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Excess Volumes for Diisopropyl Ether + Butanoic Acid and + Butyl Formate from 298.15 K to 323.15 K at Pressures up to 60 MPa

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Excess molar volumes V^E of diisopropyl ether + butanoic acid and + butyl formate 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. V^E is negative for all the mixtures studied over the whole concentration range and for all temperatures. 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 article 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 acid-, ester-, ether-, and keto-groups. Excess molar volumes for diisopropyl ether + 1-butanol and + diethyl ketone, measured by ourselves, have been reported previously (*J. Chem. Eng. Data* **1997**, *42*, 449−452). The results are implemented into a database to determine interaction parameters for a group contribution equation of state. Mixtures of diisopropyl ether with other substances were chosen, because these mixtures show mostly high molar excess volumes and are suitable for measurements at high pressures due to the experimental value range.

Experimental Section

Materials. All materials used are pro analysis grades from Merck (diisopropyl ether) and Merck-Schuchardt (butanoic acid, butyl formate) and were used without further purification. The purity of the substances was verified by gas chromatography by the manufacturers and was determined to be better than 99%. Water, used to calibrate the densimeter, was distilled four times (conductance <1 μS). All liquids were degassed by ultrasonic at first and additionally under vacuum before an experiment.

Apparatus and Procedure. Densities ρ of pure components and mixtures were determined using a vibrating tube densimeter, model DMA 60/512p of Anton Paar, Graz, as described earlier (Ulbig et al., 1997).

The densimeter 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; TRC db-1410, 1996; VDI Wärmeatlas, 1984).

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 a total mass between 15 and 35 g with an accuracy of $\pm 1 \times 10^{-4}$ 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 measured excess molar volume is accurate to $\pm 5 \times 10^{-3}$ cm^3·mol^{-1}.

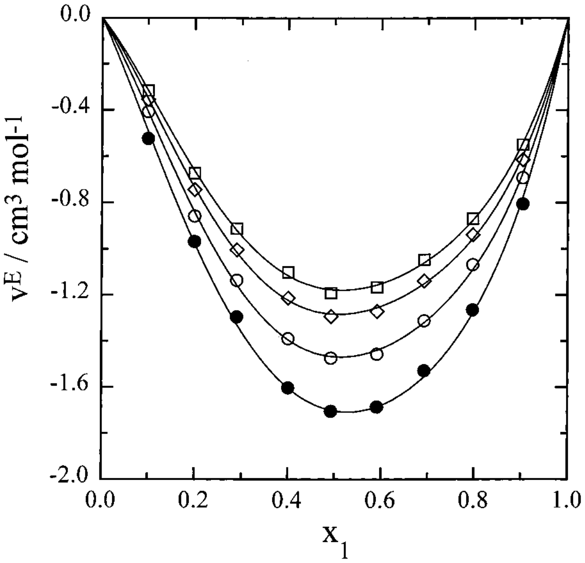

Figure 1. Excess molar volume of the binary mixture diisopropyl ether (1) + butanoic acid (2) at 298.15 K and ●, 0.1MPa; ○, 20 MPa; ◇, 40 MPa; □, 60 MPa.

The Anton Paar densimeter was evacuated from air before the samples were introduced into the vibrating tube due to the existing vacuum in the measuring cell. The advantage of this fact is that there are no losses by evaporation or impurities due to contact to air.

Results and Discussion

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

$$V^E = x_1M_1\left(\frac{1}{\rho_m} - \frac{1}{\rho^0{}_1}\right) + x_2M_2\left(\frac{1}{\rho_m} - \frac{1}{\rho^0{}_2}\right) \qquad (1)$$

with x_i being the mole fraction of component i, $\rho^0{}_i$ the density of pure component, ρ_m the density of the mixture, and M_i the molar mass of component i.

