Excess Volume of Mixtures of Selected Alkyl Esters and Ketones with Aromatic Hydrocarbons

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Excess volumes of mixing were measured at 20 °C for mixtures of four aromatic hydrocarbons (benzene, toluene, ethylbenzene, and *p*-xylene) with five alkyl acetates (methyl, ethyl, propyl, butyl, and amyl acetates) and two ketones (acetone and 2-butanone). The whole composition range was studied for all 28 binary systems. Specific interactions between the carbonyl and aromatic systems lead to rather small excess volumes, frequently even negative ones. Ketones interact more strongly than alkyl acetates.

This paper is a part of an extensive study of excess volumes of mixing for a large number of solvent pairs. This study, in turn, aims at assembling a large data base of many thermodynamic properties of binary mixtures using methods such as light scattering, inverse gas chromatography, densitometry, and calorimetry (*1*, *2*). Our goal is to assemble data that are comprehensive and internally consistent and that reveal similarities and trends among mixtures of components belonging to various chemical families. Ultimately these data should form an experimental basis for a development of a more advanced theory of mixtures.

In other papers (*3*, *4*), we have reported the dependence of excess volume on composition for binary mixtures of alkanes with carbonyl compounds and with aromatic hydrocarbons. In this paper we are presenting our measurements of excess volume of seven carbonyl compounds with four aromatic hydrocarbons. For all 28 systems, we have measured the dependence of the excess volume on composition.

Experimental Part and Results

All carbonyl compounds and aromatic hydrocarbons were obtained from Aldrich Chemical Co., with the purity better than 99%, and used as supplied. The measurement of densities was described in another paper (*3*). All experiments were performed at 20 °C.

Our experimental data are listed in Table I for all systems.

Discussion and Conclusions

The molar excess volume of mixing is defined as

$$V^E = V - x_1V_1^\circ - x_2V_2^\circ \quad (1)$$

where V is the volume of 1 mol of the mixture; x_i and V_i° are the mole fraction and molar volume of pure component i, respectively.

Experimentally, the masses m_i, the densities ρ_i of the components, and the densities ρ_m of the mixtures were measured. The volume fractions φ_i, the molar excess volumes V^E, and the relative changes in volume ΔV are then calculated as

$$\varphi_i = (m_i/\rho_i)/(m_1/\rho_1 + m_2/\rho_2) \quad (2)$$

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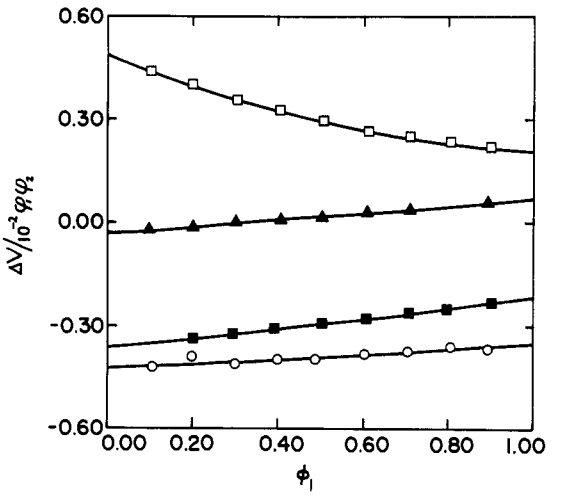

Figure 1. Variation of $\Delta V/\varphi_1\varphi_2$ with volume fraction φ_1 of propyl acetate for propyl acetate (1)–aromatic hydrocarbon (2) mixtures at 20 °C: □, benzene; ○, toluene; ▲, ethyl benzene; ■, *p*-xylene.

