Volumetric Properties of Binary Mixtures. 1. 2-Propanone + 2,2,4-Trimethylpentane and *n*-Heptane + Ethanol Mixtures

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Experimental densities over extended ranges of external conditions for the systems 2-propanone + 2,2,4-trimethylpentane and *n*-heptane + ethanol are reported. The data have been used for calculating excess volumes, isothermal compressibilities, and thermal expansion coefficients. In addition ultrasound velocity measurements are reported. These later measurements have been used for calculating isentropic compressibilities. Measured or derived properties are compared with available reliable literature data.

Introduction

Volumetric properties of fluids and their mixtures are important parameters in process design. In addition, they are needed in transforming raw data to useful thermophysical properties, such as dynamic viscosity and surface tension, and in transforming calorimetric measurements at constant pressure to data at constant volume. They are also needed in theoretical calculations, one typical example being the determination of the scaling and interaction parameters in equation-of-state theories (*1*-*3*).

In this series of papers we present consistent sets of experimental volumetric data for a number of representative systems. The first system studied is ethanol + *n*-heptane, whose volumetric properties at atmospheric pressure have been carefully studied besides others, by Benson and collaborators (*4*, *5*). Their data are used for testing in part our experimental setup. The second system studied is acetone (2-propanone) + isooctane (2,2,4-trimethylpentane), whose dynamic viscosity (*6*) and surface tension (*7*) have been measured previously.

Experimental Section

Materials. Pure liquids used in this work were pro analysi grades from Merck. Their purities were determined by gas-liquid chromatography and were better than 99.5. The mixtures were prepared by weight with precision 0.0001 g. 50 mL flasks with septum caps and magnetic stirring bars were used. The vapor space in the flask was initially 2-3 cm^3. Because of the small vapor space and the reproducibility of density measurements, no gas corrections were applied.

Density. The densities, ρ, at atmospheric pressure have been measured in a vibrating tube densitometer, Model DMA 60/602 of Anton Paar. Bidistilled water and air were used as calibrating substances. The densities of higher pressures were measured in equipment described earlier (*8*). It consisted of a high-pressure density cell, Model DMA 512 of Anton Paar, a homemade compression cell equipped with a pressure transducer, Model PDCR 610 of Druck, and a dead-weight tester, Model MTU600 of Metronex. The compression cell consisted of an outer stainless steel cylinder, along the axis of which was located a thin-wall Teflon tube containing the sample. Outside the Teflon tube was the compression fluid—a commercial hydraulic fluid. The equipment was calibrated with accurate experimental high-pressure densities of water (*9*) and methanol (*10*). No hysteresis was observed in the density measurements by increasing and then decreasing the external pressure. The temperature in the measuring cells was regulated through a Haake ultrathermostat and was kept constant to within 0.01 K. For the temperature measurements a precision digital thermometer, Model S 1220 of Systemteknik, with specially designed sensors was used. The estimated error in the density measurement at atmospheric pressure is 5×10^{-6} g cm^{-3}. The corresponding error with the high pressure cell is 1×10^{-4} g cm^{-3}.

Ultrasonic Velocity. The ultrasound velocity was measured in a sing-around equipment, Model RN-1A of DHN. The sing-around method belongs to the methods with a constant acoustic path. The equipment consisted of a stainless steel measuring vessel having the two transducers, type PXE 5 of Philips, the velocimeter RN-1A, and the frequency meter KZ 2026A for measuring the signal frequency f. The measuring vessel was immersed in a Haake thermostat with a temperature stability better than 0.01 K. The resonance frequency of the transducers was 4 MHz. The sound velocity, c, is related to f in the following way:

$$\frac{1}{f} = \frac{L}{c} + \tau \qquad (1)$$

where L is the distance between the transducers and τ is the delay time of the impulse in the circuit. L and τ are vessel constants and were obtained by calibration with 10 standard liquids of accurately known c.

