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Excess Volumes of Binary Mixtures Containing Diisopropyl Ether + 1-Butanol or Diisopropyl Ether + Diethyl Ketone and Ethanol + Heptane at High Pressures

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Excess molar volumes V^E of diisopropyl ether with 1-butanol were measured at pressures of 0.1 MPa, 20 MPa, 40 MPa, and 60 MPa and at temperatures of 278.15 K, 298.15 K, and 323.15 K; mixtures of diisopropyl ether + diethyl ketone, at 278.15 and 298.15 K. V^E is negative for all the mixtures studied over the whole concentration range and for all temperatures. Excess molar volumes V^E of ethanol with heptane were measured at 298.15 K and 0.1 MPa, 20 MPa, and 60 MPa. V^E is positive in all mixtures studied. Results were correlated by polynomial equations of the type $V^E = x_1x_2\sum_i A_i(2x_1 - 1)^i$.

Introduction

In this paper molar excess volumes of binary mixtures at a temperature range from 278.15 K to 323.15 K and up to 60 MPa are reported. The measurements are part of a long-term study to examine the dependence of excess volumes on temperature and pressure for different functional groups, in this case keto, alcohol, and ether groups. The results are input into a data base to determine interaction parameters for group contribution models.

Experimental Section

Materials. All materials used are pro analysis grades from Merck (diisopropyl ether, 1-butanol), Merck-Schuchardt (diethyl ketone, octane, ethanol, heptane), and Carl Roth (hexane, methanol). The purity of the substances was verified by gas chromatography and determined to be better than 99%; the purity of methanol was better than 99.8%. Water used to calibrate the densimeter was distilled four times (conductance <1 μS). All liquids were degassed by ultrasonic treatment and under vacuum before an experiment.

Apparatus and Procedure. Densities ρ of pure components and samples of mixtures were determined using a vibrating tube densimeter, model DMA 60/512p of Anton Paar, Graz (see Figure 1).

The required pressure up to 60 MPa was generated by a Maximator Type M hydraulic pump with water as the hydraulic fluid. The pressure was transmitted to the sample by a Ruska differential pressure cell (DPC) containing a metallic diaphragm which separated the sample and the hydraulic fluid. The pressure was controlled to ±0.01 MPa by a pressure gauge, model P3M Hottinger Baldwin Messtechnik; the output voltage was measured with a Prema 6031 digital multimeter.

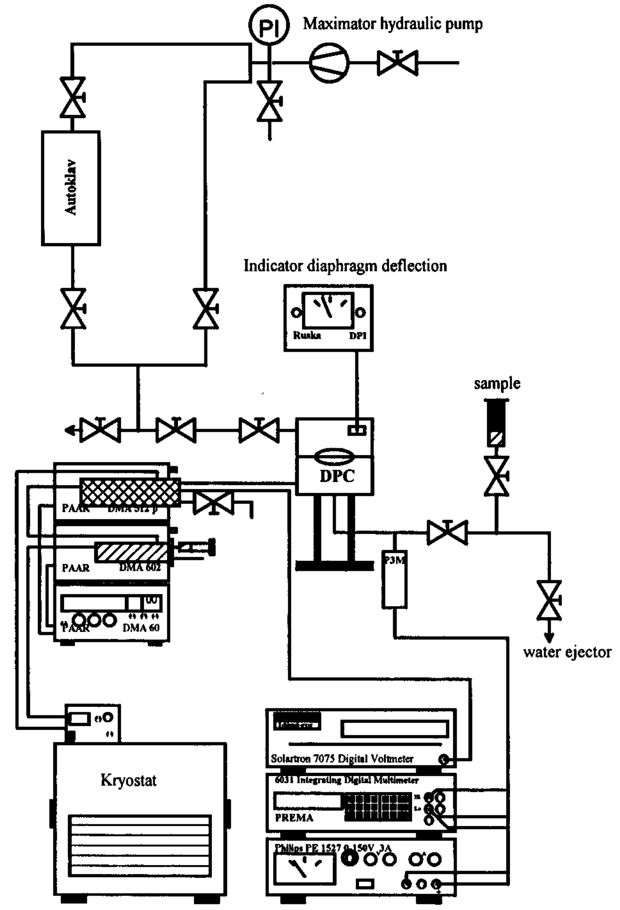

Figure 1. Experimental setup for the measurement of liquid densities at high pressures.

