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physical contribution arising from free volume effects.

A new and interesting feature revealed by the experimental results is the temperature dependence of V^E illustrated in Figure 1. Systems with strong positive V^E also show a strong positive temperature dependence, e.g., 1-propanol/nonane. With increasing chain length of the alkanol not only V^E but also its positive temperature dependence decreases and even changes its sign, e.g., in the system 1-dodecanol/nonane at higher mole fractions. This behavior indicates that in those mixtures and concentration ranges where molecular association of the alkanol molecules plays a dominant role, i.e., in case of small alkanols and/or mole fractions, V^E increases with temperature as expected from theoretical considerations (*13*). In cases where the physical or the free volume contribution dominates, i.e., in mixtures of alkanols with higher chain length and at higher mole fractions, V^E decreases with temperature in a similar manner as is often observed for alkane/alkane mixtures with components of different size. In systems such as 1-decanol/nonane and 1-dodecanol/nonane both contributions have an equally weighted influence on the temperature dependence of V^E. While positive V^E values at low alkanol concentrations increase with temperature, negative V^E values at higher concentrations decrease so that the S-shaped character of the $V^E(x)$ curve becomes even more significant at higher temperatures.

Registry No. 1-Hexanol, 111-27-3; 1-octanol, 111-87-5; 1-decanol, 112-30-1; 1-dodecanol, 112-53-8; 1-propanol, 71-23-8; nonane, 111-84-2.

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Received for review December 6, 1965. Accepted June 9, 1986. Financial support of the Max-Buchner-Forschungsstiftung (MBFSt Nr. 1142) is greatly acknowledged.

Excess Volumes of Binary 1-Alkanol/Hexane Mixtures at Temperatures between 283.15 and 323.15 K

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Measurements of V^E for binary mixtures of 1-propanol, 1-butanol, 1-hexanol, 1-octanol, and 1-decanol + hexane are reported. The results have been determined with a vibrating tube densitometer. The accuracy to be possibly achieved with such an apparatus is investigated including corrections for evaporation losses into the vapor space during the preparation of the mixtures.

Introduction

In an earlier paper V^E data of 1-alkanol/nonane mixtures measured at temperatures between 293.15 and 333.15 K have been reported (*1*). The series of experiments is continued in this work and new experimental results of the excess volume V^E of five 1-alkanol/hexane mixtures at temperatures between 283.15 and 323.15 K are presented.

The systematic study of V^E of 1-alkanol/alkane mixtures is of special interest for testing theoretical models which have been developed recently (*2-6*) for describing excess properties of mixtures containing associating components. In the present work special emphasis has been given to the study of the temperature dependence of V^E in 1-alkanol/hexane mixtures. The results make possible a sensitive test for the range of applicability of theoretical models such as the ERAS model (*2-5*).

Experimental Section

Densities of the pure liquids and liquid mixtures have been measured by using a vibrating tube densitometer. This method allows one to determine the density of liquid samples to within $\pm 2 \times 10^{-5}$ g cm^{-3}. The molar excess volume V^E is obtained from densities ρ_1 and ρ_2 of the two pure liquids and from the density ρ_M of the mixture at mole fraction $x_1 = 1 - x_2$ according to the equation

$$V^E = \frac{x_1M_1 + x_2M_2}{\rho_M} - x_1\frac{M_1}{\rho_1} - x_2\frac{M_2}{\rho_2} \qquad (1)$$

where M_1 and M_2 are the molar weights of the two components.

The densitometric method for the determination of V^E has been widely used during the past years. In order to obtain accurate V^E data not only accurate measurements of the densities are required but also very exact knowledge of the mole fraction is necessary. The principal procedure of the

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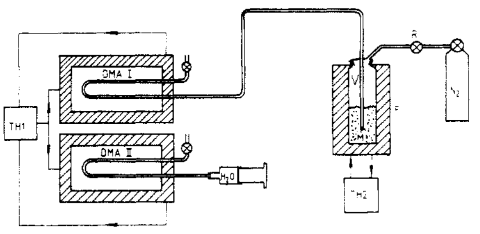

Figure 1. Schematic diagram of the vibrating tube apparatus. TH1, thermostat for temperature control of the measuring cell (DMA I) and the reference cell (DMA II). F, flask filled with liquid mixture M. TH2, thermostat for temperature control of flask F. V, vapor space volume of F. N_2, nitrogen supply with needle valve R. The dashed areas indicate the thermostated water jackets.

