Thermodynamic Interactions in Binary Mixtures of Dimethyl Sulfoxide with Benzene, Toluene, 1,3-Dimethylbenzene, 1,3,5-Trimethylbenzene, and Methoxybenzene from 298.15 to 308.15 K

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Densities, viscosities, refractive indices, and ultrasonic velocities were measured for the binary mixtures of dimethyl sulfoxide with benzene, toluene, 1,3-dimethylbenzene, 1,3,5-trimethylbenzene, and methoxybenzene at 298.15, 303.15, and 308.15 K over the entire mole fraction scale of the mixture. These results have been used to calculate the changes in volume, isentropic compressibility, and refractivity. The calculated quantities have been represented with third-degree polynomials.

Introduction

Dimethyl sulfoxide (DMSO) is a versatile dipolar aprotic solvent (having a dielectric constant $\epsilon = 46.50$) used extensively in kinetic studies and electrochemistry and as a solvent for polymers. Binary mixtures of DMSO with aromatic solvents are of interest in studies of polymer miscibility, polymer phase diagrams, and preferential interaction of polymers in mixed solvents (*1–3*). Studies of mixtures of methyl-substituted benzenes with other solvents have been reported in the earlier literature (*4–12*). This work supplements that of Absood et al. (*13*) and Gopal et al. (*14*) on the physical properties of mixtures of substituted benzenes with DMSO. We now report measurements of density ρ, viscosity η, refractive index n_D, and ultrasonic velocity u over the whole composition scale of the mixtures and in the temperature range 298.15–308.15 K.

The present investigation is a continuation of our studies of the thermodynamic and hydrodynamic properties of binary liquid mixtures containing DMSO (*15*). The measured physical properties were used to calculate changes in volume ΔV, isentropic compressibility $\Delta\beta$, and molar refraction ΔR. These properties were fitted to the third-degree polynomial, and the coefficients are tabulated for the mixtures under study.

Experimental Section

Materials. Spectral grade benzene (s.d. fine chemicals, Bombay) was used after fractional distillation using a long fractionating column. Toluene supplied by BDH, England, was dried over phosphorus pentoxide and then fractionally distilled before use. 1,3-Dimethylbenzene and 1,3,5-trimethylbenzene were both from E. Merck, Germany; 1,3-dimethylbenzene was purified by distilling twice using a fractionating column, while 1,3,5-trimethylbenzene was dried over anhydrous magnesium sulfate before distilling. Methoxybenzene, supplied by Thomas Baker, Bombay, after drying over calcium chloride was fractionally distilled before use. The spectral grade dimethyl sulfoxide (s.d. fine chemicals, Bombay) was directly used to avoid decomposition during distillation. The gas chromatographic tests using a flame ionization detector having a sensitivity better than 10^{-8} g of fatty acid/μL of solvent (Nucon series, 5700/5765 with fused silica columns) showed a purity of >99 mol %. The purity of these liquids was further corroborated by agreement of ρ, n_D, and η values with the literature data (Table I) (*16*, *17*).

Mixtures were prepared by mixing the appropriate volumes of liquids in specially designed ground-glass stoppered bottles and weighed in a single-pan Mettler balance (Switzerland) to an accuracy of ±0.05 mg. Preferential evaporation of solvents from the mixtures was kept to a minimum as evidenced by a repeated measurement of the physical properties over an interval of 2–3 days, during which time no changes in the physical properties were observed. The possible error in the mole fractions is estimated to be around 0.0001.

Measurements. Densities ρ were measured with a capillary pycnometer of about 10 cm^3 capacity. The pycnometer was calibrated with double-distilled water and benzene over the working temperature range (*18*). The standard errors in the calculation of densities of solvents and their mixtures were within 0.01%.

Viscosities were measured with Cannon Fenske viscometers (sizes 75 and 100, ASTM D445, supplied by Industrial Research Glassware Ltd., New Jersey). An electronic stop watch with a precision of ±0.01 s was used for flow time measurements. Triplicate measurements of flow times were reproducible within 0.02% or even less. Computation of the kinematic viscosity ν was done by using the relation $\nu = At - B/t$, where t is the flow time in the viscometer and A and B are viscometer constants, determined by calibrating with water and pure benzene at working temperatures. The kinematic viscosities were adjusted for kinetic energy by using the Hagenbach correction (*19*). Absolute viscosities η (mPa s) were then calculated by using the relation $\eta = \nu\rho$. The estimated error in the viscosity measurement is around 0.2% or even less in some cases. Viscosities of pure components are quite accurate as evidenced by a comparison of data given in Table I.

Refractive indices for the Na D-line were measured with a thermostated Abbe refractometer (Bellingham and Stanley Ltd, London) with an error of less than 0.0001 unit. The instrument was calibrated from time to time with the help of a glass piece of known refractive index ($n_D = 1.5159$) provided with the instrument. It was also checked by measuring the refractive index of purified water, benzene, *n*-hexane, and carbon tetrachloride at known temperatures (*16*, *17*).

