EXCESS VOLUMES OF MIXTURES OF SOME ALKYL ESTERS AND KETONES WITH ALKANOLS

Anwei QIN, Dolly E. HOFFMAN and Petr MUNK*

Department of Chemistry and Biochemistry and Center for Polymer Research, The University of Texas at Austin, Austin, Texas 78712, U.S.A.

Received April 6, 1993
Accepted April 22, 1993

Dedicated to Professor Otto Wichterle on the occasion of his 80th birthday.

Excess volumes were calculated from measured densities of binary mixtures of five linear alkanols (methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol) with five n-alkyl acetates (methyl, ethyl, propyl, butyl, and pentyl acetates) and with two ketones (acetone and 2-butanone) at 20 °C. The whole composition range was studied for all thirty-five binary systems. For a given alcohol, the $\Delta V/\varphi_1 \varphi_2$ value decreases with increasing size of the carbonyl compound. For a given carbonyl compound, it increases with the length of the alkanol. Systems with methyl acetate as one component have relatively large $\Delta V/\varphi_1 \varphi_2$ values, while systems with methanol display different compositional dependency in respect to systems with other alcohols.

For a few years, we have been working on accumulating a large quantity of thermodynamic data of binary mixtures using different methods such as light scattering, inverse gas chromatography, densitometry, and calorimetry[1,2] in order to develop a comprehensive theory which would explain simultaneously all the important aspects of liquid mixtures. In our previous papers[3-5], we have shown the dependence of excess volume on composition for binary mixtures between alkanes, carbonyl compounds and aromatic hydrocarbons. In the present paper, we are reporting the measurements of excess volumes of alcohols and some esters and ketones. The esters included methyl, ethyl, propyl, butyl, and pentyl acetate. The ketones were acetone and 2-butanone. The alcohols were five linear primary alcohols: methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol. Altogether 35 binary systems were prepared and for each system, the dependence of the excess volume on composition was studied.

* The author to whom correspondence should be addressed.

In an accompanying paper[6], the dependence of excess volumes on composition for 20 systems consisting of the same five alkanols with four aromatic hydrocarbons (benzene, toluene, ethylbenzene, and *p*-xylene) is reported.

EXPERIMENTAL

All esters, ketones and alkanols were obtained from Aldrich Chemical Co. with the purity better than 99% and used as supplied. The measurement of densities was described in our previous paper[3]. All experiments were performed at 20 °C. The experimental results are listed in Table I.

RESULTS AND DISCUSSION

By measuring the masses m_i, the densities ρ_i of the pure components, and the densities ρ_m of the mixtures, the mole fraction x_i, the volume fractions φ_i, the molar excess volumes V^E, and the relative change in volume $\Delta V = V^E/(x_1 V_1^0 + x_2 V_2^0)$ at different compositions can be calculated. V_i^0 is molar volume of pure component i.

Experimental data for V^E are usually correlated by means of a power series.

$$V^E/x_1 x_2 = \sum_j a_j (x_2 - x_1)^j . \qquad (1)$$

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

$$\Delta V/\varphi_1 \varphi_2 = \sum_j b_j (\varphi_2 - \varphi_1)^j . \qquad (2)$$

The coefficients in Eqs (*1*) and (*2*) obtained by least square fitting to the second order are collected in Table II together with the standard deviations of the fits, $\sigma(V^E/x_1 x_2)$ and $\sigma(\Delta V/\varphi_1 \varphi_2)$, which are defined as follows

$$\sigma(V^E/x_1 x_2) = [\sum (V^E_{calc}/x_1 x_2 - V^E/x_1 x_2)^2/(N - n - 1)]^{1/2} \qquad (3)$$

$$\sigma(\Delta V/\varphi_1 \varphi_2) = [\sum (\Delta V_{calc}/\varphi_1 \varphi_2 - \Delta V/\varphi_1 \varphi_2)^2/(N - n - 1)]^{1/2} , \qquad (4)$$

where N is the number of experimental points and n is the number of coefficients.

As examples, the dependencies on composition for systems of 1-butanol with various acetates and ketones are plotted in Fig. 1, the dependencies for systems of different alcohols with propyl acetate and with acetone are plotted in Figs 2 and 3, respectively.