Table I. Experimental Densities of 1-Alkanols and Hexane

substance	T/K	ρ/(g cm^{-3}) this work	ρ/(g cm^{-3}) lit
1-propanol	283.15	0.811 45	0.8116 (*8*), 0.81160 (*9*)
	298.15	0.799 63	0.79975 (*8*), 0.79991 (*9*)
	313.15	0.787 46	0.7875 (*8*), 0.78775 (*9*)
1-butanol	283.15	0.817 02	0.8170 (*8*), 0.81729 (*9*)
	298.15	0.805 76	0.8060 (*8*), 0.80583 (*9*)
	313.15	0.794 22	0.7946 (*8*), 0.79412 (*9*)
1-hexanol	288.15	0.822 14	0.8232 (*8*), 0.82259 (*9*)
	298.15	0.815 12	0.8162 (*8*), 0.81565 (*9*)
	308.15	0.807 93	0.8092 (*8*), 0.80853 (*9*)
	323.15	0.796 86	0.7979 (*8*), 0.79752 (*9*)
1-octanol	283.15	0.831 83	0.8327 (*8*), 0.83305 (*9*)
	298.15	0.821 59	0.8223 (*8*), 0.82259 (*9*)
	313.15	0.811 14	0.8117 (*8*), 0.81198 (*9*)
1-decanol	283.15	0.836 51	0.8365 (*8*), 0.83616 (*9*)
	298.15	0.826 40	0.8263 (*8*), 0.82623 (*9*)
	313.15	0.816 11	0.8159 (*8*), 0.81603 (*9*)
hexane	283.15	0.668 38	0.6683 (*10*), 0.66830 (*11*)
	288.15	0.663 80	0.6640 (*10*), 0.66388 (*11*)
	298.15	0.655 08	0.6550 (*10*), 0.65490 (*11*)
	308.15	0.645 86	0.6459 (*10*), 0.64575 (*11*)
	313.15	0.641 36	0.6412 (*10*), 0.64110 (*11*)
	323.15	0.631 82	0.6318 (*10*), 0.63169 (*11*)

densitometric determination of V^E using a vibrating tube has been described elsewhere (*7*). The improved version of the apparatus used previously (*1*) is described here in more detail including the discussion of precautions and corrections which are necessary to obtain correct V^E data.

Two vibrating tubes (DMA I and DMA II) have been used as shown in Figure 1. DMA II is filled with water and serves as a reference for counting the time units on which the determination of the frequency of DMA I is based. DMA I contains the liquid or liquid mixture of unknown density. This reference method has the advantage that temperature fluctuations in the thermostat TH1 are compensated as the liquid of TH1 circulates in parallel flows through the water jackets of both cells as indicated in Figure 1. The accuracy and reproducibility of the measured densities are improved by this device.

In order to obtain absolute values of the density, DMA I has to be calibrated with liquids of accurately known densities. Water, dry air, hexane, and cyclohexane have been used for that purpose. Table I shows the results of the densities for the pure 1-alkanols and hexane compared with data taken from literature (*8*–*11*).

In addition to the accuracy of the measured density an exact determination of the mole fraction is necessary since the excess volume according to eq 1 is determined as the small difference of large numbers and the accuracy of both, the density and the mole fraction, affect the accuracy of the resulting excess volume.

Exact values of the mole fractions are obtained in the following way. The two liquid components 1 and 2 are weighed into a flask F whose temperature is set and controlled at 25 °C by the thermostat TH2 (see Figure 1). After vapor liquid equilibrium has been established the liquid mixture is filled into the vibrating tube of cell DMA I by exerting a slight overpressure of N_2 on the liquid in flask F. The total amounts of components 1 and 2 in F expressed by the mole numbers n_1 and n_2 differ from the mole numbers n_1' and n_2' in the liquid phase because small amounts of component 1 and 2 have been evaporated into the vapor space V of the flask. n_1' and n_2' can be calculated from n_1 and n_2 if P_1^0 and P_2^0, the vapor pressures of the components at 25 °C, the vapor space volume V, and the activity coefficients γ_1 and γ_2 are known. For component 1 it follows with satisfactory accuracy