Ultrasonic velocities u were determined with a variable-path single-crystal interferometer (Mittal Enterprises, New Delhi, model M-84). This instrument is provided with a reflector plate of diameter 1.5 cm which can be moved in the cell of diameter 1.7 cm having a maximum liquid filling capacity of 12 cm^3. The maximum displacement of the reflector inside the cell is 2.5 cm.

The principle used in the measurement of ultrasonic velocity is based on the accurate determination of wavelength λ in the medium. Ultrasonic waves of known frequency f are produced by a quartz crystal fixed at the bottom of the cell. These waves are reflected by a movable metallic plate kept parallel to the quartz crystal. If the separation between these two plates is exactly a whole multiple of the ultrasonic wavelength, standing waves are formed in the medium. This acoustic resonance

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Table I. Physical Properties of Pure Components at 298.15 K

liquid	ρ/(g cm^{-3}) exptl	ρ/(g cm^{-3}) lit.	n_D exptl	n_D lit.	η/(mPa s) exptl	η/(mPa s) lit.	ref
dimethyl sulfoxide	1.0962	1.0954	1.4770	1.4775	1.975	1.991	16
benzene	0.8742	0.8736	1.4979	1.4979	0.602	0.603	17
toluene	0.8627	0.8622	1.4941	1.4941	0.552	0.553	16
1,3-dimethylbenzene	0.8602	0.8601	1.4946	1.4946	0.580	0.581	17
1,3,5-trimethylbenzene	0.8615	0.8611	1.4967	1.4968	0.656	0.650	23
methoxybenzene	0.9897	0.9893	1.5143	1.5143	0.990	1.002	24

Table II. Binary Data for Mixtures of DMSO (1) + Benzene (2)

x_1	ρ/(g cm^{-3})	η/(mPa s)	n_D	u/(m s^{-1})
		298.15 K		
0.0	0.8742	0.602	1.4979	1304
0.1043	0.8947	0.669	1.4969	1322
0.2048	0.9149	0.743	1.4951	1340
0.3059	0.9353	0.829	1.4931	1360
0.4069	0.9566	0.923	1.4910	1377
0.5105	0.9789	1.036	1.4890	1395
0.6085	1.0005	1.169	1.4869	1413
0.7063	1.0231	1.317	1.4840	1429
0.8049	1.0463	1.492	1.4819	1451
0.9029	1.0713	1.712	1.4784	1471
1.0	1.0962	1.975	1.4770	1489
		303.15 K		
0.0	0.8685	0.561	1.4948	1280
0.1043	0.8895	0.622	1.4929	1302
0.2048	0.9096	0.690	1.4919	1322
0.3059	0.9302	0.766	1.4902	1337
0.4069	0.9514	0.853	1.4880	1356
0.5105	0.9736	0.955	1.4865	1373
0.6085	0.9953	1.071	1.4837	1394
0.7063	1.0192	1.207	1.4813	1414
0.8049	1.0417	1.367	1.4792	1430
0.9029	1.0660	1.562	1.4764	1454
1.0	1.0911	1.788	1.4748	1474
		308.15 K		
0.0	0.8633	0.525	1.4918	1255
0.1043	0.8840	0.581	1.4902	1278
0.2048	0.9042	0.643	1.4899	1303
0.3059	0.9250	0.714	1.4871	1316
0.4069	0.9467	0.796	1.4856	1334
0.5105	0.9687	0.884	1.4833	1355
0.6085	0.9910	0.990	1.4813	1376
0.7063	1.0131	1.111	1.4792	1394
0.8049	1.0363	1.258	1.4768	1416
0.9029	1.0610	1.426	1.4746	1434
1.0	1.0859	1.630	1.4730	1455

Table III. Binary Data for Mixtures of DMSO (1) + Toluene (2)

x_1	ρ/(g cm^{-3})	η/(mPa s)	n_D	u/(m s^{-1})
		298.15 K		
0.0	0.8627	0.552	1.4941	1309
0.1025	0.8806	0.609	1.4930	1325
0.2029	0.8988	0.671	1.4921	1336
0.3843	0.9343	0.838	1.4902	1364
0.5040	0.9603	0.964	1.4883	1384
0.6035	0.9836	1.095	1.4863	1404
0.7049	1.0093	1.250	1.4845	1418
0.7997	1.0347	1.430	1.4821	1426
0.9017	1.0648	1.686	1.4807	1467
1.0	1.0962	1.975	1.4770	1489
		303.15 K		
0.0	0.8579	0.520	1.4905	1287
0.1025	0.8759	0.574	1.4900	1303
0.2029	0.8938	0.636	1.4897	1319
0.3843	0.9297	0.777	1.4876	1342
0.5040	0.9554	0.894	1.4858	1365
0.6035	0.9788	1.010	1.4842	1386
0.7049	1.0043	1.149	1.4816	1404
0.7997	1.0300	1.309	1.4803	1419
0.9017	1.0599	1.526	1.4781	1451
1.0	1.0911	1.788	1.4748	1474
		308.15 K		
0.0	0.8540	0.493	1.4872	1264
0.1025	0.8710	0.540	1.4877	1280
0.2029	0.8896	0.598	1.4873	1297
0.3843	0.9247	0.727	1.4854	1321
0.5040	0.9507	0.833	1.4840	1344
0.6035	0.9738	0.963	1.4815	1364
0.7049	0.9995	1.062	1.4797	1386
0.7997	1.0251	1.204	1.4779	1408
0.9017	1.0548	1.398	1.4758	1431
1.0	1.0859	1.630	1.4730	1455