TABLE I
Excess volumes of mixing for alkanols and carbonyl compounds at 20 °C

φ_1	x_1	ρ, g cm^{-3}	V^E, cm^3 mol^{-1}	$\Delta V . 10^2$
		Methanol(1)–methyl acetate(2)		
1.000	1.000	0.79165	0	0
0.904	0.949	0.80554	−0.015	−0.035
0.809	0.892	0.81934	−0.026	−0.059
0.699	0.820	0.83525	−0.043	−0.090
0.602	0.748	0.84923	−0.053	−0.106
0.503	0.664	0.86353	−0.065	−0.121
0.411	0.578	0.87665	−0.076	−0.134
0.305	0.462	0.89183	−0.080	−0.131
0.206	0.337	0.90573	−0.076	−0.114
0.102	0.182	0.92013	−0.049	−0.067
0.000	0.000	0.93405	0	0
		Methanol(1)–ethyl acetate(2)		
1.000	1.000	0.79166	0	0
0.900	0.956	0.80291	−0.016	−0.037
0.800	0.906	0.81403	−0.030	−0.065
0.699	0.849	0.82526	−0.045	−0.091
0.604	0.787	0.83591	−0.062	−0.117
0.498	0.705	0.84759	−0.070	−0.121
0.398	0.615	0.85868	−0.088	−0.141
0.296	0.504	0.86980	−0.093	−0.134
0.194	0.368	0.88077	−0.085	−0.111
0.107	0.225	0.88993	−0.064	−0.075
0.000	0.000	0.90099	0	0
		Methanol(1)–propyl acetate(2)		
1.000	1.000	0.79203	0	0
0.898	0.962	0.80202	−0.014	−0.032
0.799	0.919	0.81170	−0.025	−0.054
0.699	0.868	0.82142	−0.039	−0.078
0.600	0.810	0.83105	−0.055	−0.101
0.499	0.739	0.84077	−0.063	−0.105
0.397	0.652	0.85052	−0.075	−0.113
0.297	0.545	0.86018	−0.085	−0.114
0.193	0.405	0.86989	−0.079	−0.094
0.104	0.249	0.87815	−0.065	−0.068
0.000	0.000	0.88751	0	0

TABLE I
(*Continued*)

φ_1	x_1	ρ, g cm^{-3}	V^E, cm^3 mol^{-1}	$\Delta V \cdot 10^2$
		Methanol(1)–butyl acetate(2)		
1.000	1.000	0.79163	0	0
0.901	0.967	0.80054	–0.001	–0.003
0.804	0.930	0.80937	–0.004	–0.010
0.698	0.883	0.81891	–0.009	–0.017
0.599	0.830	0.82793	–0.017	–0.031
0.492	0.759	0.83762	–0.023	–0.037
0.393	0.678	0.84662	–0.033	–0.047
0.297	0.579	0.85526	–0.038	–0.049
0.204	0.455	0.86366	–0.045	–0.050
0.098	0.260	0.87304	–0.031	–0.028
0.000	0.000	0.88158	0	0
		Methanol(1)–pentyl acetate(2)		
1.000	1.000	0.79165	0	0
0.885	0.966	0.80144	0.005	0.011
0.795	0.934	0.80915	0.008	0.016
0.697	0.894	0.81767	0.004	0.008
0.594	0.843	0.82651	0.007	0.012
0.502	0.787	0.83472	–0.011	–0.017
0.401	0.710	0.84352	–0.023	–0.032
0.300	0.612	0.85219	–0.029	–0.035
0.196	0.472	0.86127	–0.044	–0.046
0.088	0.262	0.87047	–0.039	–0.033
0.000	0.000	0.87777	0	0
		Methanol(1)–acetone(2)		
1.000	1.000	0.79167	0	0
0.888	0.935	0.79354	–0.104	–0.244
0.802	0.880	0.79463	–0.172	–0.387
0.696	0.806	0.79557	–0.240	–0.513
0.597	0.729	0.79610	–0.289	–0.586
0.502	0.647	0.79635	–0.325	–0.624
0.396	0.543	0.79617	–0.338	–0.608
0.297	0.433	0.79564	–0.325	–0.550
0.195	0.306	0.79467	–0.276	–0.435
0.098	0.164	0.79321	–0.176	–0.259
0.000	0.000	0.79110	0	0

TABLE I
(*Continued*)

φ_1	x_1	ρ, g cm^{-3}	V^E, cm^3 mol^{-1}	$\Delta V \cdot 10^2$
		Methanol(1)–2-butanone(2)		
1.000	1.000	0.79195	0	0
0.904	0.954	0.79429	−0.054	−0.127
0.805	0.901	0.79668	−0.114	−0.251
0.704	0.840	0.79879	−0.163	−0.338
0.605	0.772	0.80060	−0.202	−0.392
0.505	0.693	0.80231	−0.238	−0.429
0.403	0.599	0.80372	−0.257	−0.427
0.306	0.493	0.80469	−0.247	−0.378
0.198	0.354	0.80572	−0.230	−0.319
0.096	0.191	0.80612	−0.154	−0.192
0.000	0.000	0.80592	0	0
		Ethanol(1)–methyl acetate(2)		
1.000	1.000	0.78989	0	0
0.899	0.924	0.80364	0.056	0.094
0.811	0.854	0.81570	0.101	0.164
0.700	0.761	0.83132	0.133	0.210
0.505	0.581	0.85898	0.173	0.258
0.407	0.483	0.87306	0.172	0.249
0.303	0.372	0.88817	0.164	0.230
0.205	0.260	0.90261	0.140	0.189
0.106	0.139	0.91747	0.091	0.119
0.000	0.000	0.93388	0	0
		Ethanol(1)–ethyl acetate(2)		
1.000	1.000	0.78989	0	0
0.887	0.930	0.80195	0.033	0.055
0.801	0.871	0.81122	0.058	0.092
0.699	0.796	0.82228	0.083	0.126
0.603	0.718	0.83279	0.104	0.149
0.495	0.622	0.84454	0.124	0.170
0.399	0.527	0.85510	0.135	0.176
0.288	0.404	0.86750	0.136	0.166
0.193	0.287	0.87822	0.122	0.141
0.083	0.132	0.89094	0.078	0.084
0.000	0.000	0.90093	0	0