Results and Discussion

The densities of the mixtures *n*-heptane + ethanol and acetone + isooctane have been measured at 30 pressures between 1 and 340 bar. Selected data for 10 pressures are reported in Tables I and II. The complete sets of data are available upon request. In Figure 1 are compared our experimental data for pure ethanol with literature data (*11*). As can be seen, our measurements are in good agreement with literature values. On the basis of the experimental densities, the molar volumes of mixing V^E at each pressure may be calculated from the equation

$$V^E = x_1M_1\left(\frac{1}{\rho} - \frac{1}{\rho_1}\right) + x_2M_2\left(\frac{1}{\rho} - \frac{1}{\rho_2}\right) \qquad (2)$$

where M_i and x_i are the molar mass and the mole fraction, respectively, of component i.

In Figures 2 and 3 are shown the excess volumes (molar volumes of mixing) of the two systems at three representative pressures. Excess volume is diminished with pressure in a similar way for both systems. In the same figures are shown excess volumes at 1 atm measured with the low-pressure

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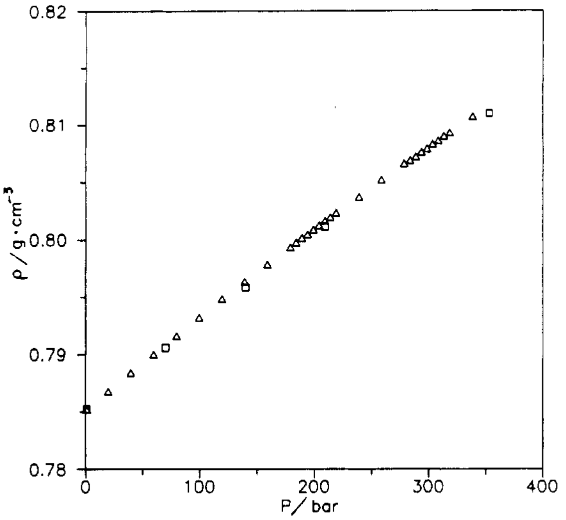

Figure 1. Experimental density ρ of pure ethanol at 298.15 K as a function of pressure P: □, Kubota et al. (*11*); △, this work.

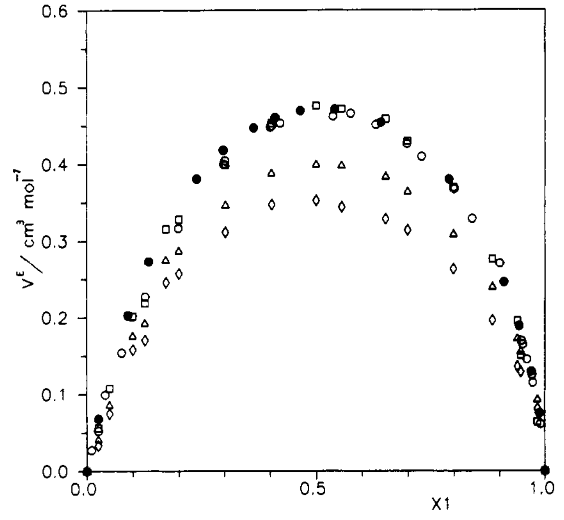

Figure 2. Excess molar volume V^E for the system n-heptane (1) + ethanol (2) at 298.15 K at various pressures P as a function of the mole fraction x_1 of heptane: ●, atmospheric pressure (*4*); ○, P = 1.01 bar with the DMA 602 cell; □, P = 1.01 bar with the DMA 512 cell; △, P = 198.9 bar; ◇, P = 338.1 bar.

