

Excess Volumes of Binary Mixtures of Tetralin with *n*-Alkanes from 293.15 to 313.15 K

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Excess volumes V^E for binary mixtures of tetralin with hexane, heptane, octane, nonane, and decane have been determined from density measurements at temperatures from 293.15 to 313.15 K. V^E is negative over the whole composition range and becomes more negative with an increase in temperature. At each temperature, V^E increases as the carbon number of the *n*-alkane decreases. The cubic expansion coefficients of tetralin and *n*-alkanes are also reported.

Introduction

Excess volumes V^E of binary mixtures containing one compound with an *n*-alkane have been measured by many researchers (1-5). However, literature data on excess volumes of binary mixtures containing a two-ring hydrocarbon are relatively limited. The excess volumes and excess enthalpies of bicyclohexyl, decalin, and tetralin in *n*-alkanes have been studied by Letcher et al. (6-11). In a previous paper (12) we reported excess volumes of tetralin + hexane at 298.15 and 308.15 K. Here excess volumes of tetralin with an *n*-alkane (C₆-C₁₀) were investigated at atmospheric pressure (nominal value 0.1 MPa) from 293.15 to 313.15 K over the entire range of composition.

Experimental Section

Materials. Hexane, heptane, octane (better than 99.5 mol %), and nonane (better than 99 mol %) were from Fluka. Tetralin and decane (better than 99 mol %) were from Aldrich and Merck, respectively. All the substances were used without further purification. Density values of the components used here are compared with those reported in the literature (13, 14) in Table 1.

Measurements. Mixtures were prepared on a mass basis using a Simadzu analytical balance (model AEG-120), and mole fractions x were calculated with an uncertainty of less than 0.0001. Densities were measured by use of a vibrating-tube densimeter (Anton Paar DMA 60/602 H) with a precision of $\pm 1.5 \times 10^{-6}$ g cm⁻³. The measuring cell of the apparatus was thermostated with a Haake F3-K thermostat bath to within 0.01 K. The densimeter was calibrated with redistilled degassed water and dry air at atmospheric pressure. The accuracy of the density is estimated to be $\pm 1 \times 10^{-5}$ g cm⁻³. The excess molar volumes V^E were calculated from the density measurements. The estimated uncertainty in V^E is less than 0.003 cm³ mol⁻¹.

Results and Discussion

The technique was checked by determining V^E for benzene + cyclohexane at 298.15 K; our results are in good agreement (better than 0.005 V^E) with literature values (15). The excess volumes obtained from the density measurements are given in Table 2 and graphically pre-

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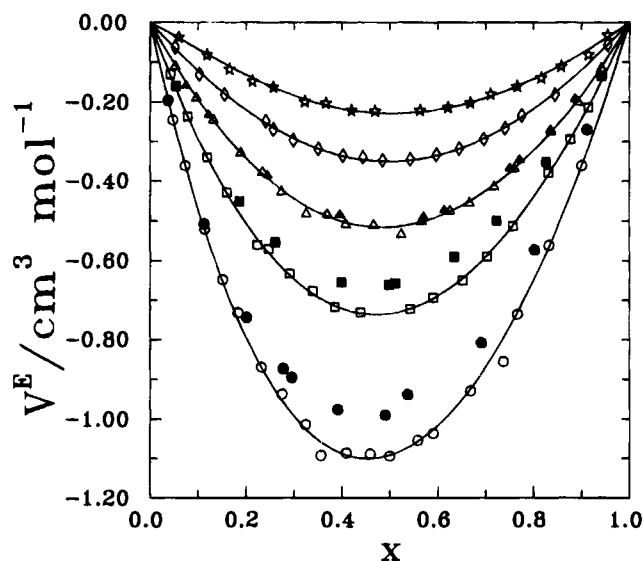