TABLE I
(*Continued*)

φ_1	x_1	ρ, g cm^{-3}	V^E, cm^3 mol^{-1}	$\Delta V \cdot 10^2$
		Ethanol(1)–propyl acetate(2)		
1.000	1.000	0.78988	0	0
0.902	0.948	0.79920	0.019	0.031
0.807	0.892	0.80834	0.035	0.054
0.702	0.823	0.81845	0.049	0.072
0.603	0.750	0.82798	0.064	0.088
0.492	0.657	0.83875	0.077	0.099
0.411	0.579	0.84664	0.088	0.107
0.304	0.463	0.85709	0.092	0.104
0.197	0.327	0.86765	0.088	0.091
0.102	0.183	0.87722	0.067	0.064
0.000	0.000	0.88775	0	0
		Ethanol(1)–butyl acetate(2)		
1.000	1.000	0.79001	0	0
0.898	0.952	0.79910	0.021	0.034
0.797	0.899	0.80813	0.036	0.055
0.696	0.838	0.81723	0.056	0.079
0.605	0.776	0.82548	0.067	0.090
0.486	0.682	0.83617	0.088	0.108
0.402	0.603	0.84385	0.099	0.114
0.297	0.489	0.85339	0.113	0.117
0.197	0.357	0.86267	0.110	0.104
0.106	0.212	0.87119	0.093	0.080
0.000	0.000	0.88165	0	0
		Ethanol(1)–pentyl acetate(2)		
1.000	1.000	0.78999	0	0
0.899	0.958	0.79863	0.018	0.029
0.801	0.911	0.80709	0.029	0.044
0.696	0.853	0.81619	0.043	0.061
0.597	0.790	0.82476	0.055	0.072
0.506	0.723	0.83265	0.068	0.082
0.398	0.627	0.84210	0.087	0.095
0.300	0.522	0.85067	0.093	0.092
0.193	0.378	0.86015	0.096	0.084
0.098	0.216	0.86867	0.080	0.062
0.000	0.000	0.87780	0	0

TABLE I
(*Continued*)

φ_1	x_1	ρ, g cm^{-3}	V^E, cm^3 mol^{-1}	$\Delta V \cdot 10^2$
		Ethanol(1)–acetone(2)		
1.000	1.000	0.79002	0	0
0.895	0.915	0.79064	−0.038	−0.064
0.790	0.826	0.79106	−0.063	−0.103
0.690	0.737	0.79131	−0.075	−0.120
0.595	0.649	0.79145	−0.080	−0.126
0.491	0.549	0.79154	−0.080	−0.123
0.395	0.451	0.79156	−0.074	−0.111
0.297	0.347	0.79151	−0.062	−0.092
0.195	0.234	0.79140	−0.045	−0.064
0.106	0.130	0.79128	−0.026	−0.037
0.000	0.000	0.79110	0	0
		Ethanol(1)–2-butanone(2)		
1.000	1.000	0.79007	0	0
0.899	0.932	0.79208	−0.032	−0.053
0.801	0.860	0.79393	−0.057	−0.091
0.704	0.785	0.79560	−0.071	−0.109
0.606	0.702	0.79724	−0.081	−0.120
0.507	0.612	0.79874	−0.080	−0.114
0.403	0.509	0.80029	−0.076	−0.103
0.306	0.403	0.80175	−0.072	−0.094
0.210	0.289	0.80301	−0.051	−0.063
0.096	0.141	0.80449	−0.021	−0.025
0.000	0.000	0.80580	0	0
		1-Propanol(1)–methyl acetate(2)		
1.000	1.000	0.80395	0	0
0.903	0.908	0.81527	0.116	0.154
0.809	0.818	0.82656	0.201	0.266
0.699	0.711	0.84018	0.268	0.353
0.593	0.608	0.85339	0.310	0.405
0.515	0.530	0.86343	0.323	0.420
0.401	0.415	0.87834	0.311	0.401
0.287	0.299	0.89362	0.271	0.348
0.201	0.211	0.90531	0.219	0.280
0.106	0.112	0.91862	0.136	0.173
0.000	0.000	0.93405	0	0

TABLE I
(*Continued*)

