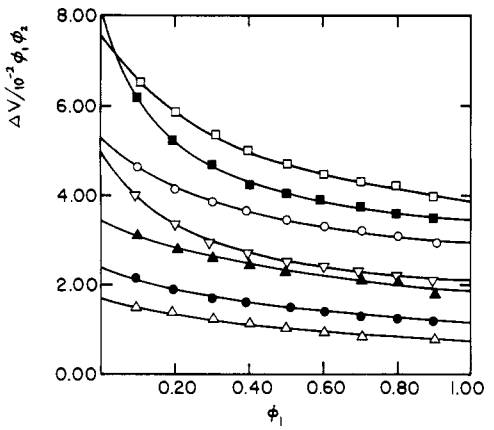

Figure 5. Variation of $\Delta V/\varphi_1\varphi_2$, eq 5, with volume fraction φ_1 of carbonyl compounds for carbonyl compounds (1)–heptane (2) mixtures at 20 °C: □, methyl acetate; ○, ethyl acetate; ▲, propyl acetate; ●, butyl acetate; △, amyl acetate; ■, acetone; ▽, 2-butanone.

cycloalkanes (cyclohexane in the present case).

$\Delta V/\varphi_1\varphi_2$ increases sharply in the region of lower concentration of the carbonyl compound. For ketones this increase is sharper than for alkyl acetates, as is apparent from Figure 5 and from the larger negative value of the fitting parameter c (Table II). This phenomenon reflects the nonregular nature of mixtures of carbonyl compounds with alkanes. The increase of volume is caused by alkane molecules disrupting the interactions of the highly dipolar molecules of the carbonyl compounds. When only a small amount of alkane is added, the carbonyl molecules rearrange themselves to preserve a larger proportion of paired dipoles than would be allowed by regular mixing. With the progressing amount of alkane being added, these "excess" dipolar pairs are disrupted as well, increasing the value of the excess volume in this concentration range.

Conclusions

Systematic measurement of compositional dependences of the excess volume of mixing on the composition for families of related pairs of compounds may reveal basic effects governing interactions among molecules. In the present study, it was found that mixtures of carbonyl compounds with alkanes exhibit a distinct nonregularity. Due to the strong interaction among the polar molecules, the number of interacting dipolar pairs disrupted by added nonpolar alkane molecules is less than would be expected for regular (random) mixing.

Registry No. Hexane, 110-54-3; heptane, 142-82-5; octane, 111-65-9; cyclohexane, 110-82-7; methyl acetate, 79-20-9; ethyl acetate, 141-78-6; propyl acetate, 109-60-4; butyl acetate, 123-86-4; amyl acetate, 628-63-7; acetone, 67-64-1; 2-butanone, 78-93-3.

Literature Cited

(1) Munk, P.; Hattam, P.; Du, Q. *J. Appl. Polym. Sci., Appl. Polym. Symp.* **1989**, *43*, 373.
(2) Cheng, W.; Abdel-Azim, A.-A. A.; El-Hibri, M. J.; Du, Q.; Munk, P. *J. Phys. Chem.* **1989**, *93*, 8248.
(3) TRC—Thermodynamic Tables—Non-hydrocarbons. Thermodynamics Research Center, The Texas A&M University System: College Station, TX, 1969; p. d-5550.
(4) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. In *Organic Solvents*, 4th ed.; Weissberger, A., Ed.; Techniques of Chemistry, Vol. II; John Wiley & Sons: New York, 1986.
(5) TRC—Thermodynamic Tables—Non-hydrocarbons. Thermodynamics Research Center, The Texas A&M University System: College Station, TX, 1952; p. d-1440 (loose-leaf data sheets).
(6) TRC—Thermodynamic Tables—Non-hydrocarbons. Thermodynamics Research Center, The Texas A&M University System: College Station, TX, 1952; p. d-1460 (loose-leaf data sheets).
(7) TRC—Thermodynamic Tables—Non-hydrocarbons. Thermodynamics Research Center, The Texas A&M University System: College Station, TX, 1952; p. d-1490 (loose-leaf data sheets).
(8) TRC—Thermodynamic Tables—Non-hydrocarbons. Thermodynamics Research Center, The Texas A&M University System: College Station, TX, 1952; p. d-2050 (loose-leaf data sheets).
(9) Grolier, J.-P. E.; Ballet, D.; Viallard, A. *J. Chem. Thermodyn.* **1974**, *6*, 895.
(10) Patel, N. C.; Sandler, S. I. *J. Chem. Eng. Data* **1985**, *30*, 218.
(11) Dusart, O.; Grolier, J.-P. E.; Viallard, A. *Bull. Soc. Chim. Fr.* **1977**, *7-8* (Part 1), 587.
(12) Jimenez, E.; Romani, L.; Paz Andrade, M. I.; Roux-Desgranges, G.; Grolier, J.-P. E. *J. Solution Chem.* **1986**, *15*, 879.
(13) Crespo Colin, A.; Compostizo, A.; Diaz Pena, M. *J. Chem. Thermodyn.* **1984**, *16*, 497.
(14) Grolier, J.-P. E.; Benson, G. C. *Can. J. Chem.* **1984**, *62*, 949.