gives rise to an electrical signal on the generator driving the quartz crystal, and the anode current of the generator becomes maximum. If the distance is increased or decreased and the variation is exactly half the wavelength ($\lambda/2$), or a multiple of it, the anode current becomes maximum. From the knowledge of λ and f, the ultrasonic velocity u ($=\lambda f$) is calculated.

A crystal control generator is used to excite the quartz crystal (at a frequency of 1 MHz) fixed at the bottom of the measuring cell at its resonance provided at the top which can lower or raise the reflector plate in the cell containing the liquid through a known distance. The measuring cell is a specially designed double-walled cell for maintaining a constant temperature of the liquid. A fine micrometer screw is used to excite the transducer at a frequency of 1 MHz, and this frequency was measured with an accuracy of 1 in 10^6 by using a digital frequency meter. The voltage variations across the transducer were observed on a microvoltmeter. Water at the desired constant temperature was circulated around the measuring cell from a thermostat. The isentropic compressibility β was calculated as $\beta = 1/u^2\rho$. Our value of u (1255 m s^{-1}) at 308.15 K for benzene is identical to that (1255 m s^{-1}) of Nath and Dixit (*11*).

In all property measurements thermostats (Toshniwal, model GL-15, and INSREF 016 AP) were maintained constant to within $\pm$0.01 K at the desired temperatures as checked by means of a calibrated (1968 temperature scale) thermometer. The results compiled in Tables II–VI are the averages of three measurements at each point.

Results and Discussion

Experimental results of ρ and η for all the binary mixtures at 298.15 K are presented in Figure 1. Results of u and n_D are shown in Figure 2. The bumps observed in n_D or η versus x_1 plots for DMSO + 1,3,5-trimethylbenzene mixtures were confirmed by repeated measurements. For mixtures of DMSO with methyl-substituted benzenes, the u versus x_1 plots cross at a single point, $x_1 \simeq 0.3$.

The changes in volume ΔV_{mix}, refractivity ΔR_{mix}, and isentropic compressibility $\Delta\beta_{\text{mix}}$ during mixing in a binary mixture are expressed as

$$V = \sum_{i=1}^{2} V_i x_i + \Delta V_{\text{mix}} \tag{1}$$

$$R = \sum_{i=1}^{2} R_i \varphi_i + \Delta R_{\text{mix}} \tag{2}$$

$$\beta = \sum_{i=1}^{2} \beta_i \varphi_i + \Delta\beta_{\text{mix}} \tag{3}$$

Here, V, R, and β represent molar volume, molar refractivity,

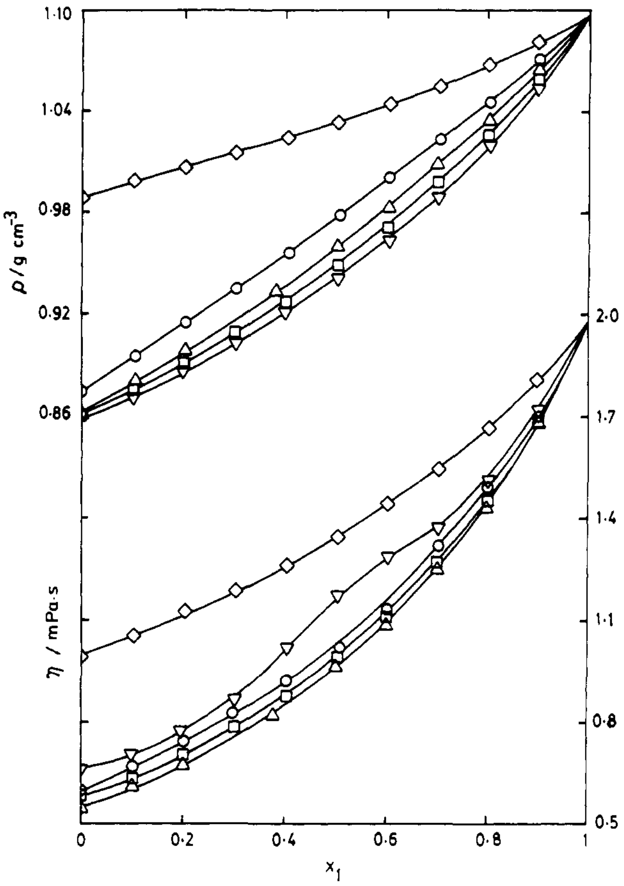

Figure 1. Density and viscosity versus mole fraction (x_1) of DMSO plots for mixtures of DMSO with benzene (○), toluene (△), 1,3-dimethylbenzene (□), 1,3,5-trimethylbenzene (▽), and methoxybenzene (◇) at 298.15 K.