φ_1	x_1	ρ, g cm^{-3}	V^E, cm^3 mol^{-1}	$\Delta V \cdot 10^2$
		1-Propanol(1)–ethyl acetate(2)		
1.000	1.000	0.80399	0	0
0.900	0.922	0.81292	0.070	0.092
0.800	0.840	0.82205	0.126	0.161
0.694	0.748	0.83190	0.171	0.212
0.600	0.663	0.84070	0.200	0.243
0.504	0.570	0.84995	0.218	0.258
0.397	0.463	0.86031	0.221	0.254
0.296	0.355	0.87023	0.209	0.233
0.194	0.239	0.88056	0.172	0.187
0.101	0.128	0.89012	0.113	0.119
0.000	0.000	0.90100	0	0
		1-Propanol(1)–propyl acetate(2)		
1.000	1.000	0.80394	0	0
0.903	0.935	0.81164	0.045	0.058
0.801	0.861	0.81996	0.078	0.097
0.706	0.787	0.82765	0.106	0.127
0.600	0.698	0.83638	0.133	0.153
0.499	0.605	0.84472	0.155	0.171
0.394	0.500	0.85358	0.164	0.173
0.300	0.397	0.86156	0.165	0.167
0.200	0.278	0.87020	0.144	0.138
0.105	0.153	0.87863	0.095	0.087
0.000	0.000	0.88828	0	0
		1-Propanol(1)–butyl acetate(2)		
1.000	1.000	0.80499	0	0
0.898	0.939	0.81248	0.033	0.042
0.802	0.877	0.81955	0.063	0.077
0.704	0.807	0.82683	0.090	0.105
0.606	0.730	0.83414	0.115	0.127
0.504	0.642	0.84174	0.142	0.149
0.406	0.546	0.84919	0.157	0.156
0.307	0.439	0.85680	0.160	0.150
0.203	0.311	0.86488	0.149	0.131
0.108	0.176	0.87254	0.111	0.091
0.000	0.000	0.88160	0	0

TABLE I
(*Continued*)

φ_1	x_1	ρ, g cm^{-3}	V^E, cm^3 mol^{-1}	$\Delta V \cdot 10^2$
		1-Propanol(1)–pentyl acetate(2)		
1.000	1.000	0.80439	0	0
0.899	0.946	0.81155	0.026	0.033
0.799	0.887	0.81868	0.048	0.058
0.701	0.823	0.82571	0.070	0.079
0.604	0.752	0.83264	0.090	0.097
0.502	0.667	0.84004	0.108	0.109
0.402	0.572	0.84728	0.124	0.117
0.301	0.461	0.85472	0.129	0.112
0.202	0.334	0.86215	0.123	0.099
0.102	0.184	0.86971	0.090	0.067
0.000	0.000	0.87780	0	0
		1-Propanol(1)–acetone(2)		
1.000	1.000	0.80447	0	0
0.900	0.899	0.80323	−0.011	−0.014
0.797	0.795	0.80188	−0.016	−0.021
0.703	0.700	0.80062	−0.017	−0.023
0.602	0.598	0.79924	−0.017	−0.023
0.501	0.497	0.79782	−0.013	−0.017
0.407	0.403	0.79651	−0.010	−0.013
0.304	0.300	0.79505	−0.005	−0.007
0.198	0.196	0.79358	−0.002	−0.003
0.092	0.090	0.79214	−0.003	−0.004
0.000	0.000	0.79086	0	0
		1-Propanol(1)–2-butanone(2)		
1.000	1.000	0.80451	0	0
0.904	0.919	0.80479	−0.015	−0.020
0.801	0.828	0.80505	−0.027	−0.034
0.702	0.739	0.80526	−0.036	−0.045
0.600	0.642	0.80537	−0.034	−0.042
0.500	0.545	0.80550	−0.034	−0.042
0.401	0.445	0.80557	−0.029	−0.035
0.301	0.341	0.80566	−0.025	−0.029
0.205	0.236	0.80568	−0.014	−0.017
0.105	0.123	0.80573	−0.005	−0.006
0.000	0.000	0.80582	0	0

TABLE I
(*Continued*)

φ_1	x_1	ρ, g cm^{-3}	V^E, cm^3 mol^{-1}	$\Delta V \cdot 10^2$
		1-Butanol(1)–methyl acetate(2)		
1.000	1.000	0.81016	0	0
0.901	0.887	0.82104	0.156	0.173
0.801	0.777	0.83222	0.280	0.316
0.703	0.672	0.84369	0.354	0.405
0.600	0.566	0.85597	0.386	0.448
0.498	0.463	0.86843	0.393	0.463
0.401	0.367	0.88074	0.369	0.440
0.302	0.272	0.89343	0.321	0.388
0.196	0.174	0.90743	0.235	0.288
0.107	0.094	0.91931	0.154	0.191
0.000	0.000	0.93437	0	0
		1-Butanol(1)–ethyl acetate(2)		
1.000	1.000	0.81005	0	0
0.794	0.805	0.82720	0.175	0.189
0.696	0.710	0.83568	0.228	0.244
0.595	0.611	0.84461	0.257	0.274
0.496	0.513	0.85342	0.274	0.290
0.389	0.405	0.86334	0.257	0.270
0.291	0.305	0.87249	0.227	0.236
0.190	0.201	0.88215	0.172	0.178
0.100	0.106	0.89101	0.107	0.110
0.000	0.000	0.90106	0	0
		1-Butanol(1)–propyl acetate(2)		
1.000	1.000	0.80996	0	0
0.899	0.918	0.81734	0.065	0.069
0.802	0.836	0.82452	0.113	0.118
0.701	0.747	0.83209	0.150	0.154
0.594	0.648	0.84024	0.179	0.179
0.498	0.555	0.84771	0.192	0.188
0.398	0.454	0.85554	0.193	0.185
0.294	0.343	0.86385	0.178	0.167
0.200	0.239	0.87143	0.148	0.135
0.099	0.121	0.87983	0.092	0.082
0.000	0.000	0.88829	0	0