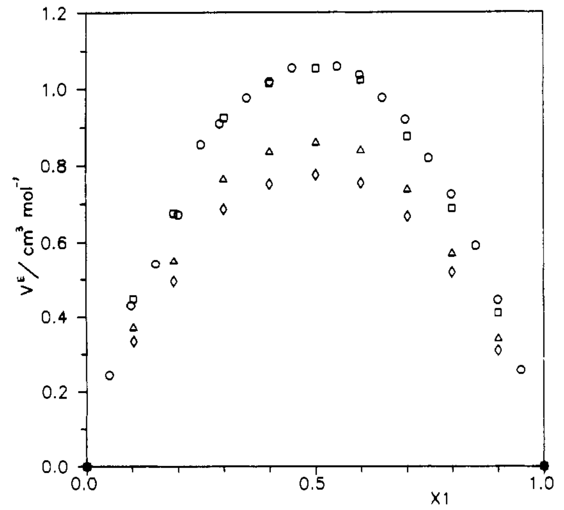

Figure 3. Excess molar volume V^E for the system acetone (1) + isooctane (2) at 298.15 K at various pressures as a function of the mole fraction x_1 of acetone: ○, P = 1.01 bar with bar with the DMA 602 cell; □, P = 1.01 bar with the DMA 512 cell; △, P = 198.9 bar; ◇, P = 338.1 bar.

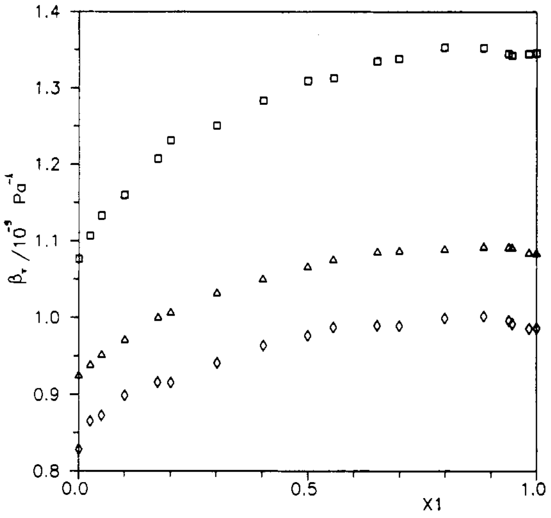

Figure 4. Isothermal compressibility β_T for the system n-heptane (1) + ethanol (2) at 298.15 K at various pressures P as a function of the mole fraction x_1 of heptane: □, P = 1.01 bar; △, P = 198.9 bar; ◇, P = 338.1 bar.

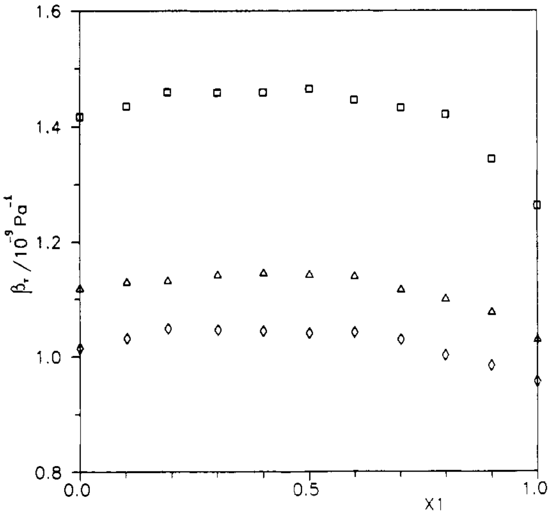

Figure 5. Isothermal compressibility β_T for the system acetone (1) + isooctane (2) at 298.15 K at various pressures P as a function of the mole fraction x_1 of acetone. Symbols as in Figure 4.

density cell, type DMA 602 of Anton Paar. As observed, the two sets of data measured with the two cells are in good agreement. In Figure 2 are also shown excess volumes at atmospheric pressure measured by Benson et al. (*5*). Our measurements are also in good agreement with these latter data.