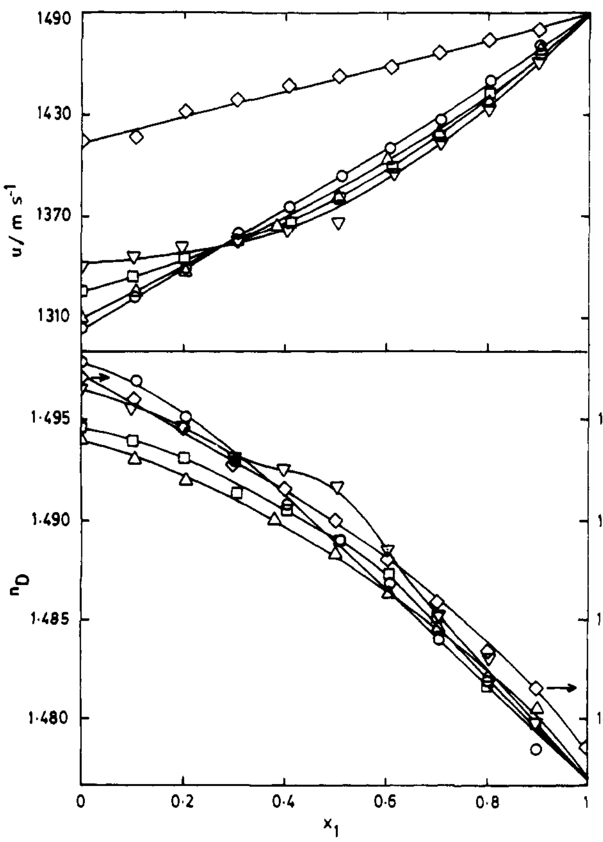

Figure 2. Ultrasonic velocity and refractive index versus x_1 at 298.15 K for the mixtures given in Figure 1.

Table IV. Binary Data for Mixtures of DMSO (1) + 1,3-Dimethylbenzene (2)

x_1	$\rho/(\mathrm{g\ cm^{-3}})$	$\eta/(\mathrm{mPa\ s})$	n_D	$u/(\mathrm{m\ s^{-1}})$
		298.15 K		
0.0	0.8602	0.580	1.4946	1326
0.1004	0.8748	0.631	1.4939	1335
0.2027	0.8913	0.700	1.4933	1346
0.3047	0.9088	0.782	1.4913	1356
0.4044	0.8279	0.877	1.4907	1367
0.5057	0.9491	0.990	1.4891	1381
0.6045	0.9721	1.116	1.4873	1396
0.7050	0.9982	1.269	1.4850	1418
0.8030	1.0267	1.450	1.4816	1442
0.9011	1.0594	1.680	1.4798	1467
1.0	1.0962	1.975	1.4770	1489
		303.15 K		
0.0	0.8559	0.548	1.4920	1304
0.1004	0.8705	0.593	1.4915	1319
0.2027	0.8871	0.657	1.4910	1326
0.3047	0.9042	0.730	1.4893	1335
0.4044	0.9232	0.815	1.4879	1346
0.5057	0.9443	0.914	1.4871	1362
0.6045	0.9674	1.026	1.4851	1376
0.7050	0.9932	1.168	1.4828	1400
0.8030	1.0219	1.325	1.4804	1420
0.9011	1.0542	1.528	1.4779	1449
1.0	1.0911	1.788	1.4748	1474
		308.15 K		
0.0	0.8514	0.519	1.4898	1283
0.1004	0.8663	0.561	1.4891	1293
0.2027	0.8822	0.617	1.4884	1308
0.3047	0.8997	0.684	1.4860	1320
0.4044	0.9187	0.760	1.4850	1329
0.5057	0.9397	0.850	1.4846	1347
0.6045	0.9625	0.952	1.4820	1362
0.7050	0.9885	1.076	1.4811	1380
0.8030	1.0171	1.219	1.4782	1405
0.9011	1.0493	1.397	1.4758	1428
1.0	1.0859	1.630	1.4730	1455

and isentropic compressibility of the mixtures; these quantities *with subscript i refer to individual components of the mixtures.* The term x_i is the mole fraction of the ith component. The volume fractions φ_i of the ith component are related to their mole fraction as

$$\varphi_i = x_i V_i / (\sum_{i=1}^{2} x_i V_i) \tag{4}$$

To avoid problems related to changes of volume upon mixing, it is convenient (and conventional) to use molar volumes of pure components when defining the volume fractions. As a first approximation, the terms ΔV_{mix}, ΔR_{mix}, and $\Delta\beta_{\mathrm{mix}}$ may be described by means of constants V^E, R^E, and β^E, respectively, according to