TABLE I
(*Continued*)

φ_1	x_1	ρ, g cm^{-3}	V^E, cm^3 mol^{-1}	$\Delta V . 10^2$
		1-Butanol(1)–butyl acetate(2)		
1.000	1.000	0.81026	0	0
0.897	0.926	0.81714	0.053	0.056
0.799	0.851	0.82381	0.095	0.098
0.705	0.775	0.83028	0.124	0.123
0.602	0.686	0.83742	0.150	0.145
0.504	0.594	0.84433	0.169	0.156
0.405	0.495	0.85141	0.172	0.154
0.306	0.388	0.85854	0.170	0.146
0.213	0.281	0.86530	0.148	0.123
0.110	0.151	0.87307	0.099	0.079
0.000	0.000	0.88159	0	0
		1-Butanol(1)–pentyl acetate(2)		
1.000	1.000	0.80997	0	0
0.894	0.932	0.81684	0.039	0.041
0.789	0.858	0.82370	0.070	0.070
0.705	0.795	0.82920	0.094	0.092
0.598	0.707	0.83631	0.119	0.110
0.510	0.628	0.84220	0.134	0.119
0.404	0.524	0.84935	0.143	0.120
0.291	0.399	0.85712	0.139	0.111
0.206	0.296	0.86301	0.123	0.094
0.110	0.166	0.86986	0.078	0.056
0.000	0.000	0.87778	0	0
		1-Butanol(1)–acetone(2)		
1.000	1.000	0.80996	0	0
0.889	0.865	0.80773	0.015	0.017
0.793	0.755	0.80580	0.027	0.032
0.701	0.653	0.80398	0.036	0.042
0.604	0.550	0.80208	0.042	0.050
0.499	0.444	0.80008	0.043	0.053
0.395	0.344	0.79815	0.038	0.048
0.291	0.248	0.79623	0.034	0.044
0.195	0.163	0.79450	0.025	0.033
0.105	0.086	0.79289	0.016	0.021
0.000	0.000	0.79109	0	0

TABLE I
(*Continued*)

φ_1	x_1	ρ, g cm^{-3}	V^E, cm^3 mol^{-1}	$\Delta V \cdot 10^2$
		1-Butanol(1)–2-butanone(2)		
1.000	1.000	0.80998	0	0
0.902	0.900	0.80955	−0.002	−0.003
0.800	0.796	0.80905	−0.001	−0.001
0.703	0.699	0.80860	0.000	0.000
0.594	0.589	0.80808	0.001	0.002
0.502	0.497	0.80765	0.001	0.002
0.404	0.398	0.80717	0.003	0.003
0.298	0.293	0.80668	0.003	0.003
0.197	0.194	0.80621	0.003	0.004
0.103	0.101	0.80577	0.003	0.003
0.000	0.000	0.80531	0	0
		1-Pentanol(1)–methyl acetate(2)		
1.000	1.000	0.81510	0	0
0.903	0.872	0.82504	0.208	0.199
0.806	0.753	0.83542	0.339	0.336
0.702	0.633	0.84693	0.431	0.442
0.608	0.532	0.85770	0.458	0.484
0.500	0.423	0.87035	0.461	0.504
0.405	0.333	0.88183	0.427	0.480
0.202	0.156	0.90749	0.260	0.311
0.097	0.073	0.92119	0.139	0.171
0.000	0.000	0.93434	0	0
		1-Pentanol(1)–ethyl acetate(2)		
1.000	1.000	0.81501	0	0
0.901	0.892	0.82248	0.130	0.122
0.801	0.785	0.83034	0.221	0.209
0.700	0.679	0.83851	0.282	0.269
0.604	0.580	0.84647	0.313	0.301
0.503	0.478	0.85505	0.317	0.308
0.402	0.378	0.86385	0.296	0.291
0.300	0.279	0.87294	0.257	0.255
0.194	0.179	0.88254	0.194	0.195
0.099	0.090	0.89149	0.105	0.106
0.000	0.000	0.90090	0	0

TABLE I
(*Continued*)