Figure 1. Excess molar volumes V^E (1 - x) *n*-alkane + x tetralin at 298.15 K: (○) hexane, present study, (●) ref 6; (□) heptane, present study, (■) ref 6; (△) octane, present study, (▲) ref 6; (◇) nonane; (☆) decane; (—) calculated from eq 1.

sented in Figure 1 at 298.15 K. The V^E data were fitted to the Redlich-Kister expansion (16)

$$V^E/(\text{cm}^3 \text{mol}^{-1}) = x(1-x)[a_0 + a_1(2x-1) + a_2(2x-1)^2 + a_3(2x-1)^3] \quad (1)$$

where a_0, a_1 , etc. are adjustable parameters and x is the mole fraction of tetralin. The values of the parameters, calculated by the least-squares method with all points weighted equally, are listed in Table 3 together with the standard deviation $\sigma(V^E)$:

$$\sigma(V^E) = [\sum (V_{\text{expt}}^E - V_{\text{calcd}}^E)^2 / (n - p)]^{1/2} \quad (2)$$

where n is the number of measurements and p is the number of parameters. Curves calculated from eq 1 are also shown in Figure 1.

Figure 1 shows that excess volumes are negative for *n*-alkanes at 298.15 K over the whole range of composition and excess volumes of this work are smaller than that measured by Letcher and Scoones (6). Table 2 indicates that the temperature coefficients $(\partial V^E / \partial T)_{P,x}$ are negative

Table 2 (Continued)