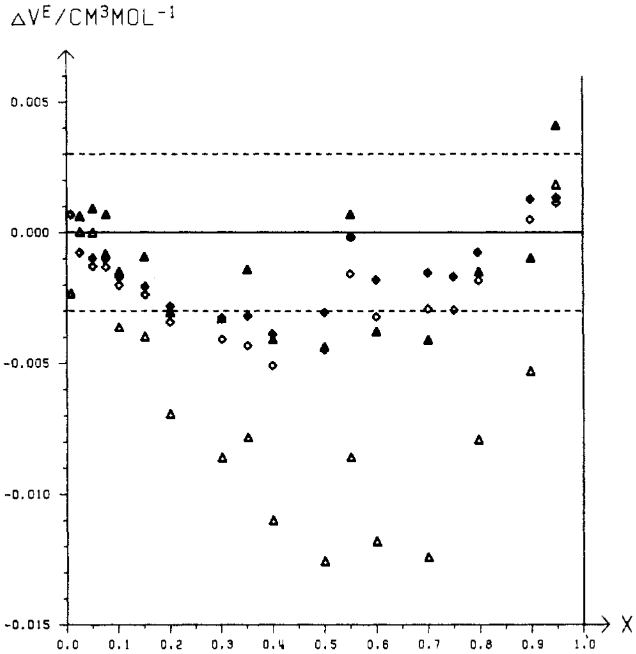

Figure 2. Experimental deviations ΔV^E for 1-hexanol/hexane to data of ref *12*. ◇, ◆ uncorrected and corrected data, respectively, for a vapor space volume V = 17 cm^3. △, ▲ uncorrected and corrected data, respectively, for a vapor space volume V = 67 cm^3. Dashed lines indicate the experimental error limit (±0.003 cm^3 mol^{-1}).

$$n_1' = n_1\left(1 - \frac{P_1^0\gamma_1 V}{n_1 + n_2}\right) \qquad (2)$$

A corresponding equation holds for component 2. $x_1 = 1 - x_2 = n_1'/(n_1' + n_2')$ is the correct mole fraction of the liquid mixture filled into DMA I. Neglecting the correction for the mole fraction can lead to erroneous excess volumes if the vapor space V is large enough and at least one of the components has a considerable vapor pressure. If these quantities are small the corrections may be neglected as has been the case for the 1-alkanol/nonane systems studied in the previous paper of this series (*1*). In the case of 1-alkanol/hexane, however, the experimental conditions require accounting for these corrections since hexane has a distinctly higher vapor pressure than nonane at 25 °C.

Successive measurements have been performed using repeatedly the same sample of liquid mixture in the flask. After each run the vapor space volume V increased. Although one run requires only about 8 mL of the liquid sample, the total increase of V is remarkable after several runs and corrections for the changes of liquid composition due to evaporation are necessary. Calculations according to eq 2 can only be made if the vapor liquid equilibrium has been reestablished after each measurement during a series of successive measurements with the same liquid sample.

As an example Figure 2 illustrates the influence of neglecting the vapor space corrections on V^E for the system 1-hexanol/hexane at 298.15 K. Treszczanowicz and Benson's results

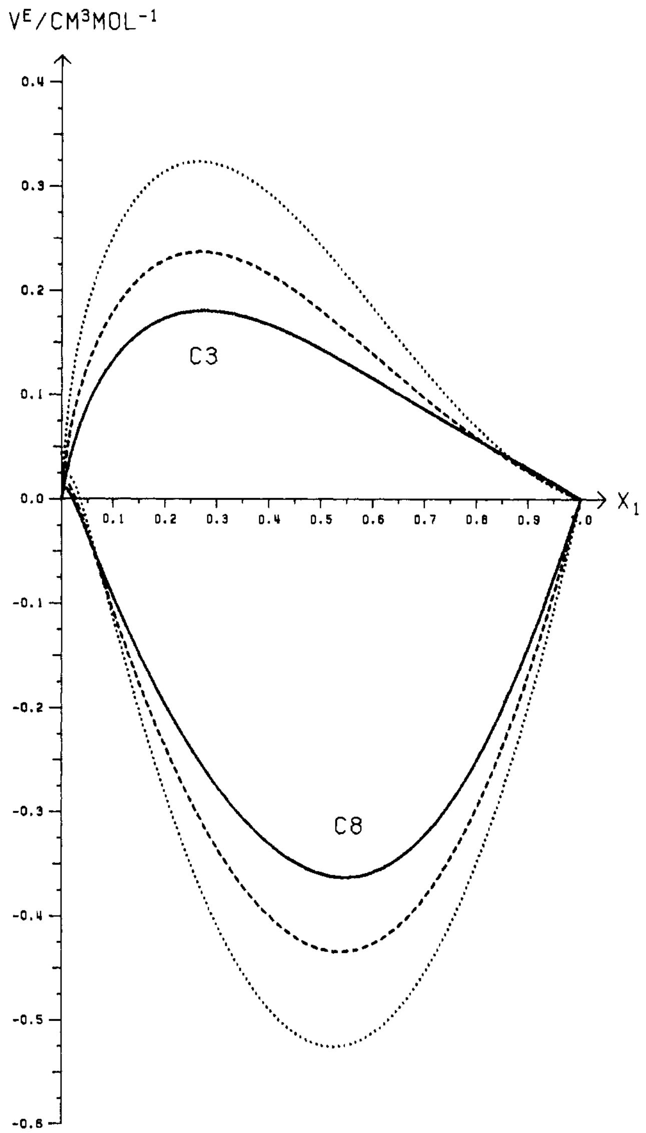

Figure 3. Experimental results of V^E for 1-propanol/hexane (C3) and 1-octanol/hexane (C8) represented by eq 3 with parameters from Table III: — 283.15 K; --- 298.15 K; ··· 313.15 K.

of V^E for this system (*12*) can be regarded as the most reliable data available in the literature and therefore have been used here for comparison. The deviation of corrected and uncorrected data obtained for this system by the method described above clearly show the necessity of vapor space corrections. The calculations have been performed assuming a total volume of 100 cm^3 for the flask and different vapor space volumes V. Two examples are demonstrated. They show the influence of vapor space corrections assuming V = 17 cm^3 and V = 67 cm^3. The results clearly show that only the corrected V^E values obtained by the vibrating tube method agree with Treszczanowicz and Benson's data within the experimental error limits of both sets of data, with the exception of a few measurement points.

