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Excess Volumes of Binary 1-Alkanol/Nonane Mixtures at Temperatures between 293.15 and 333.15 K

Dieter Wagner and Andreas Heintz*

Physikalisch-Chemisches Institut, University of Heidelberg, Im Neuenheimer Feld 253, D-6900 Heidelberg, FRG

Excess volumes V^E of 1-propanol, 1-hexanol, 1-octanol, 1-decanol, and 1-dodecanol + nonane binary mixtures have been measured at 293.15, 298.15, and 333.15 K with a vibrating tube densitometer. The temperature dependence of V^E is discussed qualitatively in terms of a chemical and a physical contribution to V^E. The data can be used to test a quantitative theoretical approach published recently which allows one to describe not only G^E, H^E, and $C_p{}^E$ but also V^E for alkanol/alkane mixtures.

Introduction

Thermodynamic excess properties of alkanol/alkane mixtures have gained large interest during the last years. Since 1984 regular workshop meetings sponsored by the IUPAC have been held annually in order to coordinate research activities in thermodynamics of 1-alkanol/*n*-alkane mixtures.

Systematic studies of the excess Gibbs energy G^E, the excess enthalpy H^E, and the excess volume V^E provide important information for better understanding of the molecular liquid structure and intermolecular interactions predominated by the association of alkanol molecules due to hydrogen bonding. With the exception of mixtures containing methanol and ethanol, only a few systematic data of V^E for higher 1-alkanol/*n*-alkane mixtures existed in literature before 1977 (*1*–*4*). More recently precise measurements of V^E have been performed for quite a number of such mixtures whereby the chain length of the alkanol and/or the alkane has been changed systematically (*5*–*12*). Most of these data, however, have been obtained only at 298.15 K. In this work new data of V^E are presented for mixtures of 1-propanol, 1-hexanol, 1-octanol, 1-decanol, and 1-dodecanol + nonane at different temperatures between 293.15 and 333.15 K. Such data allow one to test sensitively the applicability of theoretical concepts which not only describe G^E and H^E but also V^E. Recently such a theoretical approach has been developed by Heintz (*13*), which combines a free volume model with an association model.

Experimental Section

Excess volumes are measured by using a vibrating tube densitometer. This method has become a widely used technique for measuring densities of liquids and liquid mixtures. V^E data can be determined with a precision comparable with that obtained by using the more conventional dilatometric technique. The principal experimental procedure of measuring V^E by this method has already been described previously (*14*). Water and dry air have been used for calibrating the apparatus and the constancy of the parameters of the vibrating tube has been checked with the liquids hexane and cyclohexane for which the densities are accurately known from literature. In applying this densitometric method for determining V^E special care has to be taken to correct for losses of liquid into the vapor space when the liquid mixtures are prepared by weighing the components into a flask. Since V^E is determined as the small difference of large values of volumes an exact knowledge not only of the density but also of the composition of the mixture is indispensable.

Table I. Experimental Densities of 1-Alkanols and Nonane

		$\rho/(\mathrm{g\ cm^{-3}})$	
substance	T/K	this work	lit.
1-propanol	293.15	0.80378	0.80375 (*16*), 0.80386 (*17*)
	298.15	0.79981	0.79975 (*16*), 0.79991 (*17*)
	333.15	0.77058	0.7704 (*16*), 0.77080 (*17*)
1-hexanol	293.15	0.81890	0.8198 (*16*), 0.81914 (*17*)
	298.15	0.81534	0.8162 (*16*), 0.81565 (*17*)
	333.15	0.78940	0.7903 (*16*), 0.78995 (*17*)
1-octanol	293.15	0.82516	0.8258 (*16*), 0.82610 (*17*)
	298.15	0.82179	0.8223 (*16*), 0.82259 (*17*)
	333.15	0.79694	0.7970 (*16*), 0.79758 (*17*)
1-decanol	293.15	0.82982	0.8297 (*16*), 0.82957 (*17*)
	298.15	0.82644	0.8263 (*16*), 0.82623 (*17*)
	333.15	0.80202	0.8017 (*16*), 0.80203 (*17*)
1-dodecanol	298.15	0.82300	0.8308 (*16*), 0.82995 (*17*)
	333.15	0.80581	0.8063 (*16*), 0.80606 (*17*)
nonane	293.15	0.71793	0.7177 (*18*), 0.71799 (*19*)
	298.15	0.71410	0.7139 (*18*), 0.71412 (*19*)
	333.15	0.68642	0.6864 (*18*), 0.68652 (*19*)

The nonane mixtures containing the alkanols studied in this work are prepared at 25 °C. Since the components have sufficiently low vapor pressures at this temperature the corrections for losses into the vapor space are negligible compared with other experimental error sources which influence the accuracy of V^E. Therefore the procedure of correcting for the effect of evaporation on the liquid composition is discussed in more detail in a forthcoming paper (*15*) which deals with 1-alkanol/hexane mixtures where these effects play a much more dominant role.

