1946.4	−366.85	−271.74		2.03
	V^E	1.5364	−0.2015	0.1603		0.0011
1,2,4-trimethylbenzene + oxolane	H^E	−1001.9	−572.81	−577.30	−181.30	2.21
	V^E	−0.5209	0.0988	−0.0575		0.0021
1,2,4-trimethylbenzene + 1,3-dioxolane	H^E	ref 1				
	V^E	0.8933	−0.0643			0.0015

Table V. Mole Fraction at Which the Excess Functions are Maxima (or Minima)

system	$x_1(H^E(\text{max}))$	H^E(max)	$x_1(V^E(\text{max}))$	V^E(max)
benzene (1) + oxane (2)[a]	0.5042	−255.5	0.5031	−0.1613
benzene (1) + 1,4-dioxane (2)[a]	0.2058	−48.5	0.4024	−0.0753
benzene (1) + oxolane (2)[b]	0.5162	−365.8		
benzene (1) + 1,3-dioxolane (2)[b]	0.6383	75.6		
toluene (1) + oxane (2)[c]	0.4783	−237.1	0.4718	−0.1596
toluene (1) + 1,4-dioxane (2)[c]	0.4451	129.1	0.7514	−0.0224
toluene (1) + oxolane (2)[c]	0.4328	−337.1	0.4853	−0.3679
toluene (1) + 1,3-dioxolane (2)[c]	0.3956	180.6	0.5218	−0.1248
p-xylene (1) + oxane (2)[d]	0.5425	−150.3	0.5626	−0.0582
p-xylene (1) + 1,4-dioxane (2)[d]	0.5092	327.5	0.3937	0.1288
p-xylene (1) + oxolane (2)[d]	0.4967	−269.0	0.4501	−0.3435
p-xylene (1) + 1,3-dioxolane (2)[d]	0.4585	349.5	0.4522	−0.0355
1,2,4-trimethylbenzene (1) + oxane (2)	0.6808	22.4	0.4156	0.1720
1,2,4-trimethylbenzene (1) + 1,4-dioxane (2)	0.4826	488.0	0.4255	−0.1330
1,2,4-trimethylbenzene (1) + oxolane (2)	0.6396	−282.1	0.4255	−0.1330
1,2,4-trimethylbenzene (1) + 1,3-dioxolane (2)	0.4786 (*1*)	404.1 (*1*)	0.4603	0.2214

[a] Reference 4. [b] Reference 5. [c] Reference 2. [d] Reference 3.

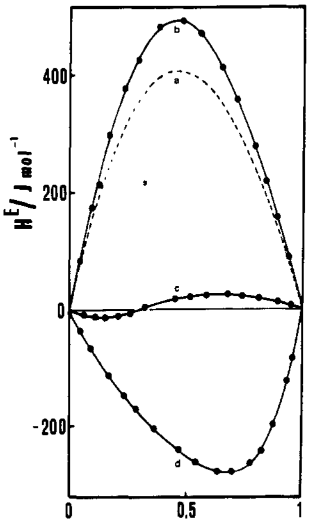

Figure 1. Excess molar enthalpies of binary mixtures for 1,2,4-trimethylbenzene (1) + 1,3-dioxolane (2) (a), + 1,4-dioxane (2) (b), + oxane (2) (c), or + oxolane (2) (d) at 298.15 K. Solid curves are least-squares representations of results by eq 1, dashed curve, ref 1.

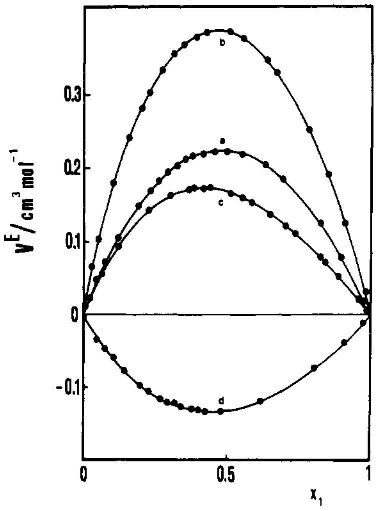

Figure 2. Excess molar volumes of binary mixtures for 1,2,4-trimethylbenzene (1) + cyclic ethers (2) at 298.5 K. The same letters are used as in Figure 1.