The temperature in the vibrating tube was controlled through an MGW Lauda Kryostat RK 20 with an accuracy of ±0.01 K. The temperature was measured with a Schlumberger Solartron 7075 digital voltmeter and a Pt 100 sensing element. The digital densimeter DMA 60/512p was calibrated with four times distilled water and hexane at temperatures of 298.15 K and 323.15 K and with four times distilled water and octane at 278.15 K. The pressure dependence of the densities of the reference substances are known with good accuracy (Benson and Winnick, 1971; Dymond, 1979; Küster and Thiel, 1982; Steam Tables, 1989; Thermodynamic Tables Hydrocarbons Vol. III; VDI Wärmeatlas, 1984). To examine the accuracy of the experimental equipment, the liquid densities of methanol at higher pressures (Table 2) and the excess volumes of the mixture ethanol + heptane (see Figure 2) at atmo-

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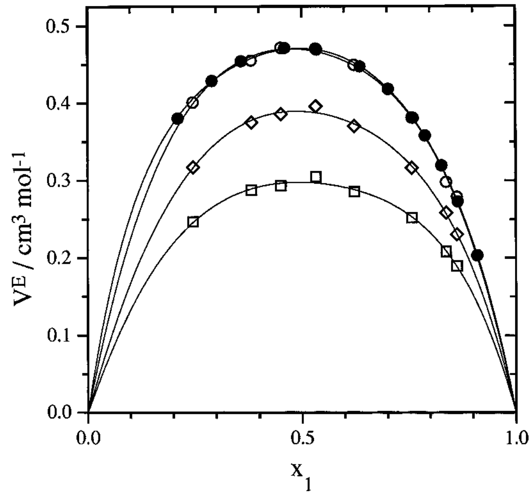

Figure 2. Excess molar volume of the binary mixture ethanol (1) + heptane (2) at 298.15 K and (●) 0.1 MPa (Treszczanowicz and Benson, 1977), (○), 0.1 MPa, (◇) 20 MPa, and (□) 60 MPa.

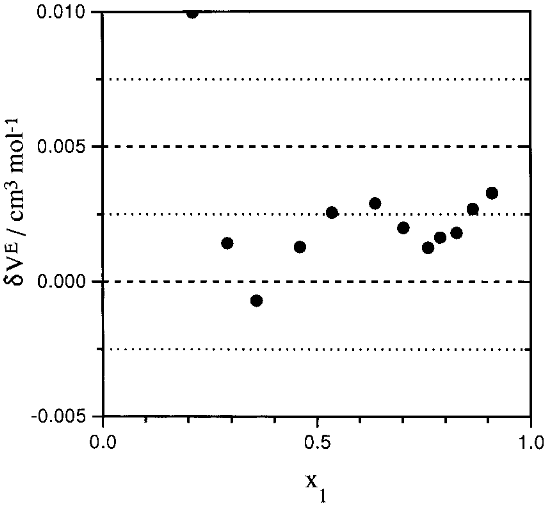

Figure 3. Comparison of measured V^E values with literature values (Treszczanowicz and Benson, 1977) of the mixture ethanol (1) + heptane (2) at 298.15 K and 0.1 MPa according to eq 3.

spheric pressure were measured and compared with literature values (Tongfan, 1988; Treszczanowicz and Benson, 1977).