All chemicals (Merck) used in the experiments were dried and degassed before use. The purity stated by the supplier was in all cases better than 99%. This was confirmed by chromatographic analysis and by the good agreement of the densities with literature data (see Table I).

Results and Discussion

The experimental results of V^E are listed in Table II for each binary 1-alkanol/hexane system at the temperatures indicated. The error limits of the mole fraction x_1 of 1-alkanol, of the density ρ, and of the excess volume V^E are ±5 × 10^{-4}, ±2 × 10^{-5} g cm^{-3}, and ±0.003 cm^3 mol^{-1}, respectively. In order to represent the experimental V^E data by suitable fitting equations Padé approximants have been used. Each set of V^E data in Table II is represented by

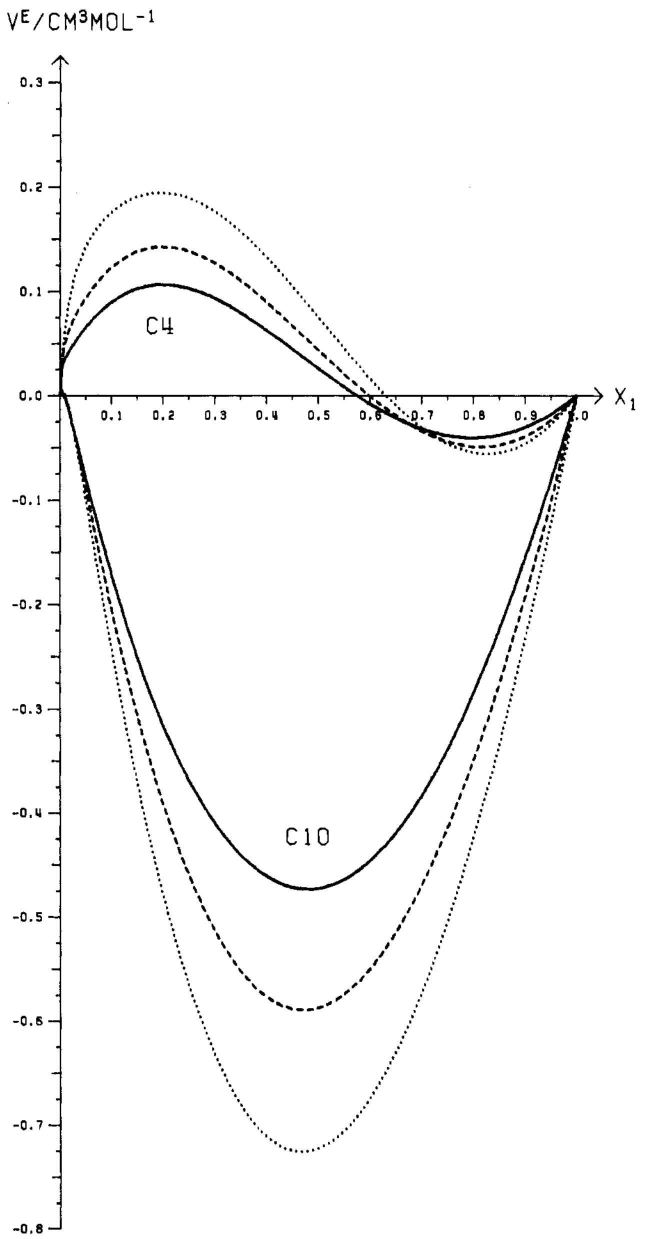

Figure 4. Experimental results of V^E for 1-butanol/hexane (C4) and 1-decanol/hexane (C10) represented by eq 3 with parameters from Table III: — 283.15 K; --- 298.15 K; ··· 313.15 K.

$$V^E = x_1(1 - x_1)\frac{\sum\limits_{i=1}^{n} A_i(2x_1 - 1)^{i-1}}{1 + \sum\limits_{j=1}^{m} B_j(2x_1 - 1)^j} \qquad (3)$$

where A_i and B_j are parameters obtained by a nonlinear least-squares fitting procedure. The parameters A_i and B_j and the standard deviation σ are listed in Table III for each system at the different temperatures indicated. The results for all 1-alkanol/hexane systems are presented graphically in Figures 3–5. The V^E curves are calculated by using eq 3 with parameters from Table III.