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Excess Volume of Mixtures of Alkanes with Aromatic Hydrocarbons

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The excess volumes of 22 binary mixtures of aromatic hydrocarbons and alkanes are reported. The excess volume of systems with the same alkane decreases with increasing size and number of substituents on the benzene ring. For systems with the same aromatic hydrocarbon it increases with the length of the alkanes. Systems with benzene or cyclohexane as one of the components show larger excess volumes than the other systems, and the dependence of their $\Delta V/\varphi_1\varphi_2$ values on composition is noticeably asymmetric.

During recent years we have been using various methods such as light scattering, inverse gas chromatography, densitometry, and calorimetry to accumulate extensive thermodynamic data concerning binary mixtures in order to develop a comprehensive theory which could interpret all the important aspects of liquid mixtures (*1*, *2*). As part of this work, we are reporting in the present paper the measurements of excess volume of mixing of alkanes and aromatic hydrocarbons. The alkanes used were three linear alkanes (hexane, heptane, and octane) and cyclohexane. The aromatic hydrocarbons included benzene, toluene, ethylbenzene, *p*-xylene, *o*-xylene, and *m*-xylene. Altogether 22 systems were prepared, and, for each system, the dependence of the excess volume on concentration was studied.

The molar excess volume of mixing V^E is defined as

$$V^E = V - x_1V^\circ_1 - x_2V^\circ_2 \quad (1)$$

where V is the volume of 1 mol of the mixture and x_i and V°_i

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Table I. Excess Volumes of Mixing for Aromatic Hydrocarbon and Alkane Mixtures at 20 °C