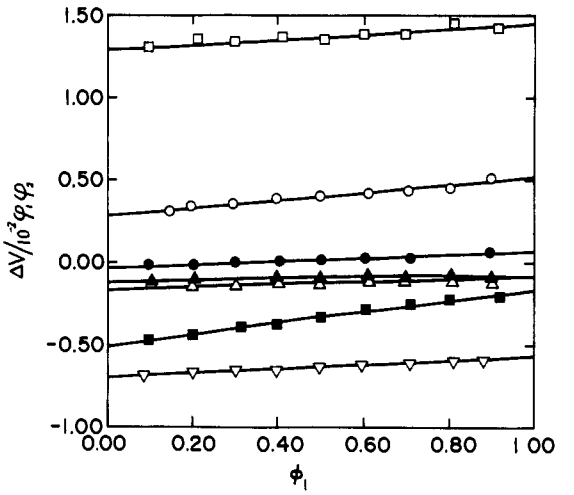

Figure 2. Variation of $\Delta V/\varphi_1\varphi_2$ with volume fraction φ_1 of carbonyl compounds for carbonyl compound (1)–ethylbenzene (2) mixtures at 20 °C: □, methyl acetate; ○, ethyl acetate; ●, propyl acetate; ▲, butyl acetate; △, amyl acetate; ■, acetone; ▽, 2-butanone.

$$V^E = [(m_1 + m_2)/\rho_m - m_1/\rho_1 - m_2/\rho_2]/(m_1/M_1 + m_2/M_2) \quad (3)$$

$$\Delta V = V^E/(x_1V_1^\circ + x_2V_2^\circ) = [(m_1 + m_2)/\rho_m - m_1/\rho_1 - m_2/\rho_2]/(m_1/\rho_1 + m_2/\rho_2) \quad (4)$$

where M_i is the molar mass of pure component i.