The most striking feature of these results is the temperature dependence of V^E. While V^E increases with temperature for systems with positive V^E, decreasing V^E values are observed

Table II. Experimental Excess Volumes V^E of (x_1) 1-Alkanol + (1 - x_1) Hexane Mixtures

T/K	x_1	V^E/(cm^3 mol^{-1})	x_1	V^E/(cm^3 mol^{-1})	x_1	V^E/(cm^3 mol^{-1})
1-Propanol/Hexane						
283.15	0.050 68	+0.0913	0.503 31	+0.1421	0.900 55	+0.0285
	0.102 02	+0.1332	0.602 45	+0.1148	0.925 14	+0.0209
	0.202 05	+0.1750	0.702 25	+0.0849	0.950 20	+0.0145
	0.288 55	+0.1806	0.801 18	+0.0577	0.974 55	+0.0071
	0.408 85	+0.1637	0.850 41	+0.0431		
298.15	0.050 68	+0.1295	0.503 21	+0.1785	0.900 49	+0.0263
	0.102 01	+0.1811	0.602 36	+0.1374	0.925 09	+0.0182
	0.202 02	+0.2304	0.702 15	+0.0964	0.950 16	+0.0114
	0.288 50	+0.2368	0.801 08	+0.0589	0.974 53	+0.0053
	0.408 77	+0.2115	0.850 34	+0.0416		
313.15	0.050 68	+0.1878	0.503 26	+0.2417	0.900 52	+0.0260
	0.102 01	+0.2542	0.602 41	+0.1805	0.925 12	+0.0175
	0.202 03	+0.3157	0.702 20	+0.1221	0.950 18	+0.0112
	0.288 53	+0.3227	0.801 13	+0.0688	0.974 54	+0.0050
	0.408 80	+0.2872	0.850 37	+0.0457		
1-Butanol/Hexane						
283.15	0.020 84	+0.0447	0.301 40	+0.0937	0.699 60	-0.0323
	0.061 75	+0.0729	0.400 62	+0.0620	0.751 53	-0.0387
	0.098 21	+0.0884	0.500 62	+0.0245	0.799 03	-0.0407
	0.151 05	+0.1007	0.550 15	+0.0072	0.849 50	-0.0378
	0.200 83	+0.1066	0.601 42	-0.0085	0.900 41	-0.0309
	0.251 14	+0.1023	0.651 39	-0.0218	0.949 89	-0.0187
298.15	0.020 84	+0.0662	0.301 34	+0.1282	0.699 48	-0.0343
	0.061 74	+0.1032	0.400 53	+0.0919	0.751 43	-0.0458
	0.098 19	+0.1231	0.500 51	+0.0431	0.798 93	-0.0479
	0.151 02	+0.1344	0.550 04	+0.0184	0.849 42	-0.0473
	0.200 79	+0.1422	0.601 30	-0.0014	0.900 33	-0.0379
	0.251 08	+0.1360	0.651 28	-0.0218	0.949 85	-0.0242
313.15	0.020 84	+0.0973	0.301 37	+0.1761	0.699 53	-0.0312
	0.061 74	+0.1523	0.400 57	+0.1331	0.751 48	-0.0470
	0.098 20	+0.1751	0.500 56	+0.0752	0.798 98	-0.0539
	0.151 04	+0.1911	0.550 09	+0.0427	0.849 46	-0.0544
	0.200 81	+0.1953	0.601 35	+0.0147	0.900 37	-0.0459
	0.251 11	+0.1856	0.651 34	-0.0103	0.949 87	-0.0293
1-Hexanol/Hexane						
288.15	0.008 43	+0.0186	0.200 01	-0.0600	0.600 08	-0.2267
	0.025 84	+0.0217	0.301 22	-0.1124	0.700 20	-0.2237
	0.050 15	+0.0146	0.351 72	-0.1370	0.797 48	-0.1859
	0.075 88	+0.0030	0.400 04	-0.1630	0.898 60	-0.1118
	0.101 72	-0.0091	0.500 40	-0.2044	0.948 97	-0.0600
	0.151 29	-0.0335	0.551 22	-0.2161		
298.15	0.008 43	+0.0264	0.199 93	-0.0628	0.599 91	-0.2486
	0.025 83	+0.0331	0.301 12	-0.1242	0.700 03	-0.2452
	0.050 14	+0.0225	0.351 60	-0.1528	0.749 60	-0.2303
	0.075 86	+0.0125	0.399 90	-0.1792	0.797 33	-0.2058
	0.101 68	-0.0025	0.500 23	-0.2236	0.898 50	-0.1237
	0.151 23	-0.0323	0.551 03	-0.2372	0.948 91	-0.0678
308.15	0.008 43	+0.0307	0.199 96	-0.0637	0.599 97	-0.2750
	0.025 83	+0.0471	0.301 15	-0.1348	0.700 09	-0.2700
	0.050 14	+0.0403	0.351 63	-0.1697	0.749 66	-0.2520
	0.075 87	+0.0239	0.399 94	-0.1987	0.797 40	-0.2267
	0.101 70	+0.0090	0.500 28	-0.2476	0.898 54	-0.1374
	0.151 25	-0.0281	0.551 08	-0.2628	0.948 93	-0.0747
323.15	0.008 43	+0.0347	0.199 98	-0.0609	0.600 02	-0.3144
	0.025 84	+0.0743	0.301 19	-0.1485	0.700 15	-0.3080
	0.050 15	+0.0752	0.351 67	-0.1891	0.749 70	-0.2872
	0.075 88	+0.0593	0.399 99	-0.2272	0.797 44	-0.2590
	0.101 71	+0.0334	0.500 33	-0.2821	0.898 57	-0.1577
	0.151 27	-0.0071	0.551 13	-0.2973	0.948 95	-0.0841
1-Octanol/Hexane						
283.15	0.008 54	+0.0107	0.102 63	-0.0989	0.602 44	-0.3588
	0.020 78	+0.0003	0.150 41	-0.1479	0.702 35	-0.3216
	0.035 27	-0.0163	0.202 58	-0.2008	0.801 82	-0.2480
	0.049 85	-0.0340	0.303 09	-0.2779	0.851 03	-0.1982
	0.065 64	-0.0529	0.403 75	-0.3320	0.902 08	-0.1386
	0.080 23	-0.0701	0.502 69	-0.3589	0.949 77	-0.0749
298.15	0.008 53	+0.0159	0.102 60	-0.1110	0.602 33	-0.4264
	0.020 77	+0.0072	0.150 37	-0.1783	0.702 22	-0.3809
	0.035 26	-0.0120	0.202 52	-0.2413	0.801 71	-0.2939
	0.049 84	-0.0335	0.303 01	-0.3382	0.850 92	-0.2350
	0.065 62	-0.0574	0.403 65	-0.4016	0.902 01	-0.1631
	0.080 20	-0.0783	0.502 57	-0.4309	0.949 72	-0.0899