φ_1	x_1	ρ/(g cm^{-3})	V^E/(cm^3 mol^{-1})	$\Delta V/10^{-2}$	φ_1	x_1	ρ/(g cm^{-3})	V^E/(cm^3 mol^{-1})	$\Delta V/10^{-2}$
				Benzene (1) + Hexane (2)					
1.000	1.000	0.879 28			0.402	0.497	0.745 35	0.403	0.367
0.908	0.936	0.858 34	0.087	0.095	0.299	0.385	0.723 03	0.374	0.327
0.801	0.856	0.833 86	0.204	0.215	0.199	0.268	0.701 68	0.319	0.267
0.700	0.775	0.811 11	0.291	0.296	0.107	0.150	0.682 25	0.211	0.170
0.599	0.687	0.788 40	0.360	0.353	0.000	0.000	0.659 84		
0.502	0.597	0.767 18	0.400	0.379					
				Benzene (1) + Heptane (2)					
1.000	1.000	0.879 31			0.399	0.523	0.758 15	0.591	0.508
0.907	0.941	0.859 67	0.157	0.170	0.302	0.417	0.739 67	0.570	0.465
0.695	0.790	0.816 21	0.444	0.440	0.209	0.304	0.722 24	0.486	0.377
0.601	0.713	0.797 50	0.532	0.505	0.103	0.159	0.702 65	0.297	0.216
0.503	0.626	0.778 25	0.584	0.529	0.000	0.000	0.684 14		
				Benzene (1) + Octane (2)					
1.000	1.000	0.879 30			0.392	0.541	0.767 48	0.716	0.584
0.906	0.946	0.860 91	0.191	0.205	0.297	0.436	0.751 27	0.690	0.529
0.798	0.879	0.840 44	0.376	0.385	0.204	0.320	0.735 79	0.576	0.414
0.703	0.812	0.822 72	0.520	0.507	0.113	0.189	0.720 85	0.388	0.261
0.602	0.734	0.804 39	0.624	0.576	0.000	0.000	0.702 78		
0.497	0.644	0.785 79	0.701	0.609					
				Benzene (1) + Cyclohexane (2)					
1.000	1.000	0.879 32			0.401	0.449	0.813 89	0.644	0.648
0.916	0.930	0.869 29	0.164	0.182	0.301	0.344	0.804 44	0.593	0.585
0.809	0.837	0.856 91	0.343	0.372	0.203	0.236	0.795 55	0.479	0.463
0.714	0.753	0.846 36	0.472	0.504	0.108	0.128	0.787 45	0.297	0.281
0.613	0.658	0.835 36	0.580	0.608	0.000	0.000	0.778 87		
0.499	0.548	0.823 58	0.640	0.656					
				Toluene (1) + Hexane (2)					
1.000	1.000	0.867 12			0.401	0.451	0.743 22	−0.054	−0.045
0.899	0.916	0.846 55	−0.040	−0.037	0.301	0.346	0.722 50	−0.041	−0.034
0.809	0.839	0.827 49	−0.044	−0.040	0.202	0.237	0.701 77	−0.028	−0.023
0.708	0.748	0.806 94	−0.056	−0.049	0.094	0.114	0.679 45	−0.009	−0.007
0.603	0.651	0.785 35	−0.086	−0.075	0.000	0.000	0.659 83		
0.495	0.547	0.762 89	−0.061	−0.052					
				Toluene (1) + Heptane (2)					
1.000	1.000	0.867 18			0.405	0.484	0.757 30	0.151	0.119
0.899	0.924	0.848 30	0.039	0.036	0.304	0.376	0.739 06	0.140	0.106
0.799	0.845	0.829 81	0.072	0.064	0.208	0.266	0.721 62	0.123	0.091
0.699	0.762	0.811 38	0.106	0.092	0.107	0.142	0.703 30	0.084	0.059
0.592	0.667	0.791 63	0.134	0.112	0.000	0.000	0.684 13		
				Toluene (1) + Octane (2)					
1.000	1.000	0.867 15			0.403	0.508	0.767 62	0.261	0.195
0.901	0.933	0.850 26	0.084	0.076	0.304	0.401	0.751 54	0.242	0.173
0.801	0.860	0.833 39	0.138	0.121	0.201	0.278	0.734 84	0.201	0.137
0.700	0.781	0.816 48	0.189	0.160	0.102	0.148	0.719 00	0.121	0.078
0.606	0.702	0.800 97	0.225	0.183	0.000	0.000	0.702 85		
0.513	0.617	0.785 62	0.254	0.199					
				Toluene (1) + Cyclohexane (2)					
1.000	1.000	0.867 14			0.406	0.410	0.810 35	0.571	0.532
0.907	0.908	0.857 62	0.163	0.153	0.302	0.306	0.801 63	0.525	0.488
0.804	0.807	0.847 34	0.316	0.297	0.199	0.202	0.793 39	0.417	0.387
0.706	0.709	0.837 76	0.433	0.406	0.096	0.098	0.785 65	0.235	0.218
0.606	0.610	0.828 33	0.519	0.485	0.000	0.000	0.778 86		
0.502	0.507	0.818 87	0.568	0.530					
				Ethylbenzene (1) + Hexane (2)					
1.000	1.000	0.867 39			0.400	0.416	0.743 94	−0.161	−0.127
0.795	0.806	0.825 51	−0.091	−0.073	0.304	0.318	0.723 78	−0.126	−0.099
0.696	0.710	0.805 121	−0.120	−0.096	0.198	0.208	0.701 48	−0.095	−0.074
0.596	0.612	0.784 50	−0.145	−0.115	0.096	0.102	0.680 07	−0.056	−0.043
0.501	0.518	0.764 80	−0.146	−0.116	0.000	0.000	0.659 89		
				Ethylbenzene (1) + Heptane (2)					
1.000	1.000	0.867 12			0.405	0.449	0.757 84	0.063	0.046
0.896	0.911	0.847 89	0.016	0.013	0.302	0.341	0.739 10	0.060	0.043
0.797	0.825	0.829 80	0.031	0.025	0.199	0.229	0.720 29	0.045	0.032
0.700	0.736	0.811 86	0.051	0.040	0.104	0.122	0.703 01	0.027	0.019
0.594	0.637	0.792 50	0.060	0.046	0.000	0.000	0.684 14		
0.500	0.544	0.775 22	0.062	0.046					

Table I (Continued)