Experiment data of V^E are usually correlated by the following power series

$$V^E/x_1x_2 = \sum_j a_j(x_2 - x_1)^j \quad (5)$$

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Table I. Excess Volumes of Mixing for Carbonyl Compounds and Aromatic Hydrocarbons 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})	$\Delta V/10^{-2}$
				Methyl Acetate (1) + Benzene (2)					
1.000	1.000	0.934 47			0.396	0.423	0.897 73	0.322	0.380
0.898	0.908	0.927 50	0.116	0.145	0.296	0.321	0.892 69	0.287	0.334
0.800	0.818	0.921 16	0.203	0.250	0.198	0.217	0.887 95	0.224	0.258
0.704	0.728	0.915 15	0.270	0.330	0.100	0.110	0.883 51	0.130	0.149
0.606	0.633	0.909 28	0.314	0.379	0.000	0.000	0.879 32		
0.500	0.529	0.903 34	0.331	0.396					
				Methyl Acetate (1) + Toluene (2)					
1.000	1.000	0.934 50			0.393	0.464	0.891 79	0.194	0.207
0.892	0.917	0.926 36	0.077	0.095	0.296	0.360	0.885 53	0.172	0.178
0.800	0.843	0.919 61	0.128	0.153	0.192	0.242	0.879 01	0.129	0.129
0.703	0.761	0.912 74	0.168	0.196	0.097	0.126	0.873 11	0.072	0.070
0.606	0.674	0.906 02	0.192	0.218	0.000	0.000	0.867 20		
0.503	0.576	0.899 05	0.201	0.222					
				Methyl Acetate (1) + Ethylbenzene (2)					
1.000	1.000	0.933 86			0.413	0.521	0.891 89	0.333	0.333
0.909	0.939	0.926 74	0.096	0.117	0.299	0.397	0.884 80	0.293	0.279
0.804	0.864	0.918 74	0.195	0.229	0.211	0.293	0.879 50	0.246	0.224
0.697	0.780	0.911 03	0.261	0.293	0.099	0.145	0.873 00	0.135	0.117
0.600	0.698	0.904 28	0.307	0.332	0.000	0.000	0.867 42		
0.507	0.613	0.898 08	0.324	0.338					
				Methyl Acetate (1) + *p*-Xylene (2)					
1.000	1.000	0.933 88			0.404	0.513	0.888 56	0.229	0.227
0.904	0.936	0.926 05	0.074	0.090	0.303	0.403	0.881 53	0.208	0.197
0.805	0.865	0.918 35	0.129	0.152	0.208	0.290	0.875 04	0.167	0.151
0.703	0.786	0.910 42	0.184	0.208	0.103	0.152	0.868 08	0.092	0.079
0.602	0.701	0.902 85	0.218	0.236	0.000	0.000	0.861 27		
0.511	0.619	0.896 18	0.238	0.248					
				Ethyl Acetate (1) + Benzene (2)					
1.000	1.000	0.901 00			0.406	0.383	0.886 79	0.139	0.150
0.900	0.891	0.898 36	0.051	0.053	0.306	0.286	0.884 72	0.127	0.139
0.806	0.791	0.895 96	0.090	0.094	0.201	0.186	0.882 70	0.100	0.110