293.15 K		298.15 K		303.15 K		308.15 K		313.15 K	
<i>x</i>	$V^E/(\text{cm}^3 \text{mol}^{-1})$	<i>x</i>	$V^E/(\text{cm}^3 \text{mol}^{-1})$	<i>x</i>	$V^E/(\text{cm}^3 \text{mol}^{-1})$	<i>x</i>	$V^E/(\text{cm}^3 \text{mol}^{-1})$	<i>x</i>	$V^E/(\text{cm}^3 \text{mol}^{-1})$
Tetralin + Nonane									
0.0520	-0.064	0.0522	-0.062	0.0506	-0.065	0.0568	-0.081	0.0557	-0.085
0.0989	-0.119	0.1031	-0.131	0.1029	-0.134	0.1104	-0.156	0.1057	-0.152
0.1499	-0.165	0.1553	-0.181	0.1422	-0.180	0.1505	-0.201	0.1501	-0.208
0.2060	-0.218	0.2410	-0.248	0.1948	-0.230	0.1983	-0.246	0.1997	-0.258
0.2414	-0.245	0.2572	-0.269	0.2465	-0.281	0.2518	-0.298	0.2504	-0.314
0.2966	-0.276	0.2985	-0.297	0.3002	-0.312	0.3564	-0.360	0.3445	-0.373
0.3432	-0.299	0.3510	-0.319	0.3448	-0.338	0.3968	-0.369	0.4008	-0.398
0.3978	-0.321	0.4027	-0.336	0.4559	-0.361	0.4374	-0.376	0.4475	-0.407
0.4478	-0.334	0.4448	-0.341	0.4928	-0.363	0.5034	-0.383	0.5002	-0.415
0.4879	-0.324	0.4855	-0.348	0.5434	-0.364	0.5460	-0.381	0.5566	-0.415
0.5458	-0.333	0.5429	-0.345	0.5957	-0.353	0.5989	-0.383	0.6400	-0.383
0.5989	-0.319	0.5972	-0.334	0.6366	-0.354	0.6551	-0.351	0.6946	-0.351
0.6424	-0.301	0.6447	-0.318	0.6926	-0.313	0.7078	-0.319	0.7464	-0.318
0.7003	-0.276	0.6962	-0.294	0.7602	-0.264	0.7491	-0.287	0.8097	-0.243
0.8033	-0.216	0.7412	-0.266	0.7986	-0.235	0.7959	-0.251	0.8422	-0.211
0.8468	-0.174	0.7760	-0.234	0.8522	-0.182	0.8531	-0.193	0.9048	-0.137
0.9030	-0.114	0.8447	-0.181	0.9032	-0.123	0.8980	-0.144		
0.9636	-0.039	0.9549	-0.056	0.9486	-0.064				
Tetralin + Decane									
0.0582	-0.049	0.0594	-0.037	0.0639	-0.052	0.0637	-0.050	0.0567	-0.055
0.1140	-0.086	0.1191	-0.081	0.1072	-0.087	0.1093	-0.092	0.1047	-0.104
0.1591	-0.112	0.1656	-0.117	0.1683	-0.154	0.1576	-0.148	0.1638	-0.152
0.2176	-0.145	0.2136	-0.147	0.2177	-0.168	0.2272	-0.181	0.2229	-0.187
0.2619	-0.160	0.2568	-0.161	0.2724	-0.206	0.2781	-0.213	0.2682	-0.222
0.3243	-0.187	0.3225	-0.198	0.3621	-0.229	0.3173	-0.220	0.3225	-0.232
0.3741	-0.205	0.3666	-0.202	0.4174	-0.239	0.3664	-0.233	0.3687	-0.255
0.4220	-0.214	0.4200	-0.220	0.4798	-0.239	0.4258	-0.251	0.4202	-0.274
0.4755	-0.224	0.4692	-0.222	0.5188	-0.239	0.4741	-0.261	0.4682	-0.280
0.5209	-0.215	0.5627	-0.220	0.6226	-0.224	0.5176	-0.259	0.5192	-0.282
0.5661	-0.219	0.6209	-0.213	0.6678	-0.216	0.5590	-0.246	0.5606	-0.270
0.6236	-0.206	0.6676	-0.201	0.7160	-0.201	0.6078	-0.245	0.6265	-0.257
0.6715	-0.195	0.7104	-0.179	0.7660	-0.169	0.6635	-0.221	0.6679	-0.236
0.7207	-0.179	0.7660	-0.160	0.8130	-0.146	0.7193	-0.214	0.7227	-0.215
0.7708	-0.148	0.8161	-0.139	0.8632	-0.115	0.7638	-0.186	0.7691	-0.198
0.8116	-0.133	0.8579	-0.109	0.9042	-0.077	0.8668	-0.116	0.8242	-0.164
0.8141	-0.134	0.9147	-0.080	0.9456	-0.045	0.9127	-0.087	0.8622	-0.137
0.8616	-0.098	0.9543	-0.032			0.9685	-0.022	0.9198	-0.078
0.9127	-0.055							0.9643	-0.035
0.9412	-0.036								

for these binary mixtures. At each temperature V^E increases in the sequence hexane < heptane < octane < nonane < decane.

In order to calculate the cubic expansion coefficient α_i of component *i* we start with the correlation between molar volume V_i of component *i* and temperature *T* as follows:

$$V_i/(\text{cm}^3 \text{mol}^{-1}) = A + B(T/K) + C(T/K)^2 \quad (3)$$

where *A*, *B*, and *C* are adjustable parameters. The cubic expansion coefficients of component *i* were derived from eq 3 using the following relation:

$$\alpha_i = V_i^{-1}(\partial V_i/\partial T)_P \quad (4)$$

Cubic expansion coefficients of *n*-alkanes and tetralin as a function of temperature have been listed in Table 4. Because values of $10^3(\partial \rho/\partial T)_P$ for hexane, heptane, octane, nonane, and decane are 0.891, 0.840, 0.803, 0.774, and 0.751, respectively, at temperatures from 273.15 to 313.15 K (17), the cubic expansion coefficients of *n*-alkanes obtained from $(\partial \rho/\partial T)_P$ are also listed in Table 4. It can be seen that the cubic expansion coefficients of *n*-alkanes measured in this work agree well with those obtained from the literature (17). Our results indicate that the cubic expansion coefficient increases with an increase in temperature and decreases with an increase in the chain length of the *n*-alkane over the whole temperature range.