The overall precision of the density measurement is estimated to be better than 5 × 10^{-5} g·cm^{-3}. The mixtures were prepared from degassed pure liquids by mass with an accuracy of ±1 × 10^{-4} g using a Mettler balance (model H 315). Correction for vapor space was performed but had only a small influence on the final mole fraction for which uncertainties of 1 × 10^{-4} were estimated. Thus, the excess molar volume is accurate to ±5 × 10^{-3} cm^3·mol^{-1}.

The samples were introduced into the vibrating tube of the Anton Paar densimeter under vacuum without losses by evaporation or impurities due to contact to air.

Results and Discussion

The experimental V^E values of the three binary mixtures are given in Table 1, the densities of pure liquids are reported in Table 2. The quantity of V^E for a mixture of two components was calulated from

$$V^E = x_1 M_1\left(\frac{1}{\rho_m} - \frac{1}{\rho_1^\circ}\right) + x_2 M_2\left(\frac{1}{\rho_m} - \frac{1}{\rho_2^\circ}\right) \qquad (1)$$

with x_i being the mole fraction of component i, ρ_i° the density of the pure component, ρ_m the density of the mixture, and M_i the molar mass of component i.

Table 1. Experimental Results for the Excess Molar Volume V^E of Diisopropyl Ether (1) + 1-Butanol (2), Diisopropyl Ether (1) + Diethyl Ketone (2), and Ethanol (1) + Heptane (2)

		V^E/cm^3·mol^{-1}			
T/K	x_1	p = 0.1 MPa	p = 20 MPa	p = 40 MPa	p = 60 MPa
		Diisopropyl Ether (1) + Diethyl Ketone (2)			
278.15	0.2015	−0.2252	−0.1613	−0.1217	−0.0882
	0.3066	−0.3361	−0.2410	−0.1968	−0.1707
	0.4257	−0.3877	−0.2805	−0.2500	−0.2194
	0.5033	−0.4041	−0.2936	−0.2589	−0.2386
	0.6058	−0.3868	−0.2816	−0.2553	−0.2180
	0.6934	−0.3532	−0.2413	−0.2164	−0.1724
	0.8068	−0.2889	−0.1859	−0.1503	−0.1140
298.15	0.2057	−0.4322	−0.3337	−0.2661	−0.2318
	0.2915	−0.5099	−0.3950	−0.3266	−0.2672
	0.4258	−0.5742	−0.4366	−0.3433	−0.2931
	0.4898	−0.5921	−0.4504	−0.3540	−0.3043
	0.6409	−0.5828	−0.4303	−0.3457	−0.3008
	0.6965	−0.5606	−0.4092	−0.3247	−0.2755
	0.7882	−0.4523	−0.3371	−0.2751	−0.2399
		Diisopropyl Ether (1) + 1-Butanol (2)			
278.15	0.2016	−0.6635	−0.5853	−0.5493	−0.5060
	0.3013	−0.8516	−0.7360	−0.6752	−0.6035
	0.4025	−0.9470	−0.8389	−0.7711	−0.7055
	0.5021	−0.9635	−0.8334	−0.7578	−0.6834
	0.6013	−0.9169	−0.7866	−0.7138	−0.6477
	0.6999	−0.8354	−0.7078	−0.6368	−0.5783
	0.8027	−0.6649	−0.5795	−0.5656	−0.5145
298.15	0.2018	−0.7790	−0.6164	−0.5323	−0.4561
	0.3023	−0.9769	−0.7546	−0.6450	−0.5580
	0.4014	−1.0556	−0.8275	−0.6988	−0.5944
	0.5013	−1.0757	−0.8411	−0.7039	−0.5928
	0.6013	−1.0392	−0.8133	−0.6871	−0.5842
	0.6999	−0.9595	−0.7422	−0.6191	−0.5202
	0.8022	−0.8318	−0.6555	−0.5519	−0.4729
323.15	0.2017	−0.8998	−0.6902	−0.5627	−0.5237
	0.2998	−1.1837	−0.8594	−0.6833	−0.5839
	0.4010	−1.2582	−0.9204	−0.7301	−0.6494
	0.5010	−1.3857	−1.0245	−0.8224	−0.7269
	0.6010	−1.3745	−1.0026	−0.7853	−0.7182
	0.7009	−1.2456	−0.9119	−0.7311	−0.6623
	0.7968	−1.0054	−0.7482	−0.5830	−0.5279
		Ethanol (1) + Heptane (2)			
298.15	0.2459	0.4007	0.3175		0.2467
	0.3818	0.4549	0.3749		0.2878
	0.4510	0.4715	0.3856		0.2934
	0.5328	0.4704	0.3957		0.3049
	0.6228	0.4491	0.3701		0.2854
	0.7575	0.3810	0.3163		0.2520
	0.8376	0.2981	0.2586		0.2079
	0.8631	0.2790	0.2304		0.1893