0.709	0.689	0.893 60	0.115	0.121	0.105	0.097	0.880 99	0.061	0.068
0.611	0.588	0.891 30	0.133	0.141	0.000	0.000	0.879 31		
0.509	0.485	0.889 00	0.141	0.151					
				Ethyl Acetate (1) + Toluene (2)					
1.000	1.000	0.901 05			0.492	0.513	0.883 99	−0.020	−0.019
0.897	0.905	0.897 56	0.000	0.000	0.389	0.409	0.880 53	−0.022	−0.022
0.799	0.812	0.894 26	−0.004	−0.004	0.291	0.308	0.877 22	−0.024	−0.024
0.699	0.717	0.890 93	−0.008	−0.008	0.100	0.107	0.870 61	−0.011	−0.010
0.597	0.617	0.887 51	−0.014	−0.014	0.000	0.000	0.867 15		
				Ethyl Acetate (1) + Ethylbenzene (2)					
1.000	1.000	0.900 99			0.397	0.452	0.880 20	0.105	0.094
0.897	0.916	0.897 16	0.047	0.047	0.295	0.344	0.876 99	0.085	0.075
0.803	0.836	0.893 82	0.073	0.072	0.195	0.233	0.873 86	0.063	0.054
0.703	0.748	0.890 35	0.095	0.091	0.146	0.177	0.872 37	0.046	0.039
0.610	0.662	0.887 17	0.107	0.101	0.000	0.000	0.867 86		
0.497	0.553	0.883 44	0.111	0.102					
				Ethyl Acetate (1) + *p*-Xylene (2)					
1.000	1.000	0.900 99			0.401	0.458	0.877 34	−0.009	−0.008
0.903	0.921	0.897 11	0.004	0.004	0.300	0.350	0.873 32	−0.010	−0.009
0.815	0.847	0.893 60	0.006	0.006	0.230	0.274	0.870 59	−0.013	−0.011
0.705	0.750	0.889 26	0.004	0.004	0.107	0.131	0.865 68	−0.008	−0.007
0.610	0.663	0.885 53	0.001	0.001	0.000	0.000	0.861 38		
0.503	0.560	0.881 31	−0.002	−0.002					
				Propyl Acetate (1) + Benzene (2)					
1.000	1.000	0.887 78			0.403	0.342	0.882 04	0.077	0.079
0.900	0.875	0.886 76	0.022	0.020	0.302	0.251	0.881 22	0.072	0.076
0.805	0.761	0.885 81	0.040	0.037	0.197	0.159	0.880 44	0.059	0.063
0.705	0.648	0.884 83	0.055	0.052	0.100	0.079	0.879 83	0.036	0.040
0.608	0.545	0.883 91	0.065	0.063	0.000	0.000	0.879 34		
0.502	0.438	0.882 92	0.074	0.074					
				Propyl Acetate (1) + Toluene (2)					
1.000	1.000	0.887 81			0.397	0.378	0.876 24	−0.105	−0.096
0.896	0.888	0.885 97	−0.039	−0.034	0.300	0.283	0.874 15	−0.094	−0.087
0.805	0.793	0.884 30	−0.064	−0.056	0.198	0.185	0.871 84	−0.067	−0.062
0.703	0.686	0.882 38	−0.087	−0.078	0.104	0.097	0.869 71	−0.042	−0.039
0.601	0.582	0.880 41	−0.102	−0.091	0.000	0.000	0.867 23		
0.485	0.465	0.878 08	−0.109	−0.099					