At each composition the complete set of experimental densities (30 data points) has been used for the determination of the coefficients of the fourth-order polynomial

$$1/(\rho/(\mathrm{g\ cm^{-3}})) = \sum_{i=0}^{4} a_i (P/\mathrm{bar})^i \tag{3}$$

Coefficients a_i of eq 3 along with the standard deviation of fit are reported in Tables III and IV. Equation 3 has subsequently been used for the evaluation of the isothermal compressibilities, β_T, of the mixtures given by

$$\beta_T = \left(\frac{\partial \ln \rho}{\partial P}\right)_T \tag{4}$$

In Figures 4 and 5 are shown isothermal compressibility data

Table I. Experimental Densities ρ for the System Heptane (1) + Ethanol (2) at 298.15 K as a Function of Pressure P and Mole Fraction x_1 of Heptane

	ρ at various P/(g cm^{-3})									
x_1	1.01 bar	20.0 bar	39.9 bar	79.6 bar	119.4 bar	159.1 bar	198.9 bar	258.6 bar	298.3 bar	338.1 bar
0.0000	0.7852	0.7866	0.7884	0.7916	0.7948	0.7978	0.8008	0.8051	0.8079	0.8107
0.0251	0.7781	0.7797	0.7814	0.7846	0.7878	0.7909	0.7939	0.7983	0.8011	0.8039
0.0498	0.7716	0.7732	0.7749	0.7782	0.7814	0.7845	0.7876	0.7919	0.7948	0.7976
0.1002	0.7598	0.7615	0.7632	0.7665	0.7698	0.7729	0.7759	0.7803	0.7832	0.7860
0.1723	0.7458	0.7474	0.7492	0.7526	0.7558	0.7590	0.7620	0.7665	0.7694	0.7722
0.2004	0.7412	0.7429	0.7447	0.7481	0.7513	0.7544	0.7575	0.7620	0.7649	0.7677
0.3017	0.7269	0.7286	0.7303	0.7337	0.7370	0.7402	0.7433	0.7478	0.7507	0.7536
0.4025	0.7154	0.7171	0.7189	0.7224	0.7257	0.7289	0.7320	0.7365	0.7394	0.7423
0.4991	0.7065	0.7083	0.7101	0.7135	0.7169	0.7201	0.7232	0.7277	0.7306	0.7335
0.5551	0.7021	0.7039	0.7056	0.7091	0.7124	0.7156	0.7188	0.7233	0.7262	0.7291
0.6515	0.6955	0.6972	0.6990	0.7025	0.7058	0.7090	0.7121	0.7166	0.7196	0.7224
0.6991	0.6926	0.6944	0.6962	0.6996	0.7029	0.7061	0.7093	0.7138	0.7167	0.7195
0.7985	0.6873	0.6891	0.6909	0.6943	0.6976	0.7008	0.7039	0.7084	0.7113	0.7142
0.8839	0.6835	0.6852	0.6870	0.6905	0.6938	0.6969	0.7000	0.7045	0.7074	0.7102
0.9387	0.6814	0.6831	0.6849	0.6883	0.6916	0.6948	0.6978	0.7023	0.7052	0.7080
0.9464	0.6813	0.6830	0.6847	0.6881	0.6914	0.6945	0.6976	0.7020	0.7049	0.7077
0.9832	0.6801	0.6817	0.6835	0.6869	0.6901	0.6932	0.6963	0.7007	0.7036	0.7064
1.0000	0.6797	0.6814	0.6832	0.6866	0.6899	0.6930	0.6961	0.7005	0.7033	0.7061

Table II. Experimental Densities ρ for the System Acetone (1) + Isooctane (2) at 298.15 K as a Function of Pressure P and Mole Fraction x_1 of Acetone