The accuracy of the V^E measurements depends on the error limits of the densities of the liquid samples and their composition. The accuracy of the measured densities is essentially determined by the constancy of the temperature in the cell which contains the vibrating tube. In order to minimize the influence of fluctuations in temperature a special method has been applied by using a second cell which serves as a reference cell. Cell 1 contains the mixture under study and cell 2 is filled with water. The frequency of cell 1 is determined electronically by using the frequency of cell 2 as the basis for

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Table II. Experimental Excess Volumes V^E of (x) 1-Alkanol + (1 − x) Nonane Mixtures

T/K	x	V^E/(cm^3 mol^{-1})	x	V^E/(cm^3 mol^{-1})	x	V^E/(cm^3 mol^{-1})
			1-Propanol/Nonane			
293.15	0.081 39	+0.1925	0.394 12	+0.3765	0.730 15	+0.2963
	0.136 53	+0.2601	0.465 35	+0.3775	0.803 13	+0.2456
	0.198 85	+0.3099	0.525 67	+0.3683	0.866 08	+0.1875
	0.268 07	+0.3450	0.601 54	+0.3521	0.932 16	+0.1142
	0.336 59	+0.3677	0.663 18	+0.3283		
298.15	0.081 39	+0.2145	0.394 12	+0.4090	0.730 15	+0.3166
	0.081 39	+0.2103	0.394 12	+0.4100	0.730 15	+0.3136
	0.136 53	+0.2825	0.465 35	+0.4091	0.803 13	+0.2630
	0.136 53	+0.2836	0.465 35	+0.4103	0.803 13	+0.2589
	0.198 85	+0.3388	0.525 67	+0.3985	0.866 08	+0.1998
	0.198 85	+0.3348	0.525 67	+0.3997	0.866 08	+0.2011
	0.268 07	+0.3775	0.601 54	+0.3782	0.932 16	+0.1216
	0.268 07	+0.3758	0.601 54	+0.3785	0.932 16	+0.1182
	0.336 59	+0.3992	0.663 18	+0.3517		
	0.336 59	+0.4030	0.663 18	+0.3521		
333.15	0.081 39	+0.4243	0.394 12	+0.7563	0.730 15	+0.5366
	0.136 53	+0.5558	0.465 35	+0.7440	0.803 13	+0.4308
	0.198 85	+0.6410	0.525 67	+0.7228	0.866 08	+0.3222
	0.268 07	+0.7100	0.601 54	+0.6717	0.932 16	+0.1785
	0.336 59	+0.7451	0.663 18	+0.6149		
			1-Hexanol/Nonane			
293.15	0.069 69	+0.1096	0.397 90	+0.1777	0.731 64	+0.0728
	0.133 12	+0.1390	0.464 12	+0.1668	0.799 10	+0.0487
	0.193 35	+0.1617	0.530 31	+0.1493	0.867 49	+0.0281
	0.264 22	+0.1768	0.598 37	+0.1269	0.932 42	+0.0127
	0.329 48	+0.1811	0.665 59	+0.0998		
298.15	0.069 69	+0.1170	0.397 90	+0.1933	0.731 64	+0.0830
	0.069 69	+0.1166	0.397 90	+0.1931	0.731 64	+0.0821
	0.133 12	+0.1567	0.464 12	+0.1832	0.799 10	+0.0566