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})	$\Delta V/10^{-2}$
				Propyl Acetate (1) + Ethylbenzene (2)					
1.000	1.000	0.887 75			0.404	0.419	0.875 61	0.003	0.002
0.896	0.902	0.885 59	0.006	0.005	0.301	0.314	0.873 54	−0.001	−0.001
0.796	0.806	0.883 55	0.008	0.007	0.203	0.214	0.871 57	−0.003	−0.002
0.707	0.720	0.881 73	0.009	0.008	0.097	0.102	0.869 40	−0.002	−0.002
0.604	0.618	0.879 63	0.008	0.007	0.000	0.000	0.867 41		
0.499	0.515	0.877 52	0.005	0.004					
				Propyl Acetate (1) + *p*-Xylene (2)					
1.000	1.000	0.887 80			0.501	0.518	0.875 27	−0.087	−0.073
0.902	0.908	0.885 39	−0.024	−0.021	0.391	0.407	0.872 38	−0.088	−0.074
0.798	0.809	0.882 83	−0.046	−0.040	0.293	0.308	0.869 75	−0.082	−0.068
0.705	0.719	0.880 50	−0.064	−0.054	0.199	0.210	0.867 15	−0.065	−0.054
0.605	0.621	0.877 96	−0.078	−0.066	0.000	0.000	0.861 43		
				Butyl Acetate (1) + Benzene (2)					
1.000	1.000	0.881 78			0.400	0.310	0.879 41	0.108	0.106
0.899	0.858	0.881 31	0.032	0.026	0.294	0.220	0.879 20	0.098	0.100
0.802	0.732	0.880 87	0.059	0.049	0.199	0.143	0.879 11	0.080	0.084
0.703	0.615	0.880 45	0.081	0.070	0.094	0.065	0.879 15	0.047	0.051
0.609	0.512	0.880 07	0.097	0.088	0.000	0.000	0.879 37		
0.500	0.403	0.879 68	0.108	0.101					
				Butyl Acetate (1) + Toluene (2)					
1.000	1.000	0.881 79			0.391	0.341	0.873 75	−0.106	−0.092
0.895	0.874	0.880 59	−0.046	−0.036	0.307	0.263	0.872 43	−0.093	−0.082
0.789	0.751	0.879 28	−0.080	−0.063	0.197	0.166	0.870 68	−0.069	−0.062
0.702	0.655	0.878 15	−0.098	−0.079	0.086	0.071	0.868 77	−0.032	−0.029
0.589	0.536	0.876 63	−0.111	−0.093	0.000	0.000	0.867 27		
0.491	0.438	0.875 25	−0.114	−0.097					
				Butyl Acetate (1) + Ethylbenzene (2)					
1.000	1.000	0.881 65			0.398	0.380	0.873 29	−0.030	−0.023
0.900	0.893	0.880 29	−0.011	−0.008	0.308	0.293	0.87 203	−0.032	−0.026
0.804	0.792	0.878 97	−0.017	−0.013	0.204	0.192	0.870 47	−0.022	−0.017
0.701	0.686	0.877 56	−0.023	−0.018	0.106	0.100	0.869 03	−0.014	−0.011
0.611	0.594	0.876 29	−0.026	−0.020	0.000	0.000	0.867 42		
0.498	0.480	0.874 70	−0.028	−0.022					
				Butyl Acetate (1) + *p*-Xylene (2)					
1.000	1.000	0.881 72			0.399	0.383	0.870 35	−0.123	−0.097
0.903	0.897	0.880 01	−0.040	−0.031	0.301	0.288	0.868 32	−0.114	−0.091
0.799	0.788	0.878 15	−0.076	−0.059	0.206	0.195	0.866 23	−0.091	−0.073
0.701	0.687	0.876 36	−0.104	−0.081	0.105	0.099	0.863 93	−0.054	−0.044
0.606	0.590	0.874 53	−0.119	−0.093	0.000	0.000	0.861 41		
0.504	0.488	0.872 52	−0.126	−0.099					
				Amyl Acetate (1) + Benzene (2)					
1.000	1.000	0.877 78			0.406	0.290	0.877 60	0.129	0.121
0.906	0.852	0.877 69	0.038	0.027	0.307	0.210	0.877 78	0.119	0.118
0.804	0.711	0.877 60	0.071	0.054	0.211	0.138	0.878 08	0.097	0.100
0.705	0.588	0.877 53	0.098	0.079	0.102	0.064	0.878 59	0.056	0.060
0.610	0.484	0.877 49	0.117	0.100	0.000	0.000	0.879 27		
0.509	0.383	0.877 51	0.128	0.114					
				Amyl Acetate (1) + Toluene (2)					
1.000	1.000	0.877 80			0.409	0.331	0.872 38	−0.123	−0.102
0.914	0.884	0.877 18	−0.047	−0.033	0.308	0.241	0.871 19	−0.104	−0.089
0.820	0.765	0.876 43	−0.088	−0.063	0.219	0.168	0.870 09	−0.081	−0.071
0.709	0.636	0.875 47	−0.118	−0.089	0.103	0.076	0.868 56	−0.041	−0.038
0.610	0.528	0.874 53	−0.131	−0.102	0.000	0.000	0.867 13		
0.501	0.418	0.873 40	−0.132	−0.106					
				Amyl Acetate (1) + Ethylbenzene (2)					
1.000	1.000	0.877 78			0.404	0.359	0.872 11	−0.043	−0.032
0.899	0.880	0.876 85	−0.013	−0.009	0.303	0.264	0.871 09	−0.039	−0.031
0.807	0.775	0.876 01	−0.025	−0.017	0.201	0.171	0.870 00	−0.029	−0.023
0.696	0.653	0.874 96	−0.034	−0.024	0.099	0.083	0.868 90	−0.017	−0.014
0.612	0.565	0.874 16	−0.040	−0.029	0.000	0.000	0.867 80		
0.497	0.449	0.873 04	−0.043	−0.032					
				Amyl Acetate (1) + *p*-Xylene (2)					
1.000	1.000	0.877 77			0.404	0.361	0.869 06	−0.168	−0.127
0.899	0.881	0.876 48	0.060	0.041	0.297	0.260	0.867 17	−0.147	−0.113
0.804	0.773	0.875 20	−0.107	−0.075	0.202	0.174	0.865 40	−0.116	−0.091
0.709	0.669	0.873 86	−0.142	−0.101	0.101	0.085	0.863 39	−0.063	−0.050
0.596	0.551	0.872 19	−0.167	−0.122	0.000	0.000	0.861 29		
0.499	0.453	0.870 65	−0.175	−0.130					