$$\Delta V_{\mathrm{mix}} = V^E x_1 x_2 \tag{5}$$

$$\Delta R_{\mathrm{mix}} = R^E \varphi_1 \varphi_2 \tag{6}$$

$$\Delta\beta_{\mathrm{mix}} = \beta^E \varphi_1 \varphi_2 \tag{7}$$

Alternatively, the constants V^E, R^E, and β^E can be expressed more generally, as functions of x_1 (or φ_1) and x_2 (or φ_2) fitted to the experimental data by a third-degree polynomial. However, to express V^E, it has been the conventional practice to use x_i rather than φ_i. Rewriting eqs 1–3, we get

$$V = \sum_{i=1}^{2} V_i x_i + x_1 x_2 \sum_{i=0}^{3} a_i (x_2 - x_1)^i \tag{8}$$

$$R = \sum_{i=1}^{2} R_i \varphi_i + \varphi_1 \varphi_2 \sum_{i=0}^{3} a_i (\varphi_2 - \varphi_1)^i \tag{9}$$

$$\beta = \sum_{i=1}^{2} \beta_i \varphi_i + \varphi_1 \varphi_2 \sum_{i=0}^{3} a_i (\varphi_2 - \varphi_1)^i \tag{10}$$

Table V. Binary Data for Mixtures of DMSO (1) + 1,3,5-Trimethylbenzene (2)

x_1	ρ/(g cm^{-3})	η/(mPa s)	n_D	u/(m s^{-1})
		298.15 K		
0.0	0.8615	0.656	1.4967	1341
0.0996	0.8702	0.699	1.4957	1347
0.1961	0.8873	0.772	1.4947	1352
0.3046	0.9037	0.865	1.4926	1355
0.4024	0.9207	1.018	1.4938	1363
0.5049	0.9408	1.168	1.4918	1366
0.6057	0.9635	1.280	1.4872	1395
0.7047	0.9896	1.367	1.4852	1414
0.8055	1.0199	1.508	1.4829	1436
0.9018	1.0542	1.711	1.4797	1461
1.0	1.0962	1.975	1.4770	1489
		303.15 K		
0.0	0.8573	0.616	1.4945	1321
0.0996	0.8660	0.654	1.4933	1328
0.1961	0.8828	0.718	1.4923	1333
0.3046	0.8994	0.799	1.4910	1338
0.4024	0.9160	0.901	1.4892	1342
0.5049	0.9364	1.029	1.4873	1353
0.6057	0.9592	1.136	1.4851	1375
0.7047	0.9846	1.241	1.4832	1396
0.8055	1.0149	1.372	1.4806	1420
0.9018	1.0494	1.553	1.4779	1448
1.0	1.0911	1.788	1.4748	1474
		308.15 K		
0.0	0.8532	0.581	1.4918	1303
0.0996	0.8616	0.616	1.4904	1306
0.1961	0.8786	0.674	1.4900	1315
0.3046	0.8948	0.747	1.4893	1317
0.4024	0.9118	0.831	1.4866	1325
0.5049	0.9322	0.935	1.4851	1334
0.6057	0.9543	1.036	1.4831	1360
0.7047	0.9801	1.135	1.4808	1376
0.8055	1.0103	1.266	1.4782	1400
0.9018	1.0445	1.420	1.4757	1426
1.0	1.0859	1.630	1.4730	1455

In the above equations the molar volume V_i is calculated from density, whereas the molar refractivity R_i is obtained from the Lorenz–Lorentz rule (*20*). However, the ideal term $\sum_{i=1}^{2} \beta_i \varphi_i$ of eq 10 is calculated from the procedure suggested elsewhere (*21*):

$$\sum_{i=1}^{2} \beta_i \varphi_i = \sum_{i=1}^{2} \varphi_i (\beta_{S,i} + TV_i/C_{P,i}) - T\left[\sum_{i=1}^{2} x_i V_i \left\{\sum_{i=1}^{2} x_i \alpha_i\right\}^2 / \left(\sum_{i=1}^{2} x_i C_{P,i}\right)\right] \quad (11)$$

where $C_{P,i}$ and α_i are, respectively, the heat capacity and thermal expansion coefficient of the individual components. The values of $C_{P,i}$ were taken from the literature (*16*), and the α_i values were calculated from a procedure suggested earlier (*22*).

The values of the coefficients a_i of eqs 8–10 were estimated from a least-squares method along with the standard errors σ between the calculated and experimental data as

$$\sigma = \left[\sum_{i=1}^{p} \{Y^E_{\text{expt}} - Y^E_{\text{calc}}\}^2 / (p - m)\right]^{1/2} \quad (12)$$

where p is the number of experimental points and m is the number of fitting parameters. The symbol Y^E represents V^E, R^E, and β^E. The calculated results are presented in Table VII.