	ρ at various P/(g cm^{-3})									
x_1	1.01 bar	20.0 bar	39.9 bar	79.6 bar	119.4 bar	159.1 bar	198.9 bar	258.6 bar	298.3 bar	338.1 bar
0.0000	0.6881	0.6899	0.6918	0.6955	0.6989	0.7023	0.7055	0.7101	0.7130	0.7160
0.1028	0.6908	0.6927	0.6946	0.6983	0.7018	0.7052	0.7085	0.7132	0.7162	0.7192
0.1921	0.6942	0.6961	0.6981	0.7019	0.7054	0.7088	0.7121	0.7169	0.7199	0.7229
0.3014	0.6990	0.7009	0.7029	0.7067	0.7103	0.7138	0.7171	0.7219	0.7250	0.7280
0.4012	0.7047	0.7067	0.7087	0.7125	0.7161	0.7197	0.7230	0.7279	0.7310	0.7340
0.5016	0.7117	0.7137	0.7157	0.7196	0.7232	0.7268	0.7302	0.7351	0.7382	0.7413
0.6000	0.7201	0.7221	0.7241	0.7280	0.7317	0.7353	0.7387	0.7436	0.7467	0.7499
0.7015	0.7311	0.7331	0.7351	0.7390	0.7427	0.7462	0.7496	0.7445	0.7576	0.7608
0.7990	0.7442	0.7462	0.7482	0.7521	0.7557	0.7593	0.7627	0.7676	0.7707	0.7739
0.9002	0.7616	0.7635	0.7655	0.7693	0.7729	0.7764	0.7798	0.7848	0.7879	0.7911
1.0000	0.7845	0.7863	0.7883	0.7920	0.7956	0.7990	0.8024	0.8072	0.8103	0.8135

Table III. Coefficients a_i in Equation 3 and Standard Deviation $\sigma(\rho)$ for the System Heptane (1) + Ethanol (2) at 298.15 K at Mole Fraction x_1 of Heptane

x_1	a_0	$a_1/10^{-3}$	$a_2/10^{-7}$	$a_3/10^{-10}$	$a_4/10^{-13}$	$\sigma(\rho)/(10^{-5}$ g cm$^{-3})$
0.0000	1.273 749	−0.137 19	0.689 93	−0.546 42	0.591 05	2
0.0251	1.285 395	−0.142 35	0.652 74		−0.607 70	3
0.0498	1.296 200	−0.147 00	0.798 72	−0.478 13		3
0.1002	1.316 220	−0.152 78	0.870 81	−0.595 94		3
0.1723	1.341 082	−0.162 10	1.083 66	−1.277 02	0.906 11	3
0.2004	1.349 301	−0.166 37	1.346 66	−2.287 72	2.234 37	3
0.3017	1.375 939	−0.172 27	1.115 89	−1.096 43	0.620 03	3
0.4025	1.397 951	−0.179 59	1.146 65	−0.809 50		3
0.4991	1.499 070	−0.185 51	1.209 99	−0.857 30		3
0.5551	1.424 426	−0.187 18	1.192 19	−0.841 13		3
0.6515	1.438 085	−0.192 17	1.371 84	−1.494 42	0.884 4	3
0.6991	1.443 940	−0.193 43	1.403 23	−1.587 94	1.004 87	3
0.7985	1.455 118	−0.197 09	1.461 35	−1.509 94	0.663 43	3
0.8839	1.463 228	−0.198 16	1.517 88	−1.863 30	1.191 05	3
0.9387	1.467 786	−0.197 57	1.340 98	−1.023 37		3
0.9464	1.468 060	−0.195 64	1.341 47	−1.330 09	0.642 66	3
0.9832	1.470 644	−0.194 49	1.293 07	−1.355 86	0.932 93	3
1.0000	1.471 458	−0.198 47	1.362 97	−0.971 59		2

for the two systems at three representative pressures. As can be seen in both systems, the isothermal compressibility is larger than the additively calculated value, the difference decreasing with increasing pressure.

Primary ultrasound velocity measurements are reported in Tables V and VI, along with the isentropic compressibilities calculated by

$$\beta_S = (\rho c^2)^{-1} \tag{5}$$

In Figure 6, our isentropic compressibility data for the system ethanol + *n*-heptane are compared with literature data (*4*). As can be seen, the two sets of data are in good agreement. Consistent sets of isothermal and isentropic compressibility data are useful quantities for the estimation of the ratio of heat capacities at constant pressure and volume by the equation

$$C_P/C_V = \beta_T/\beta_S \tag{6}$$

In Tables VII and VIII are reported experimental densities at atmospheric pressures and for temperatures different from 298.15 K. These data (at three temperatures) are not sufficient for an accurate estimation of the thermal (cubic) expansion