	0.133 12	+0.1528	0.464 12	+0.1818	0.799 10	+0.0566
	0.193 35	+0.1762	0.530 31	+0.1643	0.867 49	+0.0333
	0.193 35	+0.1769	0.530 31	+0.1641	0.867 49	+0.0329
	0.264 22	+0.1913	0.598 37	+0.1394	0.932 42	+0.0153
	0.264 22	+0.1933	0.598 37	+0.1368	0.932 42	+0.0162
	0.329 48	+0.1970	0.665 59	+0.1118		
	0.329 48	+0.1962	0.665 59	+0.1102		
333.15	0.069 69	+0.2623	0.397 90	+0.3764	0.731 64	+0.1941
	0.133 12	+0.3328	0.464 12	+0.3550	0.799 10	+0.1406
	0.193 35	+0.3657	0.530 31	+0.3286	0.867 49	+0.0870
	0.264 22	+0.3847	0.598 37	+0.2883	0.932 42	+0.0442
	0.329 48	+0.3869	0.665 59	+0.2420		
			1-Octanol/Nonane			
293.15	0.070 20	+0.0837	0.400 13	+0.0647	0.742 45	−0.0230
	0.138 39	+0.0896	0.469 60	+0.0452	0.798 45	−0.0301
	0.191 61	+0.0867	0.537 43	+0.0266	0.864 58	−0.0307
	0.264 77	+0.0816	0.601 50	+0.0130	0.928 50	−0.0215
	0.332 65	+0.0789	0.667 67	−0.0095		
298.15	0.070 20	+0.0851	0.400 13	+0.0622	0.742 45	−0.0227
	0.070 20	+0.0834	0.400 13	+0.0558	0.742 45	−0.0293
	0.138 39	+0.0912	0.469 60	+0.0459	0.798 45	−0.0277
	0.138 39	+0.0900	0.469 60	+0.0421	0.798 45	−0.0370
	0.191 61	+0.0890	0.537 43	+0.0278	0.864 58	−0.0274
	0.191 61	+0.0876	0.537 43	+0.0246	0.864 58	−0.0358
	0.264 77	+0.0834	0.601 50	+0.0114	0.928 50	−0.0193
	0.264 77	+0.0789	0.601 50	+0.0047	0.928 50	−0.0208
	0.332 65	+0.0774	0.667 67	−0.0055		
	0.332 65	+0.0649	0.667 67	−0.0134		
333.15	0.069 65	+0.1992	0.335 61	+0.1859	0.667 67	+0.0338
	0.070 20	+0.1973	0.399 18	+0.1584	0.669 14	+0.0522
	0.070 20	+0.1932	0.400 13	+0.1528	0.742 45	+0.0142
	0.133 44	+0.2195	0.400 13	+0.1537	0.742 45	+0.0100
	0.138 39	+0.2201	0.468 18	+0.1299	0.742 63	+0.0178
	0.138 39	+0.2174	0.469 60	+0.1261	0.798 45	−0.0007
	0.191 61	+0.2186	0.469 60	+0.1257	0.798 45	−0.0045
	0.191 61	+0.2155	0.535 10	+0.1006	0.800 02	+0.0090
	0.202 28	+0.2245	0.537 43	+0.0996	0.860 71	−0.0088
	0.264 77	+0.2026	0.537 43	+0.0996	0.864 58	−0.0104
	0.264 77	+0.1944	0.600 81	+0.0716	0.864 58	−0.0165
	0.267 87	+0.2023	0.601 50	+0.0706	0.928 28	−0.0073
	0.332 65	+0.1839	0.601 50	+0.0675	0.928 50	−0.0093
	0.332 65	+0.1818	0.667 67	+0.0402	0.928 50	−0.0050
			1-Decanol/Nonane			
293.15	0.022 56	+0.0442	0.106 32	+0.0298	0.530 58	−0.0776
	0.033 42	+0.0439	0.126 17	+0.0243	0.598 84	−0.0866

Table II (Continued)