φ_1	x_1	ρ/(g cm^{-3})	V^E/(cm^3 mol^{-1})	$\Delta V/10^{-2}$	φ_1	x_1	ρ/(g cm^{-3})	V^E/(cm^3 mol^{-1})	$\Delta V/10^{-2}$
				Ethylbenzene (1) + Octane (2)					
1.000	1.000	0.867 39			0.396	0.466	0.766 95	0.197	0.137
0.900	0.923	0.850 54	0.064	0.051	0.298	0.360	0.750 98	0.154	0.104
0.798	0.840	0.833 43	0.114	0.088	0.204	0.254	0.735 64	0.147	0.096
0.696	0.752	0.816 36	0.153	0.115	0.107	0.137	0.720 02	0.082	0.052
0.600	0.666	0.800 47	0.180	0.132	0.000	0.000	0.702 78		
0.497	0.568	0.783 54	0.196	0.140					
				Ethylbenzene (1) + Cyclohexane (2)					
1.000	1.000	0.867 39			0.498	0.467	0.819 24	0.518	0.452
0.898	0.886	0.857 17	0.172	0.142	0.398	0.369	0.810 43	0.513	0.453
0.793	0.772	0.846 84	0.312	0.262	0.195	0.177	0.793 57	0.361	0.326
0.699	0.672	0.837 78	0.413	0.351	0.097	0.087	0.785 86	0.219	0.200
0.600	0.570	0.828 58	0.479	0.412	0.000	0.000	0.778 85		
				o-Xylene (1) + Hexane (2)					
1.000	1.000	0.879 77			0.397	0.416	0.749 02	−0.324	−0.256
0.902	0.908	0.858 96	−0.120	−0.099	0.303	0.320	0.728 21	−0.297	−0.233
0.795	0.808	0.836 12	−0.208	−0.170	0.197	0.210	0.704 36	−0.211	−0.164
0.697	0.713	0.814 89	−0.270	−0.218	0.090	0.097	0.680 28	−0.099	−0.076
0.601	0.620	0.794 17	−0.322	−0.259	0.000	0.000	0.659 90		
0.503	0.522	0.772 54	−0.340	−0.271					
				o-Xylene (1) + Heptane (2)					
1.000	1.000	0.879 87			0.496	0.544	0.782 07	−0.159	−0.120
0.901	0.917	0.860 76	−0.044	−0.036	0.302	0.344	0.743 87	−0.121	−0.088
0.800	0.830	0.841 41	−0.092	−0.074	0.192	0.224	0.722 17	−0.090	−0.064
0.695	0.735	0.821 02	−0.126	−0.099	0.091	0.108	0.702 10	−0.049	−0.034
0.596	0.641	0.801 58	−0.144	−0.111	0.000	0.000	0.684 11		
				o-Xylene (1) + Cyclohexane (2)					
1.000	1.000	0.879 75			0.397	0.371	0.814 61	0.597	0.530
0.898	0.887	0.868 04	0.194	0.162	0.302	0.279	0.805 36	0.542	0.486
0.803	0.785	0.857 44	0.340	0.288	0.198	0.181	0.795 76	0.425	0.385
0.698	0.674	0.845 81	0.474	0.407	0.102	0.092	0.787 29	0.255	0.234
0.596	0.569	0.834 88	0.564	0.489	0.000	0.000	0.778 83		
0.498	0.471	0.824 72	0.605	0.531					
				m-Xylene (1) + Hexane (2)					
1.000	1.000	0.864 45			0.397	0.411	0.742 12	−0.184	−0.145
0.896	0.901	0.843 66	−0.071	−0.058	0.291	0.304	0.720 30	−0.156	−0.121
0.801	0.811	0.824 68	−0.124	−0.099	0.198	0.208	0.701 11	−0.116	−0.090
0.703	0.715	0.804 71	−0.166	−0.133	0.100	0.106	0.680 82	−0.059	−0.046
0.601	0.615	0.783 99	−0.186	−0.148	0.000	0.000	0.659 95		
0.503	0.518	0.763 99	−0.196	−0.155					
				m-Xylene (1) + Heptane (2)					
1.000	1.000	0.864 46			0.402	0.445	0.756 75	−0.031	−0.023
0.901	0.915	0.846 65	−0.016	−0.013	0.294	0.332	0.737 15	−0.019	−0.014
0.798	0.825	0.828 27	−0.030	−0.024	0.198	0.228	0.719 88	−0.013	−0.009
0.702	0.737	0.810 92	−0.042	−0.033	0.097	0.113	0.701 51	−0.004	−0.003
0.600	0.641	0.792 51	−0.040	−0.031	0.000	0.000	0.684 05		
0.498	0.542	0.774 21	−0.046	−0.034					
				m-Xylene (1) + Cyclohexane (2)					
1.000	1.000	0.864 44			0.397	0.367	0.807 95	0.685	0.604
0.905	0.894	0.854 96	0.195	0.161	0.298	0.272	0.799 93	0.625	0.557
0.793	0.771	0.843 94	0.391	0.327	0.199	0.180	0.792 34	0.498	0.450
0.698	0.670	0.834 84	0.527	0.447	0.102	0.091	0.785 39	0.305	0.279
0.597	0.566	0.825 54	0.617	0.530	0.000	0.000	0.778 83		
0.495	0.463	0.816 38	0.678	0.590					
				p-Xylene (1) + Hexane (2)					
1.000	1.000	0.861 44			0.398	0.412	0.741 55	−0.236	−0.185
0.905	0.910	0.842 80	−0.082	−0.066	0.304	0.316	0.722 27	−0.199	−0.155
0.798	0.808	0.821 85	−0.154	−0.123	0.210	0.220	0.703 24	−0.164	−0.127
0.700	0.712	0.802 32	−0.202	−0.161	0.110	0.116	0.682 60	−0.095	−0.073
0.601	0.615	0.782 57	−0.231	−0.183	0.000	0.000	0.659 95		
0.508	0.522	0.763 79	−0.254	−0.200					
				p-Xylene (1) + Heptane (2)					
1.000	1.000	0.861 56			0.406	0.449	0.756 67	−0.076	−0.056
0.894	0.910	0.843 02	−0.032	−0.025	0.303	0.340	0.738 17	−0.058	−0.042
0.690	0.726	0.807 06	−0.074	−0.057	0.195	0.224	0.719 00	−0.041	−0.029
0.595	0.635	0.790 10	−0.078	−0.059	0.091	0.106	0.700 36	−0.025	−0.018
0.503	0.546	0.773 76	−0.077	−0.057	0.000	0.000	0.684 14		