Table IV. Coefficients a_i in Equation 3 and Standard Deviation $\sigma(\rho)$ for the System Acetone (1) + Isooctane (2) at 298.15 K at Mole Fraction x_1 of Acetone

x_1	a_0	$a_1/10^{-3}$	$a_2/10^{-7}$	$a_3/10^{-10}$	$a_4/10^{-13}$	$\sigma(\rho)/(10^{-5}$ g cm$^{-3})$
0.0000	1.453 443	−0.206 25	1.323 04		−1.620 91	2
0.1028	1.447 722	−0.208 07	1.355 59		−1.738 71	3
0.1921	1.440 630	−0.210 48	1.463 05		−2.165 21	3
0.3014	1.430 801	−0.208 89	1.389 73		−1.858 88	3
0.4012	1.419 153	−0.207 23	1.361 86		−1.755 40	3
0.5016	1.405 295	−0.206 07	1.386 23		−1.814 22	3
0.6001	1.388 841	−0.201 00	1.303 37		−1.689 69	3
0.7015	1.367 911	−0.196 26	1.589 15	−1.356 31		3
0.7990	1.343 891	−0.191 17	1.728 53	−2.222 85	1.359 49	3
0.9002	1.313 259	−0.176 67	1.243 25	−0.928 98		3
1.0000	1.274 904	−0.161 03	0.911 89		−1.190 19	2

Table V. Experimental Sound Velocities c and Calculated Isentropic Compressibilities β_S, Equation 5, for the System Heptane (1) + Ethanol (2) at 298.15 K and Atmospheric Pressure as a Function of the Mole Fraction x_1 of Heptane

x_1	$c/(\text{m s}^{-1})$	$\beta_S/(10^{-9}\ \text{Pa}^{-1})$	x_1	$c/(\text{m s}^{-1})$	$\beta_S/(10^{-9}\ \text{Pa}^{-1})$
0.0000	1142.4	0.9757	0.4999	1111.4	1.1448
0.0497	1131.9	1.0111	0.5969	1112.9	1.1548
0.1235	1121.9	1.0519	0.6973	1114.7	1.1623
0.1763	1117.8	1.0745	0.7990	1117.6	1.1662
0.2898	1113.2	1.1093	0.8991	1121.7	1.1642
0.3979	1111.4	1.1307	0.9510	1124.6	1.1599
0.4496	1111.6	1.1384	1.0000	1130.1	1.1525

Table VI. Experimental Sound Velocities c and Calculated Isentropic Compressibilities β_S, Equation 5, for the System Acetone (1) + Isooctane (2) at 298.15 K and Atmospheric Pressure as a Function of the Mole Fraction x_1 of Acetone

x_1	$c/(\text{m s}^{-1})$	$\beta_S/(10^{-9}\ \text{Pa}^{-1})$	x_1	$c/(\text{m s}^{-1})$	$\beta_S/(10^{-9}\ \text{Pa}^{-1})$
0.0000	1081.9	1.2424	0.5485	1078.8	1.2014
0.0498	1078.4	1.2483	0.5974	1082.1	1.1869
0.0981	1075.0	1.2514	0.6477	1086.3	1.1693
0.1524	1072.8	1.2521	0.6974	1091.5	1.1494
0.2018	1072.8	1.2515	0.7482	1097.9	1.1261
0.2514	1072.1	1.2499	0.7975	1105.8	1.09970
0.2924	1072.1	1.2462	0.8512	1116.2	1.0669
0.3508	1072.3	1.2401	0.8994	1127.9	1.0328
0.4016	1073.2	1.2325	0.9497	1142.7	0.9921
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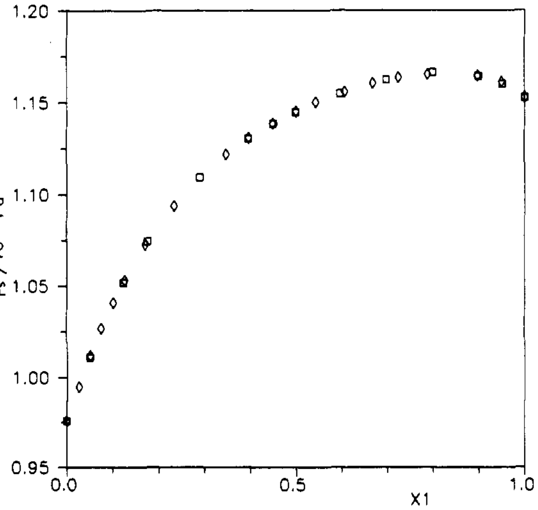