The dependence of V^E on mole fraction of DMSO for all the binary mixtures is shown in Figure 3. For mixtures of benzene or toluene with DMSO, the results of V^E vary almost identically and are negative. Similarly, for mixtures of DMSO with 1,3-dimethylbenzene or methoxybenzene, V^E values vary identically but are less negative as compared to benzene- or toluene-containing mixtures. The negative values of V^E for these mixtures suggest the presence of specific interactions between the mixing components. On the other hand, the DMSO + 1,3,5-trimethylbenzene mixture exhibits positive V^E throughout the mole fraction range, suggesting that dispersion-type interactions may be operative in these mixtures. These facts are further supported by the dependencies of R^E or β^E on volume fraction of DMSO shown in Figures 4 and 5, respectively. A comparison of viscosities of mixtures of DMSO with benzene or toluene with the results of Gopal et al. (*14*) at 303.15 K shows that they are quite comparable. Similarly, for mixtures of DMSO with benzene our V^E results at 303.15 K are also in

Table VI. Binary Data for Mixtures of DMSO (1) + Methoxybenzene (2)

x_1	ρ/(g cm^{-3})	η/(mPa s)	n_D	u/(m s^{-1})
		298.15 K		
0.0	0.9897	0.990	1.5143	1415
0.1034	0.9978	1.049	1.5121	1416
0.2030	1.0060	1.113	1.5094	1432
0.3049	1.0148	1.184	1.5058	1439
0.4058	1.0241	1.259	1.5032	1448
0.5049	1.0336	1.342	1.5001	1453
0.6063	1.0443	1.443	1.4956	1459
0.7044	1.0555	1.544	1.4917	1467
0.8039	1.0678	1.666	1.4866	1475
0.9011	1.0814	1.808	1.4826	1480
1.0	1.0962	1.975	1.4770	1489
		305.15 K		
0.0	0.9851	0.916	1.5119	1370
0.1034	0.9927	0.968	1.5097	1381
0.2030	1.0012	1.024	1.5068	1391
0.3049	1.0102	1.104	1.5035	1400
0.4058	1.0193	1.155	1.5010	1408
0.5049	1.0290	1.229	1.4976	1414
0.6063	1.0394	1.320	1.4934	1423
0.7044	1.0508	1.408	1.4896	1431
0.8039	1.0629	1.517	1.4843	1439
0.9011	1.0761	1.641	1.4802	1446
1.0	1.0911	1.788	1.4748	1455
		308.15 K		
0.0	0.9801	0.853	1.5094	1370
0.1034	0.9881	0.899	1.5072	1381
0.2030	0.9964	0.949	1.5043	1391
0.3049	1.0051	1.008	1.5014	1400
0.4058	1.0143	1.068	1.4984	1408
0.5049	1.0239	1.133	1.4951	1414
0.6063	1.0345	1.214	1.4911	1423
0.7044	1.0456	1.292	1.4870	1431
0.8039	1.0579	1.388	1.4819	1439
0.9011	1.0713	1.500	1.4780	1446
1.0	1.0851	1.630	1.4730	1455

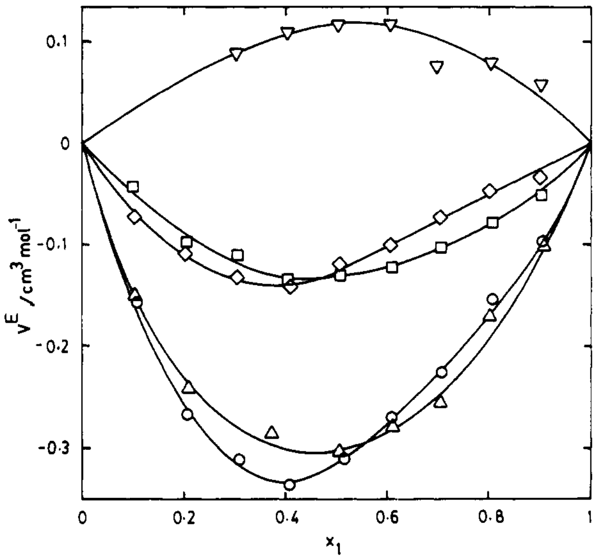

Figure 3. Dependence of V^E on x_1 at 298.15 K for mixtures given in Figure 1.