φ_1	x_1	ρ, g cm^{-3}	V^E, cm^3 mol^{-1}	$\Delta V \cdot 10^2$
		1-Pentanol(1)–propyl acetate(2)		
1.000	1.000	0.81502	0	0
0.903	0.908	0.82138	0.102	0.093
0.796	0.806	0.82877	0.155	0.142
0.703	0.715	0.83528	0.202	0.183
0.606	0.620	0.84218	0.225	0.204
0.502	0.517	0.84973	0.236	0.212
0.398	0.413	0.85737	0.229	0.204
0.306	0.319	0.86431	0.207	0.183
0.201	0.211	0.87229	0.162	0.142
0.106	0.112	0.87974	0.100	0.088
0.000	0.000	0.88829	0	0
		1-Pentanol(1)–butyl acetate(2)		
1.000	1.000	0.81533	0	0
0.895	0.912	0.82175	0.069	0.063
0.799	0.829	0.82775	0.125	0.111
0.698	0.738	0.83417	0.157	0.137
0.611	0.657	0.83983	0.177	0.153
0.508	0.557	0.84652	0.196	0.165
0.404	0.453	0.85342	0.194	0.160
0.313	0.357	0.85956	0.181	0.147
0.219	0.255	0.86603	0.152	0.121
0.109	0.130	0.87367	0.097	0.075
0.000	0.000	0.88157	0	0
		1-Pentanol(1)–pentyl acetate(2)		
1.000	1.000	0.81489	0	0
0.893	0.919	0.82115	0.068	0.061
0.697	0.759	0.83312	0.119	0.101
0.605	0.678	0.83875	0.140	0.116
0.492	0.570	0.84591	0.141	0.113
0.407	0.485	0.85119	0.152	0.118
0.302	0.372	0.85791	0.140	0.105
0.204	0.260	0.86427	0.114	0.083
0.100	0.132	0.87113	0.064	0.045
0.000	0.000	0.87780	0	0

TABLE I
(*Continued*)

φ_1	x_1	ρ, g cm^{-3}	V^E, cm^3 mol^{-1}	$\Delta V \cdot 10^2$
		1-Pentanol(1)–acetone(2)		
1.000	1.000	0.81494	0	0
0.903	0.863	0.81233	0.034	0.033
0.801	0.732	0.80966	0.060	0.061
0.708	0.622	0.80728	0.074	0.078
0.604	0.509	0.80468	0.083	0.091
0.495	0.399	0.80200	0.086	0.098
0.407	0.318	0.79991	0.080	0.095
0.304	0.229	0.79752	0.069	0.084
0.210	0.153	0.79537	0.055	0.070
0.102	0.072	0.79298	0.033	0.044
0.000	0.000	0.79088	0	0
		1-Pentanol(1)–2-butanone(2)		
1.000	1.000	0.81500	0	0
0.893	0.873	0.81381	0.019	0.018
0.790	0.757	0.81275	0.027	0.026
0.689	0.647	0.81173	0.031	0.031
0.590	0.543	0.81074	0.034	0.034
0.490	0.443	0.80981	0.029	0.030
0.385	0.341	0.80880	0.027	0.028
0.295	0.257	0.80794	0.025	0.026
0.201	0.172	0.80706	0.021	0.023
0.107	0.091	0.80622	0.014	0.015
0.000	0.000	0.80529	0	0

We were able to find a few literature data for some of our systems. The majority are quite satisfactorily comparable with ours[7 - 12].

In general, the excess volumes of this family of mixtures are small and the compositional dependencies of $\Delta V/\varphi_1 \varphi_2$ are not much pronounced. It is revealing to compare these results with excess volumes of mixtures of the same alkyl esters and ketones with alkanes[3] and with mixtures of the same alcohols with aromatic hydrocarbons[6]. In both cases, the excess volumes were large and the $\Delta V/\varphi_1 \varphi_2$ values increased steeply in the region of low concentration of the polar compound. This phenomenon can be explained in both these cases by a strong, spatially non-random, interaction between molecules of the carbonyl compounds (acetates or ketones) or between molecules of alcohols (hydrogen bonds). These interactions survive even in more dilute solutions of these polar compounds and disintegrate only at higher dilutions. Presumably, decrease of the num-