Figure 6. Isentropic compressibility β_S for the system n-heptane (1) + ethanol (2) at 298.15 K at atmospheric pressure as a function of the mole fraction x_1 of heptane: ◇, ref 4; □, this work.

coefficient of the liquids. They may, however, be used for an approximate estimation of it by the equation

$$\alpha = -\rho\left(\frac{\Delta\rho}{\Delta T}\right)_p \tag{7}$$

Table VII. Experimental Densities ρ for the System Heptane (1) + Ethanol (2) at Temperature T and Atmospheric Pressure as a Function of the Mole Fraction x_1 of Heptane

at T = 288.15 K		at T = 308.15 K	
x_1	$\rho/(\text{g cm}^{-3})$	x_1	$\rho/(\text{g cm}^{-3})$
0.0000	0.7937	0.0000	0.7765
0.0491	0.7800	0.0458	0.7637
0.2001	0.7496	0.1221	0.7464
0.3013	0.7354	0.1965	0.7329
0.4012	0.7242	0.2010	0.7321
0.5011	0.7150	0.3013	0.7178
0.6005	0.7074	0.4012	0.7065
0.6994	0.7012	0.5011	0.6973
0.8016	0.6956	0.6005	0.6898
0.9506	0.6894	0.6994	0.6835
1.0000	0.6879	0.8005	0.6783
		0.8016	0.6781
		0.8484	0.6760
		0.8967	0.6740
		0.9564	0.6719
		1.0000	0.6709

Table VIII. Experimental Densities ρ for the System Acetone (1) + Isooctane (2) at 293.15 K and Atmospheric Pressure as a Function of the Mole Fraction x_1 of Acetone

x_1	$\rho/(\text{g cm}^{-3})$	x_1	$\rho/(\text{g cm}^{-3})$
0.0000	0.7901	0.5967	0.7091
0.0493	0.7777	0.6987	0.7032
0.1985	0.7494	0.7985	0.6983
0.2503	0.7419	0.9473	0.6931
0.3977	0.7250	1.0000	0.6917

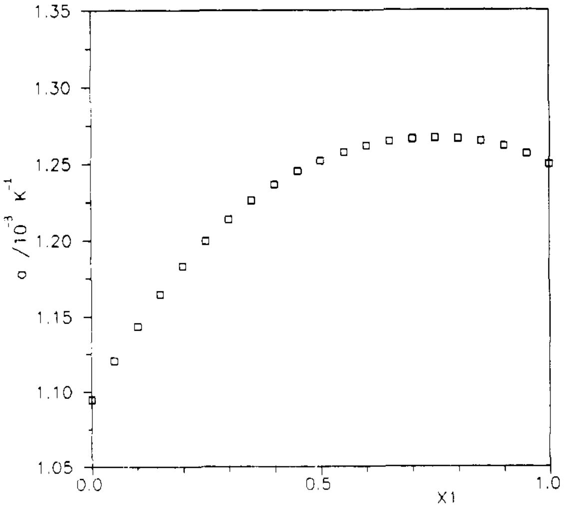

Figure 7. Cubic expansion coefficient α for the system n-heptane (1) + ethanol (2) at 298.15 K and atmospheric pressure as a function of the mole fraction x_1 of heptane.

The density data of the above tables are first fitted to Redlich–Kister polynomials for the necessary interpolations. Cubic expansion coefficients from such calculations are shown in Figure

7 for the system ethanol + *n*-heptane.