Table VII. Estimated Coefficients for Equations 8–10 and Standard Errors σ for Various Quantities

Y^E	T/K	a_0	a_1	a_2	a_3	σ
		DMSO (1) + Benzene (2)				
$V^E/(\mathrm{cm^3\ mol^{-1}})$	298.15	−1.250	−0.568	0.098	−0.368	0.015
	303.15	−1.466	−0.242	−0.729	−0.580	0.035
	308.15	−1.561	−0.473	−0.018	0.153	0.020
$\beta^E \times 10^{11}/\mathrm{Pa^{-1}}$	298.15	−18.454	−5.998	4.856	−2.900	0.071
	303.15	−19.811	−4.380	−4.468	−6.290	0.141
	308.15	−22.213	−4.291	−7.537	−8.437	0.222
$R^E_{\text{L-L}}/(\mathrm{cm^3\ mol^{-1}})$	298.15	−1.632	−0.387	0.808	−0.447	0.013
		DMSO (1) + Toluene (2)				
$V^E/(\mathrm{cm^3\ mol^{-1}})$	298.15	−1.218	−0.088	−0.494	−0.465	0.013
	303.15	−1.287	−0.140	−0.321	−0.696	0.013
	308.15	−1.153	−0.045	0.259	0.135	0.016
$\beta^E \times 10^{11}/\mathrm{Pa^{-1}}$	298.15	−13.863	−8.701	9.493	−6.351	0.382
	303.15	−15.574	−4.020	−6.715	−7.552	0.225
	308.15	−16.729	−3.639	−7.215	−5.335	0.118
$R^E_{\text{L-L}}/(\mathrm{cm^3\ mol^{-1}})$	298.15	−2.902	−0.173	−1.006	0.107	0.006
		DMSO (1) + 1,3-Dimethylbenzene (2)				
$V^E/(\mathrm{cm^3\ mol^{-1}})$	298.15	−0.528	−0.205	0.325	−0.104	0.014
	303.15	−0.456	−0.081	−0.127	−0.426	0.022
	308.15	−0.514	−0.093	−0.066	−0.791	0.007
$\beta^E \times 10^{11}/\mathrm{Pa^{-1}}$	298.15	−9.916	1.099	−0.989	−6.743	0.111
	303.15	−10.169	1.124	−5.989	−12.023	0.137
	308.15	−12.004	−1.941	−0.454	−5.295	0.190
$R^E_{\text{L-L}}/(\mathrm{cm^3\ mol^{-1}})$	298.15	4.096	−0.255	−0.137	−0.159	0.021
		DMSO (1) + 1,3,5-Trimethylbenzene (2)				
$V^E/(\mathrm{cm^3\ mol^{-1}})$	298.15	0.292	−1.380	6.269	6.095	0.136
	303.15	0.324	−1.353	6.217	6.053	0.125
	308.15	0.326	−1.340	6.759	6.401	0.135
$\beta^E \times 10^{11}/\mathrm{Pa^{-1}}$	298.15	−5.636	9.735	−14.820	1.925	0.353
	303.15	−5.872	8.711	−10.159	−1.717	0.212
	308.15	−6.174	7.406	−7.522	3.685	0.352
$R^E_{\text{L-L}}/(\mathrm{cm^3\ mol^{-1}})$	298.15	−5.274	0.127	−0.627	1.126	0.091
		DMSO (1) + Methoxybenzene (2)				
$V^E/(\mathrm{cm^3\ mol^{-1}})$	298.15	−0.484	−0.384	0.245	−0.110	0.004
	303.15	−0.534	−0.416	0.604	0.710	0.009
	308.15	−0.544	−0.411	0.445	0.001	0.006
$\beta^E \times 10^{11}/\mathrm{Pa^{-1}}$	298.15	−3.967	−3.074	4.356	3.240	0.192
	303.15	−4.213	0.172	−5.935	0.712	0.101
	308.15	−5.207	−1.837	−2.601	−2.568	0.046
$R^E_{\text{L-L}}/(\mathrm{cm^3\ mol^{-1}})$	298.15	−1.930	−0.064	−0.176	0.074	0.020

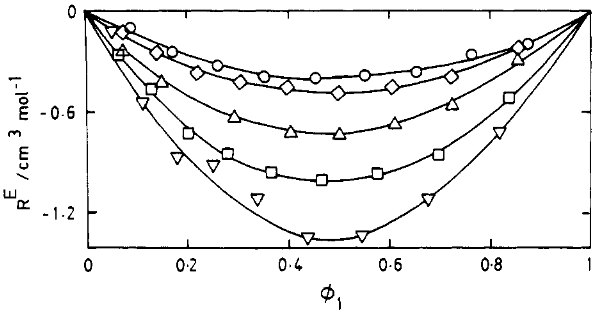

Figure 4. Dependence of R^E on φ_1 at 298.15 K for mixtures of DMSO given in Figure 1.

agreement with the results of Absood et al. (*13*). For instance, at equimolar compositions our V^E is −0.3665 cm³/mol, whereas Absood et al. got −0.2773 cm³/mol.

Conclusions

In the present paper some thermodynamic mixing functions have been derived from the results of densities, refractive indices, and ultrasonic velocities of mixtures of aromatic hydrocarbons with DMSO. Some of these mixtures have been studied previously; however, no extensive data base exists on the mixtures studied here. The results of our study indicate the effect of methyl and methoxy substitutions in benzene on its mixing properties with DMSO as shown from the dependencies of V^E, β^E, and R^E on mixture compositions.