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Table 1. Experimental Results for the Excess Molar Volume V^E of Diisopropyl Ether (1) + Butanoic Acid (2) and Diisopropyl Ether (1) + Butyl Formate (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) + Butanoic Acid (2)			
278.15	0.1009	−0.4796	−0.3839	−0.3348	−0.3075
	0.1999	−0.9031	−0.7803	−0.7062	−0.6493
	0.2975	−1.2239	−1.0682	−0.9496	−0.8830
	0.4022	−1.4278	−1.2697	−1.1352	−1.0482
	0.5016	−1.5298	−1.3400	−1.2034	−1.1231
	0.5954	−1.5275	−1.3412	−1.1990	−1.1208
	0.6985	−1.4027	−1.2278	−1.0798	−1.0132
	0.7955	−1.1691	−1.0119	−0.9137	−0.8462
	0.9080	−0.7317	−0.6318	−0.5609	−0.5190
298.15	0.1005	−0.5232	−0.4075	−0.3548	−0.3159
	0.1997	−0.9683	−0.8581	−0.7439	−0.6731
	0.2897	−1.2947	−1.1357	−1.0033	−0.9121
	0.4008	−1.6026	−1.3891	−1.2132	−1.1014
	0.4929	−1.7044	−1.4738	−1.2919	−1.1914
	0.5911	−1.6862	−1.4566	−1.2711	−1.1663
	0.6924	−1.5283	−1.3112	−1.1390	−1.0468
	0.7967	−1.2641	−1.0681	−0.9381	−0.8687
	0.9042	−0.8049	−0.6920	−0.6146	−0.5501
323.15	0.1008	−0.6184	−0.4884	−0.4142	−0.3403
	0.1998	−1.2092	−0.9803	−0.8434	−0.7500
	0.3033	−1.6691	−1.3087	−1.1512	−1.0208
	0.3965	−1.9540	−1.5640	−1.3230	−1.1871
	0.4952	−2.0793	−1.6359	−1.4053	−1.2752
	0.5953	−2.0533	−1.5962	−1.3633	−1.2470
	0.7098	−1.8773	−1.4279	−1.3221	−1.1293
	0.7982	−1.5470	−1.2127	−1.0238	−0.9543
	0.9151	−0.9196	−0.7482	−0.6731	−0.6110
		Diisopropyl Ether (1) + Butyl Formate (2)			
278.15	0.0988	−0.1423	−0.0942	−0.0613	−0.0469
	0.1985	−0.2703	−0.1767	−0.1393	−0.1198
	0.3003	−0.3610	−0.2600	−0.2052	−0.1738
	0.3989	−0.4278	−0.3125	−0.2539	−0.2185
	0.4997	−0.4602	−0.3403	−0.2752	−0.2459
	0.5999	−0.4718	−0.3439	−0.2714	−0.2383
	0.6995	−0.4192	−0.3000	−0.2360	−0.2030
	0.8016	−0.3361	−0.2267	−0.1811	−0.1527
	0.9005	−0.2078	−0.1255	−0.0959	−0.0726
298.15	0.1001	−0.2296	−0.1281	−0.0967	−0.0797
	0.1999	−0.3634	−0.2533	−0.2000	−0.1698
	0.3010	−0.4661	−0.3334	−0.2682	−0.2202
	0.3988	−0.5289	−0.3988	−0.3152	−0.2784
	0.4997	−0.5477	−0.4213	−0.3358	−0.2965
	0.5992	−0.5288	−0.3995	−0.3168	−0.2808
	0.6996	−0.4788	−0.3631	−0.2762	−0.2423
	0.7996	−0.3662	−0.2639	−0.1962	−0.1702
	0.9002	−0.2202	−0.1401	−0.1140	−0.0883
323.15	0.1004	−0.3202	−0.2121	−0.1739	−0.1519
	0.2001	−0.4837	−0.3493	−0.2764	−0.2527
	0.3020	−0.5891	−0.4488	−0.3600	−0.3112
	0.3984	−0.6595	−0.4983	−0.4112	−0.3622
	0.5028	−0.6606	−0.5151	−0.4162	−0.3707
	0.6016	−0.6043	−0.4659	−0.3789	−0.3450
	0.6987	−0.5092	−0.3952	−0.3212	−0.2905
	0.8019	−0.3839	−0.2802	−0.2314	−0.2042
	0.8960	−0.2365	−0.1522	−0.1203	−0.1219

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	0.7388	0.7581	0.7737	0.7869
	butanoic acid	0.9722	0.9869	0.9997	1.0102
	butyl formate	0.9108	0.9258	0.9386	0.9502
298.15	diisopropyl ether	0.7182	0.7397	0.7571	0.7719
	butanoic acid	0.9525	0.9688	0.9827	0.9952
	butyl formate	0.8896	0.9069	0.9212	0.9339
323.15	diisopropyl ether	0.6913	0.7167	0.7369	0.7532
	butanoic acid	0.9277	0.9456	0.9613	0.9747
	butyl formate	0.8644	0.8837	0.9003	0.9146

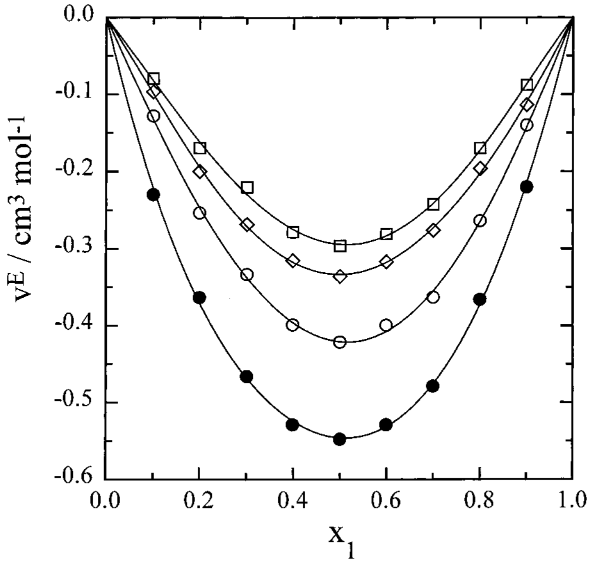

Figure 2. Excess molar volume of the binary mixture diisopropyl ether (1) + butyl formate (2) at 298.15 K and ●, 0.1 MPa; ○, 20 MPa; ◇, 40 MPa; □, 60 MPa.