Table I (Continued)

φ_1	x_1	ρ/(g cm^{-3})	V^E/(cm^3 mol^{-1})	$\Delta V/10^{-2}$	φ_1	x_1	ρ/(g cm^{-3})	V^E/(cm^3 mol^{-1})	$\Delta V/10^{-2}$
				p-Xylene (1) + Octane (2)					
1.000	1.000	0.861 41			0.393	0.461	0.765 04	0.030	0.021
0.891	0.915	0.844 09	−0.001	−0.001	0.294	0.354	0.749 30	0.036	0.024
0.788	0.830	0.827 72	0.005	0.004	0.192	0.239	0.733 28	0.027	0.018
0.683	0.740	0.811 09	0.025	0.019	0.093	0.119	0.717 52	0.019	0.012
0.590	0.655	0.796 30	0.025	0.019	0.000	0.000	0.702 89		
0.495	0.564	0.781 17	0.032	0.023					
				p-Xylene (1) + Cyclohexane (2)					
1.000	1.000	0.861 44			0.405	0.374	0.807 80	0.635	0.558
0.899	0.887	0.851 81	0.189	0.156	0.304	0.277	0.799 81	0.583	0.520
0.802	0.781	0.842 63	0.352	0.294	0.203	0.182	0.792 25	0.468	0.422
0.702	0.674	0.833 42	0.485	0.410	0.100	0.089	0.785 15	0.272	0.248
0.602	0.570	0.824 46	0.579	0.496	0.000	0.000	0.778 85		
0.504	0.471	0.816 02	0.631	0.548					