Table II (Continued)

T/K	x_1	V^E/(cm^3 mol^{-1})	x_1	V^E/(cm^3 mol^{-1})	x_1	V^E/(cm^3 mol^{-1})
313.15	0.008 54	+0.0220	0.102 61	−0.1219	0.602 38	−0.5121
	0.020 77	+0.0194	0.150 39	−0.2036	0.702 28	−0.4546
	0.035 26	−0.0004	0.202 55	−0.2883	0.801 77	−0.3485
	0.049 84	−0.0246	0.303 04	−0.4112	0.850 97	−0.2785
	0.065 63	−0.0533	0.403 70	−0.4877	0.902 05	−0.1949
	0.080 22	−0.0798	0.502 63	−0.5235	0.949 75	−0.1048
			1-Decanol/Hexane			
283.15	0.002 90	+0.0032	0.100 76	−0.1730	0.600 79	−0.4447
	0.008 82	−0.0016	0.202 17	−0.3202	0.703 37	−0.3812
	0.013 86	−0.0078	0.300 62	−0.4117	0.801 54	−0.2831
	0.025 32	−0.0315	0.400 75	−0.4610	0.872 35	−0.1921
	0.050 76	−0.0796	0.500 96	−0.4734	0.949 89	−0.0797
298.15	0.002 90	+0.0035	0.100 73	−0.2077	0.600 62	−0.5498
	0.008 82	+0.0027	0.202 11	−0.3978	0.703 22	−0.4664
	0.013 85	−0.0043	0.300 53	−0.5144	0.801 42	−0.3475
	0.025 31	−0.0302	0.400 62	−0.5766	0.872 26	−0.2364
	0.050 75	−0.0904	0.500 82	−0.5867	0.949 85	−0.0996
313.15	0.002 90	+0.0014	0.100 74	−0.2462	0.600 70	−0.6736
	0.008 82	+0.0017	0.202 13	−0.4847	0.703 29	−0.5685
	0.013 85	−0.0024	0.300 57	−0.6354	0.801 48	−0.4217
	0.025 31	−0.0294	0.400 68	−0.7118	0.872 31	−0.2866
	0.050 75	−0.1026	0.500 88	−0.7214	0.949 87	−0.1211