T/K	x	V^E/(cm^3 mol^{-1})	x	V^E/(cm^3 mol^{-1})	x	V^E/(cm^3 mol^{-1})
	0.039 59	+0.0451	0.128 82	+0.0207	0.664 94	−0.0911
	0.047 78	+0.0436	0.151 81	+0.0164	0.732 23	−0.0877
	0.058 87	+0.0414	0.200 26	−0.0004	0.796 26	−0.0803
	0.067 45	+0.0363	0.263 23	−0.0187	0.861 85	−0.0658
	0.070 99	+0.0402	0.331 54	−0.0347	0.929 61	−0.0390
	0.077 30	+0.0379	0.398 46	−0.0514		
	0.088 09	+0.0344	0.464 35	−0.0650		
298.15	0.022 56	+0.0489	0.088 09	+0.0413	0.464 35	−0.0651
	0.022 56	+0.0492	0.106 32	+0.0413	0.464 35	−0.0701
	0.033 42	+0.0468	0.106 32	+0.0360	0.530 58	−0.0802
	0.033 42	+0.0486	0.126 17	+0.0317	0.530 58	−0.0834
	0.039 59	+0.0512	0.126 17	+0.0306	0.598 84	−0.0869
	0.039 59	+0.0504	0.128 82	+0.0307	0.598 84	−0.0947
	0.047 78	+0.0522	0.128 82	+0.0265	0.664 94	−0.0911
	0.047 78	+0.0504	0.151 81	+0.0236	0.664 94	−0.0966
	0.058 87	+0.0487	0.151 81	+0.0206	0.732 23	−0.0891
	0.058 87	+0.0492	0.200 26	+0.0078	0.732 23	−0.0918
	0.067 45	+0,0455	0.200 26	+0.0055	0.796 26	−0.0818
	0.067 45	+0.0450	0.263 23	−0.0133	0.796 26	−0.0844
	0.070 99	+0.0474	0.263 23	−0.0159	0.861 85	−0.0655
	0.070 99	+0.0466	0.331 54	−0.0309	0.861 85	−0.0699
	0.077 30	+0.0461	0.331 54	−0.0350	0.929 61	−0.0392
	0.077 30	+0.0442	0.398 46	−0.0495	0.929 61	−0.0394
	0.088 09	+0.0442	0.398 46	−0.0540		
333.15	0.022 56	+0.0931	0.106 32	+0.1327	0.530 58	−0.0800
	0.033 42	+0.1139	0.126 17	+0.1252	0.598 84	−0.0957
	0.039 59	+0.1242	0.128 82	+0.1226	0.664 94	−0.1030
	0.047 78	+0.1325	0.151 81	+0.1120	0.732 23	−0.1058
	0.058 87	+0.1372	0.200 26	+0.0859	0.796 26	−0.0982
	0.067 45	+0.1358	0.263 23	+0.0476	0.861 85	−0.0765
	0.070 99	+0.1409	0.331 54	+0.0078	0.929 61	−0.0451
	0.077 30	+0.1411	0.398 46	−0.0264		
	0.088 09	+0.1381	0.464 35	−0.0576		
			1-Dodecanol/Nonane			
298.15	0.010 73	+0.0256	0.084 74	+0.0076	0.465 80	−0.1482
	0.010 73	+0.0298	0.105 29	−0.0059	0.465 80	−0.1551
	0.022 99	+0.0312	0.105 29	−0.0019	0.534 23	−0.1547
	0.022 99	+0.0359	0.127 52	−0.0174	0.534 23	−0.1585
	0.030 40	+0.0311	0.127 52	−0.0192	0.602 84	−0.1541
	0.030 40	+0.0336	0.131 15	−0.0278	0.602 84	−0.1582
	0.041 61	+0.0269	0.131 15	−0.0277	0.665 77	−0.1482
	0.041 61	+0.0299	0.150 62	−0.0305	0.665 77	−0.1522
	0.051 11	+0.0220	0.150 62	−0.0310	0.733 64	−0.1335
	0.051 11	+0.0252	0.193 84	−0.0611	0.733 64	−0.1409
	0.058 98	+0.0201	0.193 84	−0.0617	0.797 35	−0.1126
	0.058 98	+0.0238	0.264 65	−0.0955	0.797 35	−0.1166
	0.063 68	+0.0182	0.264 65	−0.0987	0.860 39	−0.0872
	0.063 68	+0.0193	0.334 98	−0.1266	0.860 39	−0.0873
	0.065 62	+0.0176	0.334 98	−0.1349	0.931 74	−0.0442
	0.065 62	+0.0202	0.394 88	−0.1360	0.931 74	−0.0481
	0.084 74	+0.0054	0.394 88	−0.1438		
333.15	0.010 73	+0.0435	0.105 29	+0.0599	0.534 23	−0.2251
	0.022 99	+0.0711	0.127 52	+0.0399	0.602 84	−0.2238
	0.030 40	+0.0833	0.131 15	+0.0282	0.665 77	−0.2101
	0.041 61	+0.0918	0.150 62	+0.0143	0.733 64	−0.1860
	0.051 11	+0.0900	0.193 84	−0.0324	0.797 35	−0.1542
	0.058 98	+0.0886	0.264 65	−0.0953	0.860 39	−0.1153
	0.063 68	+0.0832	0.334 98	−0.1502	0.931 74	−0.0590
	0.065 62	+0.0877	0.394 88	−0.1799		
	0.084 74	+0.0734	0.465 80	−0.2088		