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})	$\Delta V/10^{-2}$
				Acetone (1) + Benzene (2)					
1.000	1.000	0.791 30			0.392	0.439	0.845 39	−0.071	−0.087
0.896	0.912	0.800 63	−0.015	−0.020	0.290	0.331	0.854 23	−0.056	−0.067
0.792	0.822	0.809 86	−0.029	−0.039	0.195	0.227	0.862 46	−0.047	−0.055
0.692	0.731	0.818 77	−0.041	−0.053	0.098	0.116	0.870 80	−0.026	−0.030
0.598	0.643	0.827 15	−0.052	−0.066	0.000	0.000	0.879 12		
0.502	0.550	0.835 65	−0.061	−0.075					
				Acetone (1) + Toluene (2)					
1.000	1.000	0.791 42			0.402	0.493	0.838 15	−0.164	−0.182
0.900	0.928	0.799 39	−0.037	−0.049	0.296	0.378	0.846 10	−0.162	−0.173
0.795	0.849	0.807 71	−0.078	−0.100	0.199	0.265	0.853 10	−0.133	−0.136
0.701	0.772	0.815 16	−0.111	−0.137	0.094	0.131	0.860 57	−0.081	−0.079
0.597	0.682	0.823 27	−0.140	−0.168	0.000	0.000	0.866 99		
0.498	0.590	0.830 83	−0.157	−0.180					
				Acetone (1) + Ethylbenzene (2)					
1.000	1.000	0.791 54			0.401	0.528	0.837 93	−0.087	−0.090
0.917	0.949	0.797 98	−0.012	−0.015	0.314	0.433	0.844 50	−0.084	−0.083
0.800	0.870	0.807 03	−0.027	−0.034	0.199	0.293	0.853 18	−0.075	−0.069
0.710	0.803	0.814 10	−0.044	−0.052	0.098	0.153	0.860 68	−0.047	−0.041
0.604	0.718	0.822 27	−0.058	−0.067	0.000	0.000	0.867 77		
0.500	0.625	0.830 38	−0.077	−0.084					
				Acetone (1) + *p*-Xylene (2)					
1.000	1.000	0.791 34			0.399	0.527	0.834 37	−0.120	−0.123
0.897	0.936	0.798 84	−0.029	−0.037	0.304	0.424	0.840 88	−0.117	−0.115
0.798	0.869	0.805 97	−0.054	−0.067	0.199	0.295	0.848 06	−0.102	−0.094
0.703	0.799	0.812 88	−0.079	−0.095	0.098	0.154	0.854 87	−0.072	−0.062
0.601	0.716	0.820 12	−0.094	−0.108	0.000	0.000	0.861 16		
0.490	0.617	0.827 99	−0.116	−0.126					
				2-Butanone (1) + Benzene (2)					
1.000	1.000	0.806 17			0.405	0.403	0.850 65	−0.100	−0.112
0.905	0.904	0.813 55	−0.046	−0.052	0.308	0.307	0.857 53	−0.081	−0.091
0.810	0.809	0.820 75	−0.078	−0.087	0.205	0.204	0.864 84	−0.053	−0.060
0.713	0.711	0.828 10	−0.099	−0.111	0.101	0.100	0.872 15	−0.022	−0.025
0.614	0.612	0.835 43	−0.111	−0.124	0.000	0.000	0.879 30		
0.501	0.500	0.843 68	−0.110	−0.124					
				2-Butanone (1) + Toluene (2)					
1.000	1.000	0.806 18			0.405	0.447	0.844 44	−0.229	−0.232
0.904	0.918	0.812 71	−0.076	−0.084	0.303	0.340	0.850 40	−0.201	−0.200
0.810	0.835	0.818 93	−0.133	−0.145	0.200	0.229	0.856 24	−0.154	−0.151
0.712	0.746	0.825 34	−0.182	−0.194	0.100	0.117	0.861 75	−0.086	−0.082
0.607	0.647	0.832 05	−0.216	−0.227	0.000	0.000	0.867 16		
0.506	0.549	0.838 30	−0.233	−0.240					
				2-Butanone (1) + Ethylbenzene (2)					
1.000	1.000	0.805 31			0.397	0.474	0.844 28	−0.165	−0.155
0.880	0.909	0.813 29	−0.057	−0.061	0.302	0.372	0.850 09	−0.152	−0.138
0.810	0.853	0.817 93	−0.085	−0.090	0.201	0.255	0.856 18	−0.122	−0.107
0.708	0.768	0.824 59	−0.120	−0.124	0.087	0.115	0.862 82	−0.064	−0.054
0.596	0.668	0.831 81	−0.150	−0.149	0.000	0.000	0.867 79		
0.498	0.575	0.838 02	−0.163	−0.157					
				2-Butanone (1) + *p*-Xylene (2)					
1.000	1.000	0.805 29			0.380	0.458	0.841 52	−0.190	−0.176
0.902	0.927	0.811 26	−0.056	−0.061	0.298	0.369	0.845 99	−0.175	−0.158
0.780	0.830	0.818 60	−0.116	−0.121	0.183	0.236	0.852 06	−0.128	−0.111
0.682	0.747	0.824 42	−0.153	−0.156	0.082	0.109	0.857 28	−0.071	−0.059
0.595	0.669	0.829 47	−0.176	−0.175	0.000	0.000	0.861 37		
0.504	0.583	0.834 65	−0.192	−0.185					