Table 2. Densities of Pure Liquid Components at Different Temperatures and Pressures

		ρ/g·cm^{-3}			
T/K	component	p = 0.1 MPa	p = 20 MPa	p = 40 MPa	p = 60 MPa
278.15	diisopropyl ether	0.7418	0.7612	0.7769	0.7899
	diethyl ketone	0.8300	0.8446	0.8570	0.8677
	1-butanol	0.8206	0.8331	0.8440	0.8539
283.15	methanol		0.8190	0.8324	0.8444
	methanol (Tongfan, 1988)		0.8170	0.8313	0.8437
298.15	diisopropyl ether	0.7108	0.7325	0.7504	0.7655
	diethyl ketone	0.8037	0.8190	0.8328	0.8450
	1-butanol	0.8060	0.8193	0.8311	0.8418
	ethanol	0.7814	0.7975		0.8235
	heptane	0.6739	0.6906		0.7170
323.15	diisopropyl ether	0.6903	0.7162	0.7357	0.7523
	1-butanol	0.7854	0.8004	0.8133	0.8252

Table 3. Parameters A_i of Equation 2 and Standard Deviation

system	T/K	p/MPa	A_0	A_1	A_2	A_3	100σ/cm^3·mol^{-1}
diisopropyl ether + 1-butanol	278.15	0.1	−3.8575	0.2557	−0.8504	−0.8762	0.388
		20	−3.3337	0.4197	−0.8220	−1.2261	0.869
		40	−3.0087	0.5740	−1.2095	−1.9377	1.714
		60	−2.7192	0.4654	−1.1753	−1.5362	2.389
	298.15	0.1	−4.2861	0.3264	−2.0514	−1.7724	0.389
		20	−3.3375	0.2504	−1.6943	−1.3376	0.946
		40	−2.8046	0.2723	−1.5514	−1.0891	1.164
		60	−2.3753	0.3317	−1.4092	−1.1816	1.466
	323.15	0.1	−5.5013	−0.7235	−1.1217	0.6679	1.861
		20	−4.0069	−0.6200	−1.2566	1.0223	1.558
		40	−3.1818	−0.5478	−1.0359	1.3146	1.786
		60	−2.8250	−0.8553	−1.1426	2.3833	1.388
diisopropyl ether + diethyl ketone	278.15	0.1	−1.6084	0.0348	−0.0299	−1.1085	0.795
		20	−1.1692	0.0394	0.2102	−0.5312	1.262
		40	−1.0504	−0.1045	0.5249	−0.2031	0.915
		60	−0.9361	0.0423	0.8262	−0.5559	1.714
	298.15	0.1	−2.3880	−0.3856	−0.8783	0.9383	0.685
		20	−1.7979	−0.1068	−0.6952	0.3532	0.468
		40	−1.4220	−0.0253	−0.6809	0.0385	1.592
		60	−1.2107	−0.1089	−0.6208	0.2724	1.178
ethanol + heptane	298.15	0.1	1.8784	−0.0998	0.9013	0.0721	1.281
		20	1.5571	−0.0469	0.6221	0.2623	0.907
		60	1.1910	−0.0173	0.6119	0.2401	1.128