TABLE II
Coefficients in Eqs (*1*) and (*2*) and standard deviations

System	a_0	a_1	a_2	$\sigma(V^E/x_1x_2)$ cm^3 mol^{-1}	$b_0 \cdot 10^2$	$b_1 \cdot 10^2$	$b_2 \cdot 10^2$	$[\sigma(\Delta V/\varphi_1\varphi_2)] \cdot 10^2$
ML–MA	−0.311	−0.036	−0.007	0.015	−0.498	−0.232	−0.116	0.019
ML–EA	−0.362	−0.011	−0.009	0.015	−0.516	−0.247	−0.127	0.018
ML–PA	−0.331	−0.011	−0.046	0.014	−0.428	−0.224	−0.157	0.020
ML–BA	−0.174	−0.025	0.115	0.008	−0.155	−0.186	−0.046	0.013
ML–AA	−0.186	−0.134	0.239	0.027	−0.044	−0.316	−0.146	0.025
ML–AC	−1.338	0.214	−0.218	0.014	−2.480	−0.285	−0.328	0.013
ML–BU	−1.029	0.150	−0.139	0.030	−1.700	−0.387	−0.214	0.062
EL–MA	0.698	−0.017	0.144	0.015	1.019	0.113	0.218	0.024
EL–EA	0.544	0.108	0.088	0.007	0.666	0.300	0.222	0.024
EL–PA	0.359	0.077	0.105	0.010	0.393	0.202	0.201	0.011
EL–BA	0.431	0.137	0.156	0.019	0.414	0.277	0.293	0.024
EL–AA	0.366	0.110	0.160	0.027	0.325	0.223	0.268	0.018
EL–AC	−0.307	0.150	−0.075	0.007	−0.494	0.180	−0.066	0.008
EL–BU	−0.310	0.191	−0.033	0.016	−0.474	0.167	0.043	0.024
PL–MA	1.283	−0.014	0.147	0.010	1.667	0.028	0.190	0.014
PL–EA	0.889	0.035	0.160	0.003	1.028	0.165	0.207	0.011
PL–PA	0.651	0.057	0.126	0.027	0.675	0.190	0.184	0.017
PL–BA	0.636	0.138	0.086	0.008	0.584	0.289	0.189	0.015
PL–AA	0.509	0.094	0.089	0.007	0.434	0.221	0.170	0.010
PL–AC	−0.049	0.061	−0.033	0.008	−0.066	0.083	−0.046	0.011
PL–BU	−0.131	0.095	0.013	0.008	−0.170	0.100	0.035	0.010
BL–MA	1.575	0.075	0.157	0.048	1.849	−0.037	0.185	0.051
BL–EA	1.075	−0.024	0.091	0.017	1.136	0.010	0.098	0.019
BL–PA	0.773	0.015	0.134	0.004	0.749	0.092	0.140	0.006
BL–BA	0.693	0.024	0.138	0.007	0.620	0.121	0.143	0.008
BL–AA	0.572	−0.008	0.026	0.015	0.478	0.106	0.047	0.011
BL–AC	0.167	0.039	−0.008	0.007	0.208	0.023	−0.016	0.009
BL–BU	0.009	0.028	−0.009	0.006	0.010	0.030	−0.011	0.007
AL–MA	1.861	0.108	0.130	0.017	2.004	−0.186	0.147	0.021
AL–EA	1.273	−0.029	0.083	0.017	1.235	−0.088	0.086	0.017
AL–PA	0.928	−0.072	0.256	0.042	0.834	−0.043	0.226	0.036
AL–BA	0.782	−0.009	0.142	0.016	0.654	0.049	0.120	0.014
AL–AA	0.578	−0.145	0.240	0.050	0.469	−0.057	0.163	0.030
AL–AC	0.327	0.101	0.092	0.015	0.383	0.050	0.070	0.011
AL–BU	0.124	−0.014	0.075	0.006	0.124	−0.021	0.079	0.005

ML methanol; EL ethanol; PL 1-propanol; BL 1-butanol; AL 1-pentanol; MA methyl acetate; EA ethyl acetate; PA propyl acetate; BA butyl acetate; AL pentyl acetate; AC acetone; BU 2- butanone.

ber of such interactions is accompanied by an increase of volume. The above phenomenon was not observed for the presently studied systems despite the fact that these strong interactions exist in both components of the mixtures in their pure state. Apparently, the strong interactions among the molecules of each component are replaced by possibly even stronger interspecies interactions. This conclusion reflects, of course, the well-known tendency of carbonyl groups to form hydrogen bonds with hydroxy groups of alcohols or other compounds. In our previous study[5] we have observed a similar phenomenon: mixtures of alkyl acetates or ketones with aromatic hydrocarbons also did

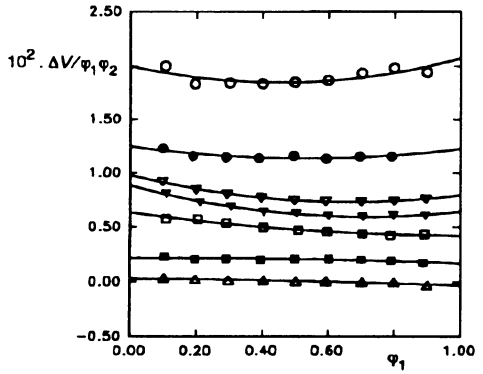

FIG. 1
Variation of $\Delta V/\varphi_1 \varphi_2$ with volume fraction φ_1 of 1-butanol for 1-butanol(1)–carbonyl compound(2) mixtures at 20 °C. ○ methyl acetate; ● ethyl acetate; ▽ propyl acetate; ▼ butyl acetate, ❐ pentyl acetate; ■ acetone; △ 2-butanone