Accordingly ΔV can be expressed as

$$\Delta V/\varphi_1\varphi_2 = \sum_j b_j(\varphi_2 - \varphi_1)^j \quad (6)$$

Coefficients in eqs 5 and 6 were obtained by least-squares fitting and are assembled 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 definitions as follows

$$\sigma(V^E/x_1x_2) = [\sum(V^E_{calc}/x_1x_2 - V^E/x_1x_2)^2/(N - n - 1)]^{1/2} \quad (7)$$

$$\sigma(\Delta V/\varphi_1\varphi_2) = [\sum(\Delta V_{calc}/\varphi_1\varphi_2 - \Delta V/\varphi_1\varphi_2)^2/(N - n - 1)]^{1/2} \quad (8)$$

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

We were able to find only a few literature data to compare with our systems. The literature data were all measured at 25 °C. Our experimental values and literature values of V^E interpolated to molar fraction 0.5 are listed in Table III. We consider the agreement to be quite acceptable.

As a group, the mixtures of carbonyl compounds and aromatic hydrocarbons exhibit quite small excess volumes of mixing; they are frequently even negative. The compositional dependence of $\Delta V/\varphi_1\varphi_2$ is in most cases rather small. This contrasts with the excess volumes of carbonyl compounds/alkanes mixtures that were very large and strongly composition

Table II. Parameters of Equations 5 and 6 and Standard Deviations[a]

system	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}
MA-BE	1.329	−0.040	0.041	0.007	1.584	0.041	0.048	0.008
MA-TO	0.795	−0.219	0.050	0.005	0.892	−0.111	0.003	0.005
MA-EB	1.302	−0.358	0.101	0.023	1.371	−0.076	0.002	0.021
MA-PX	0.919	−0.298	0.026	0.024	0.971	−0.087	−0.055	0.022
EA-BE	0.562	0.101	0.083	0.006	0.608	0.082	0.080	0.006
EA-TO	−0.082	−0.073	0.040	0.005	−0.078	−0.076	0.033	0.006
EA-EB	0.424	−0.171	0.038	0.018	0.403	−0.113	0.053	0.015
EA-PX	−0.025	−0.084	0.022	0.004	−0.014	−0.080	0.001	0.004
PA-BE	0.278	0.171	0.098	0.004	0.295	0.138	0.055	0.002
PA-TO	−0.429	−0.057	−0.001	0.011	−0.390	−0.036	0.003	0.010
PA-EB	0.018	−0.059	0.006	0.002	0.017	−0.049	0.002	0.002
PA-PX	−0.351	−0.079	0.006	0.001	−0.292	−0.076	0.000	0.001
BA-BE	0.386	0.272	0.161	0.014	0.401	0.188	0.055	0.006
BA-TO	−0.454	−0.050	0.006	0.008	−0.386	0.000	0.010	0.006
BA-EB	−0.116	−0.034	−0.025	0.009	−0.093	−0.024	−0.018	0.008
BA-PX	−0.507	−0.103	−0.023	0.008	−0.401	−0.068	−0.013	0.006
AA-BE	0.450	0.352	0.215	0.010	0.462	0.214	0.041	0.002
AA-TO	−0.531	−0.078	0.014	0.002	−0.427	0.010	0.019	0.002
AA-EB	−0.170	−0.059	−0.003	0.004	−0.129	−0.032	0.005	0.003
AA-PX	−0.692	−0.152	0.000	0.008	−0.520	−0.064	0.017	0.005
AC-BE	−0.255	−0.049	0.054	0.015	−0.308	−0.094	0.050	0.019
AC-TO	−0.669	−0.073	0.038	0.014	−0.729	−0.223	−0.012	0.015
AC-EB	−0.341	−0.074	0.058	0.012	−0.326	−0.170	−0.010	0.012
AC-PX	−0.483	−0.043	−0.053	0.015	−0.482	−0.163	−0.099	0.021
BU-BE	−0.443	0.161	0.079	0.014	−0.495	0.182	0.088	0.015
BU-TO	−0.926	0.097	0.021	0.012	−0.955	0.016	0.029	0.012
BU-EB	−0.663	0.036	0.010	0.002	−0.631	−0.065	0.005	0.002
BU-PX	−0.770	0.074	−0.005	0.010	−0.735	−0.047	0.000	0.010