Table II. Parameters of Equations 2 and 3 and Standard Deviations

system[a]	a_0	a_1	a_2	$\sigma(V^E/x_1x_2)$/(cm^3 mol^{-1})	$b_0/10^{-2}$	$b_1/10^{-2}$	$b_2/10^{-2}$	$\sigma(\Delta V/\varphi_1\varphi_2)/10^{-2}$
BE-HX	1.658	0.018	−0.133	0.072	1.509	0.322	−0.064	0.057
BE-HP	2.393	−0.363	0.185	0.023	2.117	0.194	0.111	0.025
BE-OC	2.840	−0.678	0.343	0.030	2.436	0.131	0.117	0.018
BE-CH	2.596	0.104	−0.007	0.009	2.626	0.364	0.039	0.009
TO-HX	−0.237	0.212	−0.056	0.060	−0.218	0.160	−0.015	0.048
TO-HP	0.601	0.073	0.033	0.021	0.468	0.131	0.052	0.019
TO-OC	1.015	−0.150	0.162	0.051	0.780	0.038	0.105	0.029
TO-CH	2.282	0.449	0.061	0.010	2.126	0.436	0.064	0.009
EB-HX	−0.607	−0.019	0.051	0.033	−0.480	−0.032	0.041	0.026
EB-HP	0.262	0.023	−0.057	0.013	0.194	0.037	−0.038	0.009
EB-OC	0.769	−0.111	0.029	0.040	0.551	−0.002	0.009	0.030
EB-CH	2.030	0.615	0.270	0.035	1.794	0.431	0.175	0.027
PX-HX	−0.980	0.044	0.040	0.022	−0.773	0.012	0.033	0.017
PX-HP	−0.304	0.095	−0.026	0.021	−0.232	0.051	−0.007	0.016
PX-OC	0.141	0.087	−0.083	0.027	0.091	0.079	−0.041	0.017
PX-CH	2.483	0.899	0.196	0.013	2.199	0.641	0.076	0.010
OX-HX	−1.354	0.120	0.115	0.057	−1.081	0.051	0.095	0.047
OX-HP	−0.612	0.087	0.101	0.031	−0.464	0.017	0.085	0.021
OX-CH	2.378	0.686	0.143	0.013	2.112	0.488	0.065	0.010
MX-HX	−0.783	0.102	0.101	0.012	−0.621	0.060	0.083	0.011
MX-HP	−0.152	0.121	0.049	0.016	−0.121	0.077	0.052	0.011
MX-CH	2.654	0.981	0.303	0.022	2.354	0.711	0.163	0.017

[a] Abbreviations: BE, benzene; TO, toluene; EB, ethylbenzene; OX, *o*-xylene; MX, *m*-xylene; PX, *p*-xylene; HX, hexane; HP, heptane; OC, octane; CH, cyclohexane.

are mole fraction and molar volume of pure component i, respectively. Experimentally, by measuring the densities of pure components and their mixtures, the molar excess volume of mixing can be calculated. We have found it convenient to express the volume changes also as fractional changes of volume upon mixing $\Delta V \equiv V^E/(x_1V^\circ_1 + x_2V^\circ_2)$. The experimental data are listed in Table I for all systems.

A polynomial function is often used to correlate the experimental data of V^E/x_1x_2

$$V^E/x_1x_2 = \sum_j a_j(x_2 - x_1)^j \quad (2)$$

Similarly, $\Delta V/\varphi_1\varphi_2$ is expressed by the following power series

$$\Delta V/\varphi_1\varphi_2 = \sum_j b_j(\varphi_2 - \varphi_1)^j \quad (3)$$

The correlation coefficients in eqs 2 and 3 obtained by least-squares fitting to the second order are collected in Table II, together with the standard deviations of the fits, $\sigma(V^E/x_1x_2)$ and $\sigma(\Delta V/\varphi_1\varphi_2)$, which have the forms as follows

$$\sigma(V^E/x_1x_2) = [\sum(V^E_{calc}/x_1x_2 - V^E/x_1x_2)^2/(N - n - 1)]^{1/2} \quad (4)$$

$$\sigma(\Delta V/\varphi_1\varphi_2) = [\sum(\Delta V_{calc}/\varphi_1\varphi_2 - \Delta V/\varphi_1\varphi_2)^2/(N - n - 1)]^{1/2} \quad (5)$$

There, N is the number of values measured, and n is the number of adjusted parameters.

Table III. V^E at $x_1 = 0.5$[a]

system[b]	V^E(lit.)	V^E(expt)	V^E(lit.)/V^E(expt)[c]
BE-HP	0.591 (20 °C)	0.598	0.988 (*4*)
BE-HP	0.590	0.598	0.987 (*4*)
BE-CH	0.651 (20 °C)	0.649	1.003 (*5*)
BE-CH	0.654	0.649	1.008 (*5*)
BE-CH	0.650	0.649	1.001 (*6*)
BE-CH	0.638	0.649	0.982 (*7*)
BE-CH	0.651	0.649	1.004 (*8*)
TO-CH	0.551	0.571	0.966 (*7*)
EB-HX	−0.147	−0.152	0.967 (*9*)
EB-OC	0.195	0.192	1.014 (*9*)
PX-CH	0.588	0.621	0.945 (*7*)

[a] Literature values were measured at 25 °C except where indicated. [b] See guide for abbreviations in footnote *a* of Table II. [c] Literature references are given in parentheses.