Table III. Values of the Parameters A_i and B_1 according to Eq 3 and Standard Deviation σ for 1-Alkanol/Hexane Mixtures at the Temperatures Indicated

alkanol	T/K	A_1/ (cm^3 mol^{-1})	A_2/ (cm^3 mol^{-1})	A_3/ (cm^3 mol^{-1})	A_4/ (cm^3 mol^{-1})	A_5/ (cm^3 mol^{-1})	B_1	σ/ (cm^3 mol^{-1})
1-propanol	283.15	0.573 122	−0.012 573	−0.145 174	0.172 030		0.910 686	0.0010
1-propanol	298.15	0.720 477	−0.103 642	−0.353 468	0.202 300		0.954 735	0.0009
1-propanol	313.15	0.970 412	−0.192 442	−0.605 063	0.185 239		0.964 288	0.0009
1-butanol	283.15	0.102 410	−0.631 084	−0.482 965	0.193 034		0.998 968	0.0008
1-butanol	298.15	0.172 835	−0.765 655	−0.662 987	0.157 787		0.992 698	0.0018
1-butanol	313.15	0.298 281	−0.917 967	−0.927 073	0.114 912	0.157 561	0.965 009	0.0013
1-hexanol	288.15	−0.812 877	−1.471 873	−0.575 044	0.187 028	0.192 553	0.979 966	0.0010
1-hexanol	298.15	−0.894 288	−1.600 683	−0.608 630	0.123 691	0.148 913	0.980 596	0.0011
1-hexanol	308.15	−0.989 910	−1.747 562	−0.626 135	0.096 577	0.158 290	0.968 358	0.0010
1-hexanol	323.15	−1.137 019	−1.971 785	−0.531 761			0.958 232	0.0038
1-octanol	283.15	−1.437 985	−1.706 463	−0.216 850	0.147 326	0.158 579	0.985 570	0.0010
1-octanol	298.15	−1.726 177	−1.964 283	−0.172 586	0.086 194	0.119 029	0.979 827	0.0009
1-octanol	313.15	−2.095 948	−2.255 809				0.967 738	0.0015
1-decanol	283.15	−1.891 058	−1.699 210	0.142 617	0.072 540	0.158 368	0.980 702	0.0011
1-decanol	298.15	−2.349 391	−2.004 074	0.319 713	−0.086 946		0.978 890	0.0013
1-decanol	313.15	−2.890 307	−2.372 641	0.472 238	−0.125 706		0.962 066	0.0014

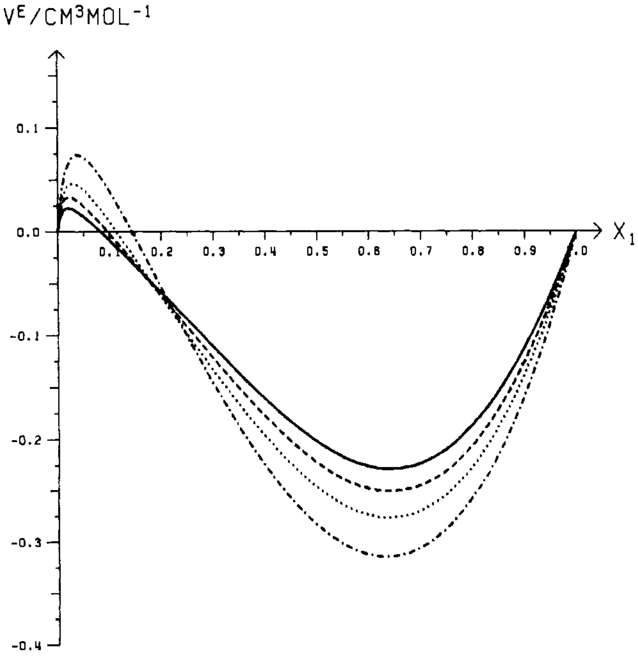

Figure 5. Experimental results of V^E for 1-hexanol/hexane represented by eq 3 with parameters from Table III: — 288.15 K; --- 298.15 K; ··· 308.15 K; -·-·-· 323.15 K.

for systems or concentration ranges where V^E is negative. This behavior has already been observed in 1-alkanol/nonane mixtures (*1*) and appears to be even more significant in 1-alkanol/hexane systems.

The V^E curves of the 1-butanol/hexane and 1-hexanol/hexane systems shown in Figures 4 and 5 suggest the existence of a crossover point where the V^E curves at different temperatures intersect indicating an inversion of their temperature dependence. Since there exist only small positive values of V^E in the diluted region of 1-alkanol this point of temperature inversion is not so clearly revealed in case of 1-octanol/hexane and 1-decanol/hexane. Its existence, however, is suggested from the behavior of the 1-butanol and 1-hexanol systems.

More recently attempts have been made to interpret the general behavior of V^E in 1-alkanol/alkane systems theoretically. The first theoretical approach developed for mixtures containing a self-associating compound is the ERAS model (*2*, *3*). This model combines an association model for chainlike molecules with the free volume theory of Flory and his collaborators (*13*, *14*). Another theoretical approach recently published is the model by Treszczanowicz and Benson (*6*). The ERAS model is able to predict V^E qualitatively in the correct manner provided experimental H^E data have been used for adjusting the binary parameter in the ERAS model. Theoretical results of V^E calculated by this method have already been published in literature for alkanol/alkane systems including 1-alkanol/hexane systems (*3*–*5*).