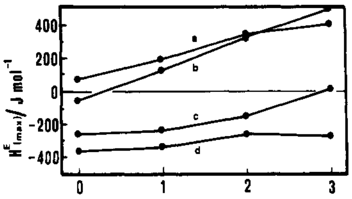

Figure 3. Values of H^E(max) plotted against the number of methyl groups in the methyl-substituted benzene compounds. (a)–(d) refer to the 1,3-dioxolane, 1,4-dioxane, oxane, and oxolane + benzene (*4*, *5*), + toluene (*2*), + *p*-xylene (*3*), and + 1,2,4-trimethylbenzene systems, respectively.

In Figures 3 and 4, excess enthalpies H^E(max) and excess volumes V^E(max) at maximum (or minimum) have been plotted as a function of number of methyl groups in the methyl-substituted benzene compounds. The values reported in Table V are from this work together with those from our previous measurements (*1*–*3*) and from the literature (*4*, *5*).

Figures 1 and 2 show the trend toward more positive H^E values in going from mono- to biethers and from five-atom-ring to six-atom-ring ethers. The same behavior is shown for the binary mixtures of the same ethers with benzene, toluene, and *p*-xylene. From Figure 3, we see that increasing the number of methyl groups in the benzene ring leads to increasing H^E(max) values for mixtures with any ether as a second component. Also 1-methylnaphthalene (*12*) displays a similar excess enthalpy in mixtures with the same ethers. However, values of H^E are more negative probably due to the double benzene ring interacting with the ether molecule since the methyl group

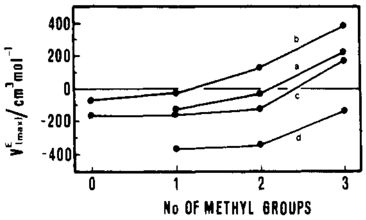

Figure 4. Values of V^E(max) plotted against the number of methyl groups in the methyl-substituted benzene compounds. The same letters are used as in Figure 3. No values of V^E(max) for benzene + 1,3-dioxolane and benzene + oxolane have been found in the literature.

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.

Literature Cited

(1) Francesconi, R.; Comelli, F. *Thermochim. Acta* **1991**, *179*, 149.
(2) Francesconi, R.; Comelli, F. *J. Chem. Eng. Data*, submitted for publication.
(3) Francesconi, R.; Lunelli, B.; Comelli, F. *Thermochim. Acta*, submitted for publication.
(4) Andrews, A. W.; Morcom, K. W. *J. Chem. Thermodyn.* **1971**, *3*, 513, 519.
(5) Inglese, A.; Wilhelm, E.; Grolier, J.-P. E.; Kehlaian, H. V. *J. Chem. Thermodyn.* **1981**, *13*, 229.
(6) Dreisbach, R. R. *Physical Properties of Chemical Compounds-II*; American Chemical Society: Washington, DC, 1959.
(7) Inglese, A.; Grolier, J.-P. E.; Wilhelm, E. *J. Chem. Eng. Data* **1983**, *28*, 124.
(8) Fermeglia, M.; Lapasin, J. *J. Chem. Eng. Data* **1988**, *33*, 415.
(9) Monk, P.; Wadso, I. *Acta Chem. Scand.* **1968**, *22*, 1842.
(10) Benson, G. C. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1974**, 19.
(11) Francesconi, R.; Comelli, F. *J. Chem. Eng. Data* **1986**, *31*, 250.
(12) Comelli, F.; Francesconi, R. *J. Chem. Eng. Data* **1991**, *36*, 382.

Received for review December 6, 1991. Accepted April 20, 1992.

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