Experimental Part and Results

All aromatic hydrocarbons and alkanes obtained from Aldrich Chemical Co. were of purity higher than 99% and were used as supplied. The measurement of densities was described in another paper (*3*). All experiments were done at 20 °C.

Discussion and Conclusions

We were able to compare some results of our systems with literature data (*4*–*9*) for the compositional dependence of V^E. Most of the literature data were measured at 25 °C. Our ex-

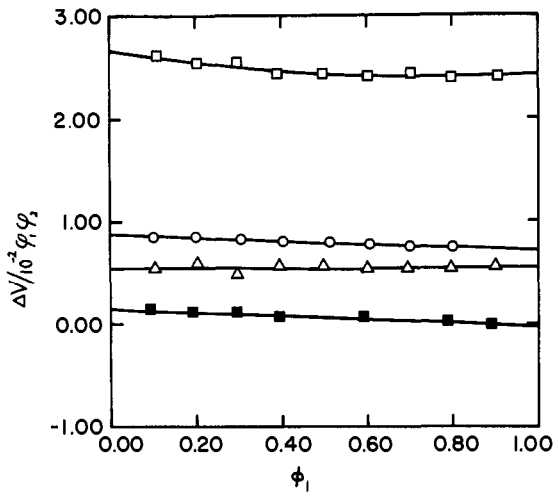

Figure 1. Variation of $\Delta V/\varphi_1\varphi_2$ with volume fraction φ_1 of the aromatic hydrocarbon for aromatic hydrocarbon (1)–octane (2) mixtures at 20 °C: □, benzene; O, toluene; △, ethylbenzene; ■, *p*-xylene.

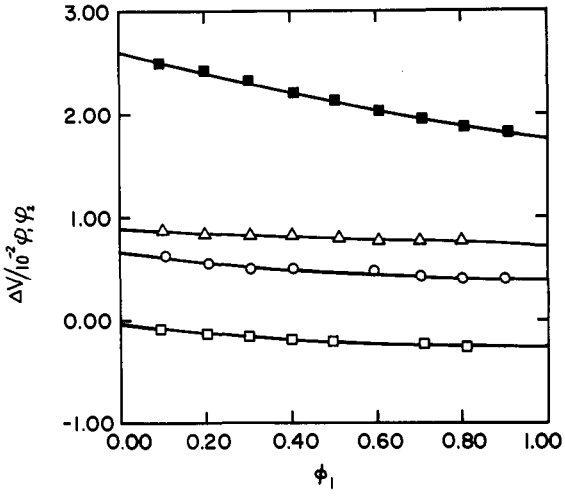

Figure 2. Variation of $\Delta V/\varphi_1\varphi_2$ with volume fraction φ_1 of toluene for toluene (1)–alkane (2) mixtures at 20 °C: □, hexane; O, heptane; △, octane; ■, cyclohexane.

perimental values and literature values of V^E interpolated to molar fraction 0.5 are listed in Table III. For all these systems, the values calculated from our interpolation formula (eq 2 and Table II) were very close to the values obtained from the literature formula. For the majority of the systems, the discrepancy between literature values and our data is less than 3%; this may be partially due to the different temperature used. The overall agreement assures us about the reliability of our data.

The dependences of excess volumes on composition are very clearly demonstrated by the plots of $\Delta V/\varphi_1\varphi_2$ versus composition. From Figure 1 it can be seen that for systems with octane as one component the excess volume decreases with the increase of the size and the number of the substituents on the benzene ring. This is also true for other linear alkanes. When a given aromatic hydrocarbon is mixed with a series of alkanes, the excess volume increases regularly with the increasing length of the alkane (Figure 2).

The behavior of mixtures with benzene or cyclohexane as one component is strikingly different from the other systems. First, in comparison with the other members of their family, these systems have distinctly higher excess volumes (Figures 1 and 2). Second, $\Delta V/\varphi_1\varphi_2$ values of all these systems are remarkably composition dependent (Figures 3 and 4), while the other systems are almost independent of composition. The $\Delta V/\varphi_1\varphi_2$ values in benzene-containing mixtures increase with the decreasing amount of benzene. However, in cyclohexane-containing mixtures, they increase with the increasing amount of cyclohexane. We believe that this behavior is related to the geometry of the molecules involved and to the peculiarities of their packing in pure liquids and in mixtures.