[a] ME, methyl acetate; EA, ethyl acetate; PA, propyl acetate; BA, butyl acetate; AA, amyl acetate; AC, acetone; BU, 2-butanone; BE, benzene; TO, toluene; EB, ethylbenzene; PX, *p*-xylene.

Table III. V^E at $x_1 = 0.5$

system[a]	V^E(expt)	V^E(lit.)
MA-BE	0.332	0.309 (*5*)
EA-BE	0.141	0.117 (*5*)
EA-TO	−0.021	−0.026 (*5*)
EA-EB	0.110	0.108 (*5*)
AC-BE	−0.061	−0.067 (*6*)
AC-BE	−0.061	−0.070 (*7*)
AC-TO	−0.167	−0.162 (*7*)
AC-PX	−0.121	−0.110 (*7*)
BU-BE	−0.111	−0.116 (*8*)

[a] Abbreviations are defined in footnote *a* of Table II.

dependent (*3*). ($\Delta V/\varphi_1\varphi_2$ increased for mixtures poor in the carbonyl compound.) We have explained that behavior by the strong polar character of the carbonyl compounds: the increase of the volume is related to the energetically unfavorable disruption of the interaction of the strongly polar carbonyls by the alkane molecules. Moreover, the dipolar interactions of the carbonyls tended to produce a nonregular mixture with a pronounced compositional dependence of the $\Delta V/\varphi_1\varphi_2$ value. This peculiar behavior of carbonyl compounds is absent in their mixtures with aromatic hydrocarbons.

In Figure 1 the $\Delta V/\varphi_1\varphi_2$ values are plotted for mixtures of propyl acetate and the four aromatic compounds. (Very similar plots could be drawn for all carbonyl compounds.) By comparing families of similar mixtures, it can be seen that the excess volume increases with the increasing aliphatic content of the aromatic hydrocarbon: from toluene to *p*-xylene to ethylbenzene. However, the behavior of benzene is out of line.

The $\Delta V/\varphi_1\varphi_2$ values of mixtures of ethylbenzene with all our carbonyl compounds were plotted in Figure 2. (Other aromatics yield similar pictures.) The $\Delta V/\varphi_1\varphi_2$ values decrease with the increasing length of the alkyl groups. The lowest values are for ketones. Apparently, the specific interaction of ketones with aromatics is stronger than that of esters.

Registry No. BE, 71-43-2; TO, 108-88-3; EB, 100-41-4; PX, 106-42-3; MA, 79-20-9; EA, 141-78-6; PA, 109-60-4; BA, 123-86-4; AA, 628-63-7; AC, 67-64-1; BU, 78-93-3.

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