Table 3. Parameters A_i of Equation 2 and Standard Deviation

T/K	p/MPa	A_0/cm^3· mol^{-1}	A_1/cm^3· mol^{-1}	A_2/cm^3· mol^{-1}	A_3/cm^3· mol^{-1}	100σ/cm^3· mol^{-1}
		Diisopropyl Ether + Butanoic Acid				
278.15	0.1	−6.0918	−0.6989	−1.1430	−2.0169	1.34
	20	−5.3800	−0.4964	−0.6199	−2.1941	1.14
	40	−4.8082	−0.3799	−0.5288	−2.1114	1.14
	60	−4.4832	−0.4421	−0.4097	−1.8127	1.05
298.15	0.1	−6.7609	−0.7144	−0.7291	−2.2234	2.17
	20	−5.8718	−0.3017	−0.3716	−2.6145	1.73
	40	−5.1314	−0.1691	−0.3608	−2.5889	1.45
	60	−4.7102	−0.2777	−0.2130	−2.1788	1.23
323.15	0.1	−8.2998	−0.7801	−1.0827	−3.1520	1.84
	20	−6.4922	−0.1438	−1.0315	−3.3993	2.35
	40	−5.5524	0.0568	−1.0378	−3.4284	2.43
	60	−5.0432	−0.1577	−0.8105	−3.1591	1.98
		Diisopropyl Ether + Butyl Formate				
278.15	0.1	−1.8520	−0.3441	−0.1447	−0.1021	0.45
	20	−1.3708	−0.2815	0.2480	0.0961	0.27
	40	−1.1052	−0.1708	0.3148	−0.1114	0.20
	60	−0.9740	−0.1816	0.4127	0.0163	0.31
298.15	0.1	−2.1846	−0.0801	−0.3806	0.2026	0.55
	20	−1.6839	−0.1158	0.2390	0.0705	0.53
	40	−1.3336	0.0109	0.2603	−0.1361	0.45
	60	−1.1772	−0.0821	0.3695	0.0825	0.55
323.15	0.1	−2.5973	0.4562	−0.4608	0.2180	1.26
	20	−2.0289	0.2809	0.1188	0.2373	0.45
	40	−1.6512	0.2006	0.1310	0.2244	0.56
	60	−1.4661	0.1323	0.0511	0.2005	0.63

In Figures 1 and 2, the plots of experimental excess volumes are shown. The solid curves were calculated by fitting to the experimental data using the Redlich−Kister polynomial

$$V^E(x_1) = x_1 x_2 \sum_{i=0}^{n} A_i (2x_1 - 1)^i \qquad (2)$$

with the A_i being adjustable parameters obtained by a least-squares method. The parameters A_i and the standard deviations of the experimental values to the fitting curves are listed in Table 3. The values of $\sigma(V^E)$ were obtained by using the equation

$$\sigma(V^E) = \left[\frac{\sum (V^E_{\mathrm{calcd}} - V^E_{\mathrm{exptl}})^2}{n - P}\right]^{1/2} \qquad (3)$$

where n is the number of experimental data and P is the number of parameters.

The molar excess volumes of the mixtures diisopropyl ether + butanoic acid and + butyl formate are negative, their absolute values decreasing with an increase in pressure and increasing with an increase in temperature.

A comparison with results of diisopropyl ether + 1-butanol, + diethyl ketone previously measured (*J. Chem. Eng. Data* **1997**, *42*, 449−452) shows that the values of the excess molar volumes depend on the structure respectively of the functional groups of the used components. The absolute values of the data points increase with an increase in polarity as well; both butyl formate ($V^E{}_{max} \approx -0.5$ $cm^3 \cdot mol^{-1}$, e.g., at 298.15 K and 0.1 MPa) and diethyl ketone ($V^E{}_{max} \approx -0.6$ $cm^3 \cdot mol^{-1}$) have similar small absolute values of molar excess volumes, whereas 1-butanol ($V^E{}_{max} \approx -1.1$ $cm^3 \cdot mol^{-1}$) and butanoic acid ($V^E{}_{max} \approx -1.7$ $cm^3 \cdot mol^{-1}$) above all do have large absolute values obviously due to their hydrogen bondings, which are typical of alcohols and organic acids.

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