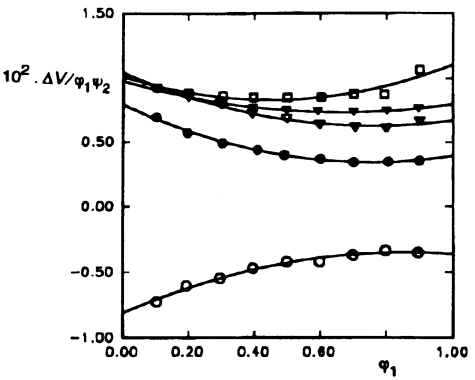

FIG. 2
Variation of $\Delta V/\varphi_1 \varphi_2$ with volume fraction φ_1 of alkanol for alkanol(1)–propyl acetate(2) mixtures at 20 °C. ○ methanol; ● ethanol; ▽ 1-propanol; ▼ 1-butanol; ❐ 1-pentanol

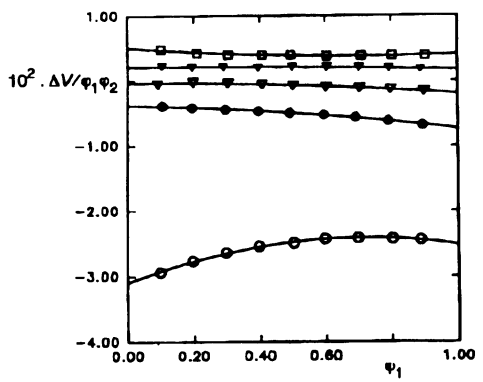

FIG. 3
Variation of $\Delta V/\varphi_1 \varphi_2$ with volume fraction φ_1 of alkanol for alkanol(1)–acetone(2) mixtures at 20 °C. ○ methanol; ● ethanol; ▽ 1-propanol; ▼ 1-butanol; ❐ 1-pentanol

not display the strong asymmetry of the $\Delta V/\varphi_1 \varphi_2$ dependencies on composition that was observed for their mixtures with aliphatic hydrocarbons. The values of excess volumes for these mixtures were also small, often negative. In that case, the inter-carbonyl interactions were replaced by strong carbonyl-aromatic interactions. The existence of such interactions was clearly shown in our light scattering study[13].

A more detailed inspection reveals the following facts. For systems with a given alcohol (Fig. 1), the $\Delta V/\varphi_1 \varphi_2$ values decrease as the length of alkyl group is increasing in acetates. Mixtures with methyl acetate have remarkably higher $\Delta V/\varphi_1 \varphi_2$ values than mixtures of the same alcohol with other esters. Systems with ketones have the smallest $\Delta V/\varphi_1 \varphi_2$ values among the systems studied. For systems with a given ester or ketone (Figs 2 and 3), the $\Delta V/\varphi_1 \varphi_2$ values increase when the alkyl length of the alcohols is increasing. The increase of $\Delta V/\varphi_1 \varphi_2$ from methanol to ethanol is exceptionally large when comparing the differences between other alcohols. It is interesting that the $\Delta V/\varphi_1 \varphi_2$ values of systems of methanol with esters or ketones have a noticeably different compositional dependence from those of other alcohols. The values of $\Delta V/\varphi_1 \varphi_2$ increase as the concentration of methanol increases whereas the $\Delta V/\varphi_1 \varphi_2$ values of other alcohol–ester or alcohol–ketone systems seem much less composition dependent or have a decreasing trend. The peculiarity of the behavior of methyl acetate and methanol was also found in mixtures of esters and aromatic hydrocarbons[5] and in mixtures of alcohols with aromatic hydrocarbons[6].

This research was supported by National Science Foundation (Grant DMR-8815784).

REFERENCES

1. Munk P., Hattam P., Du Q.: J. Appl. Polym. Sci.: Appl. Polym. Symp. *43*, 373 (1989).
2. Cheng W., Abdel-Azim A-A. A., El-Hibri M. J., Du Q., Munk P.: J. Phys. Chem. *93*, 8248 (1989).
3. Qin A., Hoffman D. E., Munk P.: J. Chem. Eng. Data *37*, 55 (1992).
4. Qin A., Hoffman D. E., Munk P.: J. Chem. Eng. Data *37*, 61 (1992).
5. Qin A., Hoffman D. E., Munk P.: J. Chem. Eng. Data *37*, 66 (1992).
6. Munk P., Qin A., Hoffman D. E.: Collect. Czech. Chem. Commun. *58*, 2612(1993).
7. Kato M.: Bull. Chem. Soc. Jpn. *53*, 1937 (1980).
8. Winnick J., Kong J.: Ind. Eng. Chem., Fundam. *13*, 292 (1974).
9. Nakanishi K., Shirai H.: Bull. Chem. Soc. Jpn. *43* 1634 (1970).
10. Inarrea J., Valero J., Perez P., Gracia M., Losa C. G.: J. Chem. Thermodyn. *20*, 193 (1988).
11. Ortega J., Paz-Andrade M. I., Rodriquez-Nunez E., Romani L.: Aust. J. Chem. *38*, 1435 (1985).
12. Ortega J., Pena J. A., Paz-Andrade M. I.: Aust. J. Chem. *39*, 1685 (1986).
13. Qin A., Abdel-Azim A. A., Cheng W., Munk P.: Thermochim. Acta *181*, 237 (1991).