counting the time units of cell 1. The temperature of the cells is set and controlled by a thermostat. The circulating liquid of the thermostat is divided in parallel currents when it passes the water jackets of the two cells. This device allows elimination of long time fluctuations of temperature generated by changes of room temperature during a day and improves the accuracy and reproducibility of the measured densities. The error limit of the density $\Delta\rho$ is estimated to be $\pm 2 \times 10^{-5}$ g cm^{-3}. The accuracy of the mole fraction depends on the uncertainty of the weights of the liquids in the flask where the mixtures are prepared. The experimental error limit of the mole fraction Δx is $\pm 3 \times 10^{-5}$ provided corrections for losses by evaporation can be neglected as discussed above.

According to Gauss's law of error propagation the error limit of the excess volume ΔV^E is ± 0.003 cm^3 mol^{-1} at 293.15 and 298.15 K and ± 0.005 cm^3 mol^{-1} at 333.15 K. The densities of the pure components measured in this work are given in Table I including reliable literature data for comparison (*16–19*).

The chemicals (Merck) used in the experiments were dried and degassed before use. The purities are in all cases better than 99% with the exception of 1-dodecanol (>98%).

Results

The experimental results of V^E are listed in Table II for all 1-alkanol/nonane systems at the temperatures indicated. Each

Table III. Values of the Parameters A_i and B_j according to Eq 1 and Standard Deviation σ for 1-Alkanol/Nonane 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})	B_1	B_2	B_3	σ/(cm^3 mol^{-1})
1-propanol	293.15	1.496 065	−0.138 869	−0.371 555	0.068 590	−0.595 770		0.0013
1-propanol	298.15	1.620 991	−0.266 999	−0.536 377	0.018 579	−0.663 543		0.0018
1-propanol	333.15	2.936 690	−0.628 891	−1.151 795	0.059 440	−0.687 996		0.0025
1-hexanol	293.15	0.636 004			0.878 484	0.978 697	0.923 501	0.0014
1-hexanol	298.15	0.692 614			0.840 595	0.815 871	0.778 047	0.0010
1-hexanol	333.15	1.368 810			0.665 445	0.218 764	0.393 512	0.0013
1-octanol	293.15	0.157 751	−0.560 991		−0.289 931	−0.275 736	0.850 499	0.0027
1-octanol	298.15	0.144 182	−0.548 421		−0.247 318	−0.314 894	0.793 066	0.0035
1-octanol	333.15	0.458 221	−0.761 608		0.269 751	−0.237 401	0.351 964	0.0043
1-decanol	293.15	−0.290 464	−0.488 092		0.537 972	−0.435 221		0.0013
1-decanol	298.15	−0.300 682	−0.534 858		0.572 096	−0.388 633		0.0022
1-decanol	333.15	−0.279 579	−0.906 260		0.743 223	−0.170 198		0.0016
1-dodecanol	298.15	−0.634 882	−0.782 833		0.969 383			0.0035
1-dodecanol	333.15	−0.869 643	−1.292 358		1.084 149	0.161 384		0.0024

set of results has been fitted to a Padé (n,m) approximant according to the following equation for V^E

$$V^E = x(1-x)\frac{\sum_{i=1}^{n} A_i(2x-1)^{i-1}}{1+\sum_{j=1}^{m} B_j(2x-1)^j} \qquad (1)$$

x in eq 1 is the mole fraction of the alkanol. A_i and B_j are parameters obtained by a nonlinear least-squares fitting procedure. Parameters A_i and B_j together with the standard deviation σ are listed for each set of V^E data in Table III. Special care has been taken to ensure that no singularities appear in eq 1 for values of x within the range of 0–1. Rational functions such as Padé approximants have turned out to be superior to polynomials in fitting experimental data (*20*) and have already been used successfully for describing thermodynamic excess properties (*21*, *22*). V^E data presented here show a strongly asymmetric dependence on mole fraction x. Considerably less adjustable parameters are necessary for representing these data within the experimental error limits with eq 1 instead of, e.g., Redlich–Kister polynomials.