Registry No. 1-Propanol, 71-23-8; 1-butanol, 71-36-3; 1-hexanol, 111-27-3; 1-octanol, 111-87-5; 1-decanol, 112-30-1; hexene, 110-54-3.

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Received for review December 26, 1985. Accepted June 9, 1986. Financial support of the Max Buchner-Forschungsstiftung (MBFST Nr. 1142) and the Deutsche Forschungsgemeinschaft is greatly acknowledged.

Speed of Sound in and Isothermal Compressibility and Isobaric Expansivity of Pure Liquids at 298.15 K

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The speed of sound u, the isothermal compressibility κ_T, and the isobaric expansivity α have been determined at 298.15 K for several hydrocarbons containing 5, 6, 10, and 12 carbon atoms. Values of the isentropic compressibility κ_S were also calculated from the speed of sound experimental results.

Introduction

The isothermal compressibility $\kappa_T = -V^{-1}(\partial V/\partial p)_T$ and the isobaric expansitivity $\alpha = V^{-1}(\partial V/\partial T)_p$ together with the molar volume V are thermodynamic properties used in recent theories of liquids to calculate the characteristic parameters P^*, V^*, and T^* of pure substances. Currently, Letcher and Baxter (*1*) are studying the Flory theory of mixtures including the substances we measure in this paper, so experimental data of κ_T and α are indispensable. In this work we report results of κ_T, α, and u for several substances containing six carbon atoms and for others including aromatic and nonaromatic rings.

Experimental Section

The solvents 1-hexene and 1-hexyne from Fluka and cyclohexene, cyclopentane, and cyclohexylbenzene from Aldrich were distilled and dried. Bicyclohexyl (EGA Chemic), 1,3-cyclohexadiene (Aldrich), 1,4-cyclohexadiene (Aldrich), and tetralin (BDH) were used without further purification. Their purities, determined by gas liquid chromatography, were 98% for cyclohexylbenzene and 1,4-cyclohexadiene and better than 99% for the other. Experimental densities at 298.15 K were determined with a Paar densimeter and are reported in Table I.

The experimental methods used in measuring κ_T and α (direct piezometric technique), including the piezometer filling, and in measuring u (pulse-echo-overlap method) have been described elsewhere (*2-6*). Values of κ_T and α are obtained with a precision better than 0.2% while the precision of u is better than 0.1 m·s^{-1}.

Results and Discussion

Measurements of isothermal compressibility κ_T, and isobaric expansivity α at 298.15 K were run twice. Table I reports average values of those thermodynamic magnitudes for several hydrocarbons containing 5, 6, 10, and 12 carbon atoms. The speed of sound u has been determined by action of waves of 2.25 MHz on the same substances, and the results obtained are also reported in Table I. In that table are values for the same

Table I. Experimental Results of Pure Liquids at 298.15 K

substance	ρ[a]	κ_T[b]	$10^3\alpha$[c]	u[d]	κ_S[e]
n-hexane	655.04	1669[f]	1.381[j]	1076.78[l]	1316.68
1-hexene	669.01	1689 (1711)[g]	1.414	1066.06 (1065)[m]	1315.24
1-hexyne	729.29	1404	1.371	1132.35 (1140)[m]	1069.40
cyclopentane	737.36	1332 (1331)[h]	1.351 (1.347)[h]	1200.89	940.40
cyclohexane	773.87	1120[i]	1.215[h]	1253.86[l]	821.93
cyclohexene	805.88	1036 (1041)[g]	1.177	1274.44 (1278)[m]	764.00
1,3-cyclohexadiene	841.60	962 (1012)[g]	1.142	1279.03	726.33
1,4-cyclohexadiene	851.03	944 (917)[g]	1.141	1326.40	667.89
benzene	873.69	966[f]	1.218[j]	1299.40[l]	677.78
bicyclohexyl	882.73	674	0.819 (0.784)[k]	1441.51	545.17
cyclohexylbenzene	938.97	627	0.818 (0.753)[k]	1458.11 (1457)[m]	500.92
tetralin	964.55	607	0.824 (0.745)[k]	1469.29 (1466)[m]	480.24

[a] In kg·m^{-3}. [b] In TPa^{-1}. [c] In K^{-1}. [d] In m·s^{-1}. [e] In TPa^{-1}. [f] Reference 4. [g] Reference 8. [h] Reference 7. [i] Reference 9. [j] Reference 10. [k] Reference 1. [l] Reference 6. [m] Reference 11. The other values have been measured in this work.

0021-9568/86/1731-0492$01.50/0