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Volumetric Properties of Binary Mixtures. 2. Mixtures of *n*-Hexane with Ethanol and 1-Propanol

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In the second part of this series of papers we report experimental densities for the binary mixtures *n*-hexane + ethanol and *n*-hexane + 1-propanol. The pressure range at 298.15 K is from 1 to 340 bar. At atmospheric pressure the densities have been measured also at 288.15 and 308.15 K. The data have been used for calculating excess volumes, isothermal compressibilities, and thermal expansion coefficients. In addition ultrasound velocity measurements are reported that have been used for calculating isentropic compressibilities.

Introduction

Mixtures of 1-alkanols with *n*-alkanes have attracted particular attention in the thermodynamic literature. IUPAC has already organized five international workshops on the vapor-liquid equilibria and related properties of these systems. New theoretical approaches for data correlation and prediction in alkanol + alkane mixtures are based on equation-of-state theories, which are extended to account for hydrogen bonding and formation of association complexes (*1*-*3*). Volumetric properties of pure components and mixtures are of particular importance in the implementation of these new theoretical approaches. However, as it was pointed out in part 1 of this series of paper (*4*), the usefulness of volumetric properties is not confined to equation-of-state theories.

In the second part of this series of papers we report experimental densities at 298.15 K and in the pressure range from 1 to 340 bar for the mixtures of *n*-hexane with ethanol and 1-propanol. Densities at atmospheric pressure and at two other temperatures are also reported. In addition, ultrasound velocity measurements have been conducted, and the results have been used for calculating isentropic compressibilities.

Experimental Section

Materials. Pure ethanol and *n*-hexane used in this work were pro analysi grades from Merck while 1-propanol was a puriss. grade from Fluka. Their purity was determined by gas-liquid chromatography and was better than 99.8% for ethanol, better than 99.0% for *n*-hexane, and better than 99.5% for 1-propanol. Pure liquids have been used as received without any further purification. The mixtures were prepared by weight with precisions of 0.0001 g. 50 mL flasks with septum caps and magnetic stirring bars were used. The initial vapor space in the flask was less than 3 cm^3. Because of the small vapor space and the reproducibility of density measurements, no gas corrections were applied.

Density. The experimental setup for the density measurements was described previously (*4*). At atmospheric pressure the densities, ρ, have been measured in a vibrating tube densitometer, Model DMA 60/602 of Anton Paar. At higher pressures, a high-pressure density cell was used that consisted of a high-pressure density cell, Model DMA 512 of Anton Paar, a homemade compression cell, and a dead-weight tester, Model MTU600 of Metronex. No hysteresis was observed in the density measurements by increasing and then decreasing the external pressure. The temperature in the measuring cells was regulated through a Haake ultrathermostat and was kept constant to within 0.01 K, as measured by a precision digital thermometer, Model S1220 of Systemteknik. The estimated error in the density measurement at atmospheric pressure is 5×10^{-6} g/cm^3. The corresponding error with the high-pressure cell is 1×10^{-4} g/cm^3.

Ultrasonic Velocity. As previously reported (*4*), the ultrasound velocity was measured in sing-around equipment, Model RN-1A of DHN, at a resonance frequency of 4 MHz. The sound velocity, c, is related to the signal frequency, f, as follows:

$$\frac{1}{f} = \frac{L}{c} + \tau \qquad (1)$$

where L is the distance between the transducers and τ is the delay time of the impulse in the circuit. These are equipment constants.

Results and Discussion

The densities of the binary mixtures at each composition have been measured at 30 pressures between 1 and 340 bar. Selected data for 10 pressures are reported in Tables I and II. The complete sets of data are available upon request. In Figure 1 are compared our experimental data with literature data (*5*). As can be seen, our experimental data are in good agreement with literature values. The sets of data that have been used for calibrating our density cell are those of Kell and Whalley (*6*) for water and those of Machado and Street (*7*) for methanol. On the basis of the experimental densities, we may calculate the molar volume of mixing V^E (excess volume) at each pressure according to eq 2 of the previous paper in this

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