Discussion

The results for the 1-alkanol/nonane systems are presented graphically at 298.15 and 333.15 K in Figure 1 which illustrates the general behavior of V^E with increasing chain length of the alkanol. While the V^E values of 1-propanol/nonane and 1-hexanol/nonane are positive over the whole range of composition the 1-octanol/nonane mixture shows an S-shaped concentration dependence with positive V^E values at lower alkanol mole fractions and negative values at higher mole fractions. In the case of the 1-decanol and 1-dodecanol systems negative values of V^E for a wide range of mole fraction are observed. Only at very low alkanol mole fractions V^E has small positive values. Treszczanowicz and Benson (*6–8*) have pointed out that this general behavior can be interpreted by assuming two essential contributions to V^E, one arising from the association of the alkanol molecules which is positive, and another one which is negative and has its origin in the change of free volume upon mixing. It depends on the chain length of the alkanols which contribution prevails.

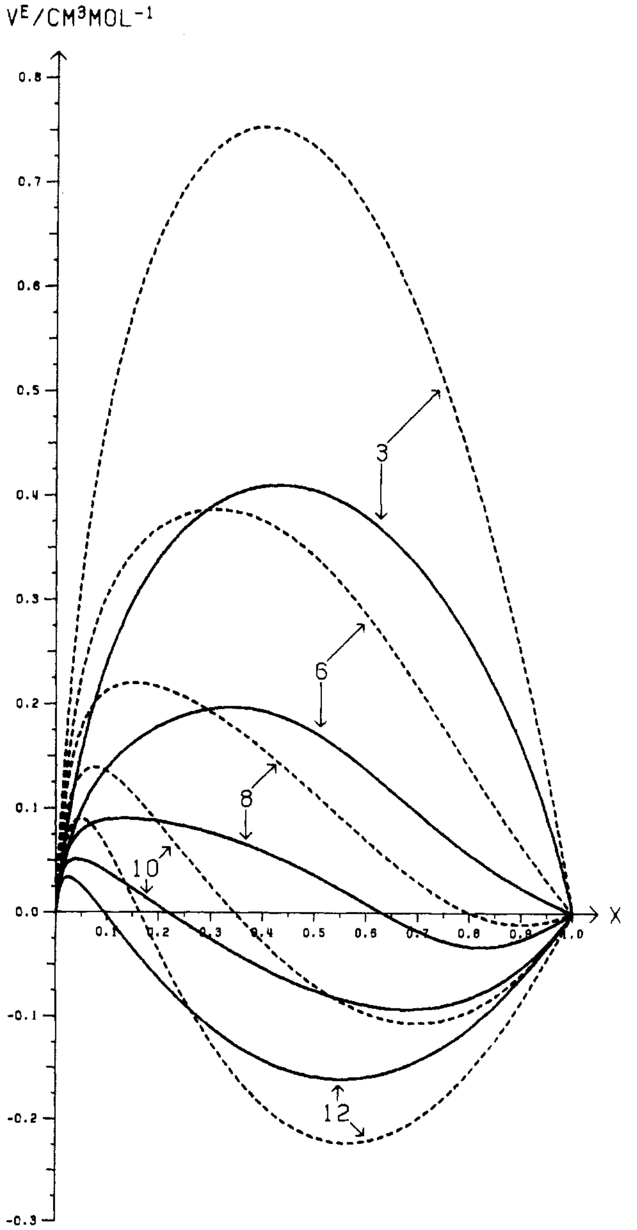

Figure 1. V^E as function of mole fraction x (alkanol) for 1-alkanol/nonane mixtures according to eq 1 with parameters from Table III. — data at 298.15 K; --- data at 333.15 K. (The numbers indicate the alkanol molecule corresponding to its number of C atoms.)

From these considerations it is obvious that a quantitative explanation of the mixing properties can be given by combining an association model which accounts for a positive reaction energy and reaction volume of hydrogen bonding with a suitable free volume theory of chainlike molecules, e.g., the Flory–Prigogine theory. Such a theoretical approach has been developed by Heintz (*13*). It describes successfully not only G^E and H^E but also V^E of alkanol/alkane mixtures (*23*, *24*). It turns out that V^E can be split into a chemical contribution due to hydrogen bonding containing the reaction volume Δv^* and a 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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Excess Volumes of Binary 1-Alkanol/Hexane Mixtures at Temperatures between 283.15 and 323.15 K

Andreas Heintz,* Bernd Schmittecker, Dieter Wagner, and Rüdiger N. Lichtenthaler
Physikalisch-Chemisches Institut, University of Heidelberg, Im Neuenheimer Feld 253, D-6900 Heidelberg, FRG

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 ±2 × 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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