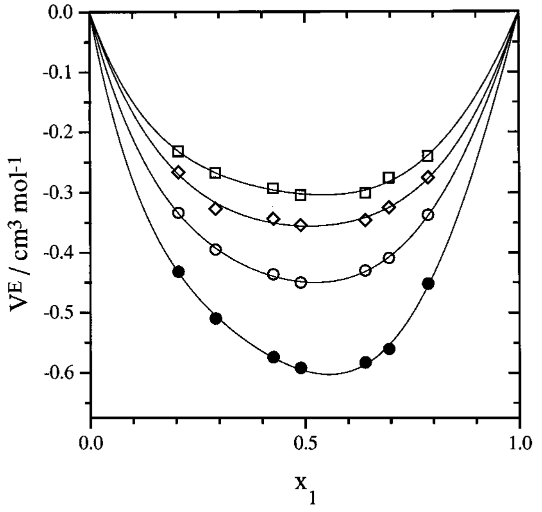

Figure 4. Excess molar volume of the binary mixture diisopropyl ether (1) + diethyl ketone (2) at 298.15 K and (●) 0.1 MPa, (○) 20 MPa, (◇) 40 MPa, and (□) 60 MPa.

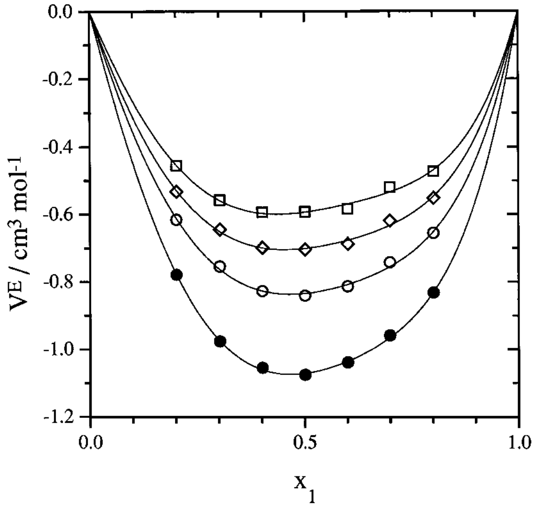

Figure 5. Excess molar volume of the binary mixture diisopropyl ether (1) + 1-butanol (2) at 298.15 K and (●) 0.1 MPa, (○) 20 MPa, (◇) 40 MPa, and (□) 60 MPa.

In Figures 2, 4, and 5, the plots of experimental excess volumes are shown. The solid curves were calculated by fitting to the experimental data using the Redlich−Kister polynomial

$$V^{E}(x_1) = x_1x_2\sum_{i=0}^{n}A_i(2x_1 - 1)^i \tag{2}$$

with the A_i being adjustable parameters obtained by a least-squares method. The parameters A_i and the standard deviations are listed in Table 3.

The molar excess volume of the mixture ethanol + heptane is positive over the whole concentration range and decreases with pressure. The measured V^E values at 0.1 MPa and 298.15 K are compared with values taken from the literature (Treszczanowicz and Benson, 1977) according to

$$\delta V^{E} = V^{E}_{\text{lit.}} - V^{E}_{\text{calc.}} \tag{3}$$

The results of this comparison are given in Figure 3. It can be seen that the supposed accuracy of our measured values of ±5 × 10^{-3} cm^3·mol^{-1} is indeed justified in most cases. The measured values for the pure liquid densities of methanol at 283.15 K and pressures of 20 MPa, 40 MPa, and 60 MPa are in good agreement with values taken from the literature (Tongfan, 1988).

The V^E values of the mixtures diisopropyl ether + 1-butanol or diisopropyl ether + diethyl ketone are negative, decreasing with an increase in pressure and show a positive temperature coefficient.

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