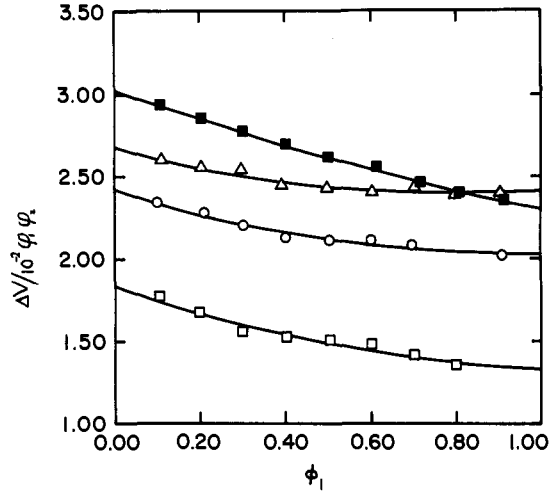

Figure 3. Variation of $\Delta V/\varphi_1\varphi_2$ with volume fraction φ_1 of benzene for benzene (1)–alkane (2) mixtures at 20 °C: □, hexane; O, heptane; △, octane; ■, cyclohexane.

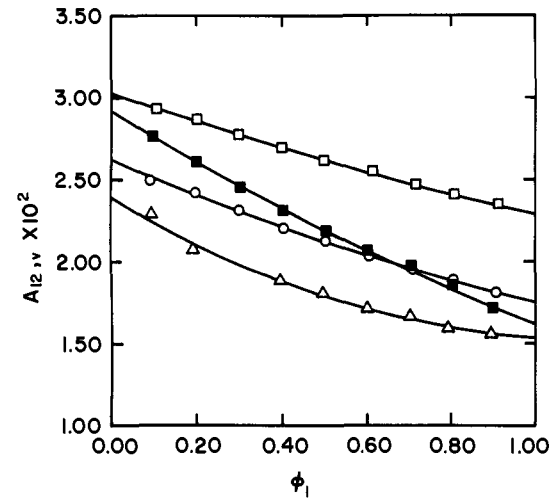

Figure 4. Variation of $\Delta V/\varphi_1\varphi_2$ with volume fraction φ_1 of aromatic hydrocarbon for aromatic hydrocarbon (1)–cyclohexane (2) mixtures at 20 °C: □, benzene; O, toluene; △, ethylbenzene; ■, *p*-xylene.

Registry No. BE, 71-43-2; TO, 108-88-3; EB, 100-41-4; OX, 95-47-6; MX, 108-38-3; PX, 106-42-3; HX, 110-54-3; HP, 142-82-5; OC, 111-65-9; CH, 292-64-8.

Literature Cited

(1) Munk, P.; Hattam, P.; Du, Q. *J. Appl. Polym. Sci.: Appl. Polym. Symp.* **1989**, *43*, 373. Munk, P.; Hattam, P.; Du, Q.; Abdel-Azim, A. A. *Ibid.* **1990**, *45*, 289.
(2) Cheng, W.; Abdel-Azim, A.-A. A.; El-Hibri, M. J.; Du, Q.; Munk, P. *J. Phys. Chem.* **1989**, *93*, 8248.
(3) Qin, A.; Hoffman, D. E.; Munk, P. *J. Chem. Eng. Data*, first of three papers in this issue.
(4) Takenaka, M.; Tanaka, R.; Murakami, S. *J. Chem. Thermodyn.* **1982**, *14*, 399.
(5) Takenaka, M.; Tanaka, R.; Murakami, S. *J. Chem. Thermodyn.* **1980**, *12*, 849.
(6) Stokes, R. H.; Levien, B. J.; Marsh, K. N. *J. Chem. Thermodyn.* **1970**, *2*, 43.
(7) Acree, W. E., Jr.; Gholami, K.; McHan, D. R.; Rytting, J. H. *J. Chem. Eng. Data* **1985**, *30*, 182.
(8) Grolier, J.-P. E.; Wilhelm, E.; Hamedi, M. H. *Ber. Bunsen-Ges, Phys. Chem.* **1978**, *82*, 1282.
(9) Caceres Alonso, M.; Poveda Vilches, J. L.; Sanchez-Pajares, R. G.; Nunez Delgado, J. *Fluid Phase Equilib.* **1985**, *20*, 81.

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