Table 3. Parameters a_i and Standard Deviations $\sigma(V^E)$ (in Eqs 1 and 2) for Tetralin + *n*-Alkane

<i>T/K</i>	a_0	a_1	a_2	a_3	$\sigma(V^E)/(\text{cm}^3 \text{mol}^{-1})$
Tetralin + Hexane					
293.15	-4.1089	0.6779	-0.4401	0.1177	0.010
298.15	-4.3833	0.6827	-0.4149	0.1177	0.018
303.15	-4.5504	0.5305	-0.3579	0.3357	0.019
308.15	-4.8269	0.6893	-0.0872	0.1584	0.012
313.15	-5.0817	0.7335	-0.3387	0.2610	0.010
Tetralin + Heptane					
293.15	-2.7810	0.2649	-0.1031		0.004
298.15	-2.9372	0.3316	-0.0599		0.006
303.15	-3.0996	0.3149	-0.0637		0.003
308.15	-3.2239	0.2941	-0.0531	0.1425	0.004
313.15	-3.3983	0.3641	-0.0454		0.008
Tetralin + Octane					
293.15	-1.9557	0.1167	0.0041	0.0508	0.005
298.15	-2.0609	0.1287	-0.0571	-0.0910	0.007
303.15	-2.1452	0.0668	0.0091	0.0941	0.003
308.15	-2.2773	0.1027	0.0059	0.0615	0.004
313.15	-2.4046	0.1531	0.0011	0.1956	0.005
Tetralin + Nonane					
293.15	-1.3439	0.0293	0.1069		0.006
298.15	-1.4034	0.0107	0.0994		0.004
303.15	-1.4966	0.0226	0.1396		0.006
308.15	-1.5513	0.0076	-0.0016		0.004
313.15	-1.6668	-0.0203	0.1102	0.0796	0.004
Tetralin + Decane					
293.15	-0.8891	-0.1192	0.1338	0.3111	0.005
298.15	-0.9148	-0.0192	0.1615	-0.0941	0.006
303.15	-0.9964	0.0284	0.1056		0.008
308.15	-1.0424	0.0535	0.1027	-0.1488	0.007
313.15	-1.1131	-0.0007	0.0640		0.006

Table 4. Cubic Expansion Coefficients α/K^{-1} of Tetralin and *n*-Alkanes at Various Temperatures

substance	$10^3 \alpha/K^{-1}$				
	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
tetralin	0.8003	0.8087	0.8173	0.8257	0.8340
hexane	1.3436	1.3692	1.3943	1.4187	1.4426
	1.352 (17)	1.361 (17)	1.370 (17)	1.381 (17)	1.390 (17)
heptane	1.2304	1.2461	1.2614	1.2764	1.2910
	1.229 (17)	1.236 (17)	1.244 (17)	1.252 (17)	1.260 (17)
octane	1.1500	1.1401	1.1649	1.1892	1.2129
	1.143 (17)	1.150 (17)	1.156 (17)	1.163 (17)	1.170 (17)
nonane	1.0674	1.0791	1.0907	1.1020	1.1132
	1.078 (17)	1.084 (17)	1.090 (17)	1.096 (17)	1.102 (17)
decane	1.0197	1.0320	1.0440	1.0559	1.0675
	1.029 (17)	1.034 (17)	1.039 (17)	1.045 (17)	1.050 (17)

Acknowledgment

We express our gratitude to the Thermodynamics Research Center (The Texas A&M University System) for the permission to use data from the TRC Thermodynamic Tables.

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Received for review December 2, 1994. Accepted February 28, 1995.* Acknowledgment is made to the National Science Council of the Republic of China (Grant No. NSC 83-0402-E006-007) for financial support of this work.

JE940259V

* Abstract published in *Advance ACS Abstracts*, April 1, 1995.