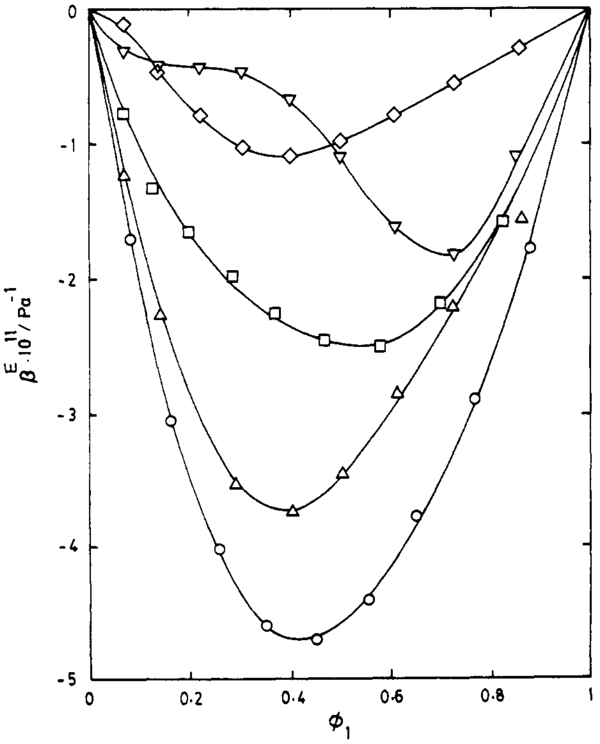

Figure 5. Dependence of β^E on φ_1 at 298.15 K for mixtures given in Figure 1.

Registry No. DMSO, 67-68-5; benzene, 71-43-2; toluene, 108-88-3; 1,3-dimethylbenzene, 108-38-3; 1,3,5-trimethylbenzene, 108-67-8; methoxybenzene, 100-66-3.

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Sorption and Separation of Divalent Metals by a Macromolecular Resin Containing Organophosphorus Acids

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Studies have been conducted on the equilibrium distribution of divalent zinc ion between aqueous solution and macromolecular resin impregnated with phosphoric acid bis(2-ethylhexyl ester) (D2EHPA). The mechanism of Zn(II) sorption on the impregnated sorbent is different from that for the solvent extraction, being expressed by a simple ion-exchange reaction, with the equilibrium constant of 0.036 kg of sorbent/dm^3. The separations of Zn(II)/Cu(II) using D2EHPA-impregnated sorbent and of Co(II)/Ni(II) by the resin impregnated with (2-ethylhexyl)phosphonic acid mono(2-ethylhexyl ester) (EHPNA) have also been conducted in a batch operation. It was found that the selective sorptions of Zn(II) to Cu(II) and of Co(II) to Ni(II) can be attained satisfactorily with the separation factors of 55.2 and 6.73, respectively.

Introduction

The fields of application of ion exchange for separation are extremely widespread from the treatment of low-cost materials such as water to the purification of expensive pharmaceutical derivatives. There is a need for specific ion-exchange materials having high affinities to the objective substances.

Extractant-impregnated sorbents and Levextrel resins have had special attention because of their great potential for highly selective separation and concentration of metal ions from aqueous solutions (*1*–*4*); their features and applications are reviewed by Warshawsky (*5*). Compared with typical chelating resins, impregnated sorbents have some advantages such as simplicity in preparation, high selectivity, and complete desorptibility. The most attractive feature of this type of the sorbent is in the availability of an extractant fitted in with a metal separation system; furthermore, the sorption characteristics can be evaluated from previous data on the solvent extraction.

In a previous work (*6*), we studied the equilibrium sorption and separation of Zn(II) by a tri-*n*-octylamine-impregnated sorbent. These showed that the stoichiometric relation of the sorption equilibrium follows that of the solvent extraction, and Zn(II) could be separated from Cu(II) continuously in a column operation.

The present study has been made on the sorption and separation characteristics of divalent metals by sorbents impregnated with two organophosphorus acid reagents: D2EHPA and EHPNA as phosphoric and phosphonic acid type extractants, respectively. Solvent extraction using these extractants has been studied extensively for the separation of lanthanoids and transition-metal ions.

Experimental Section

Preparation of Impregnated Sorbent. Two types of organophosphorus acid reagents, D2EHPA (Tokyo Kasei Co., Ltd.) and EHPNA (trade name PC-88A; Daihachi Chemicals Industry Co., Ltd.), were used as active components without further purification. Amberlite XAD-2 (Organo Co., Ltd.), washed with acetone and water, and fractionated in the particle size range of 500–710 µm prior to the impregnation with an extractant, was used as a matrix resin.

A sorbent impregnated with each extractant was prepared as follows. An appropriate volume of 0.1 M solution of the extractant in *n*-hexane was mixed with a given weighed amount of XAD-2, and the diluent was then evaporated in a rotatory evaporator. Subsequently the impregnated sorbent was placed in a vacuum at 50 °C for 2 h to be sure of the complete