

EXCESS VOLUMES OF MIXTURES OF ALKANOLS WITH AROMATIC HYDROCARBONS

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

The excess volumes of twenty binary mixtures of four aromatic hydrocarbons (benzene, toluene, ethylbenzene, and *p*-xylene) and five linear alkanols (methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol) at 20 °C are reported. The excess volume of systems with the same alkanol increases 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 alkanols. The dependence of $\Delta V/\varphi_1 \varphi_2$ values on composition is noticeably asymmetric. Systems with benzene as one of the component show larger $\Delta V/\varphi_1 \varphi_2$ values than other systems and systems with methanol show different compositional dependence patterns.

In our previous papers¹⁻³, 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 volume of five alcohols (methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol) with four aromatic hydrocarbons (benzene, toluene, ethylbenzene, and *p*-xylene) at 20 °C. Altogether twenty systems were prepared and, for each system, the dependence of the excess volume on composition was studied. Excess volumes of a few of these mixtures were studied previously⁴⁻⁸ and were found to be rather anomalous, especially in the region of very low mole fractions of alcohol. However, we are mainly interested in measuring a larger number of closely related systems within wider ranges of compositions. This should serve our ultimate goal: we want to accumulate a large number of thermodynamic data, in order to lay an experimental foundation for a development of a comprehensive theory of mixtures that would explain simultaneously all the important aspects of liquid mixtures.

The compositional dependence for systems of the same five alkanols with some esters and ketones was also studied, the results are presented separately as an accompanying paper⁹.

EXPERIMENTAL

All aromatic hydrocarbons 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 paper¹. All experiments were performed at 20 °C. The experimental data are listed in Table I for all systems.

RESULTS AND DISCUSSION

Experimentally, by measuring the masses m_i , the densities ρ_i of the pure components, and the densities ρ_m of the mixtures the volume fractions φ_i , the molar excess volumes V^E , and the relative change in volume ΔV at different compositions can be easily calculated as

$$\varphi_i = (m_i/\rho_i)/(m_1/\rho_1 + m_2/\rho_2) \quad (1)$$

$$V^E = [(m_1 + m_2)/\rho_m - m_1/\rho_1 - m_2/\rho_2]/(m_1/M_1 + m_2/M_2) \quad (2)$$

$$\begin{aligned} \Delta V &= V^E/(x_1V_1^0 + x_2V_2^0) = \\ &= [(m_1 + m_2)/\rho_m - m_1/\rho_1 - m_2/\rho_2]/(m_1/\rho_1 + m_2/\rho_2), \end{aligned} \quad (3)$$

where M_i , x_i and V_i^0 are molar mass, mole fraction and molar volume of pure component i , respectively.

Experimental data of V^E are usually correlated by means of a power series or by a rational function. For alkanol and aromatic hydrocarbon mixtures reported in this paper the fitting using a rational function seems more satisfactory. The function is written as

$$V^E/x_1x_2 = [a_0 + a_1(x_2 - x_1)]/[1 + c(x_2 - x_1)]. \quad (4)$$

Similarly, ΔV can be expressed as

$$\Delta V/\varphi_1\varphi_2 = [b_0 + b_1(\varphi_2 - \varphi_1)]/[1 + d(\varphi_2 - \varphi_1)]. \quad (5)$$

The coefficients in Eqs (4) and (5) obtained by least-square fitting 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 were defined as follows

$$\sigma(V^E/x_1x_2) = \left[\sum (V_{\text{calc}}^E/x_1x_2 - V^E/x_1x_2)^2/(N - n - 1) \right]^{1/2} \quad (6)$$

$$\sigma(\Delta V/\varphi_1\varphi_2) = \left[\sum (\Delta V_{\text{calc}}/\varphi_1\varphi_2 - \Delta V/\varphi_1\varphi_2)^2/(N - n - 1) \right]^{1/2}, \quad (7)$$

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

TABLE I
Excess volumes of mixing for aromatic mixtures of hydrocarbons and alkanols at 20 °C

φ_1	x_1	ρ , g cm ⁻³	V^E , cm ³ mol ⁻¹	$\Delta V \cdot 10^2$
Methanol(1)–benzene(2)				
1.000	1.000	0.79186	0	0
0.900	0.952	0.80083	-0.010	-0.023
0.800	0.898	0.80963	-0.017	-0.038
0.701	0.837	0.81839	-0.023	-0.047
0.608	0.773	0.82651	-0.024	-0.047
0.499	0.686	0.83607	-0.023	-0.041
0.404	0.598	0.84426	-0.017	-0.028
0.304	0.490	0.85282	-0.008	-0.012
0.209	0.366	0.86103	0.006	0.009
0.101	0.198	0.87034	0.017	0.022
0.000	0.000	0.87935	0	0
Methanol(1)–toluene(2)				
1.000	1.000	0.79165	0	0
0.896	0.958	0.79992	-0.023	-0.053
0.795	0.911	0.80789	-0.044	-0.096
0.699	0.859	0.81537	-0.063	-0.126
0.508	0.731	0.82994	-0.082	-0.142
0.405	0.641	0.83763	-0.084	-0.131
0.305	0.535	0.84502	-0.078	-0.110
0.205	0.403	0.85233	-0.062	-0.077
0.110	0.244	0.85916	-0.032	-0.036
0.000	0.000	0.86712	0	0
Methanol(1)–ethylbenzene(2)				
1.000	1.000	0.79166	0	0
0.894	0.962	0.79975	-0.001	-0.003
0.807	0.927	0.80642	-0.003	-0.007
0.699	0.875	0.81466	-0.005	-0.010
0.602	0.820	0.82208	-0.006	-0.011
0.502	0.753	0.82963	-0.006	-0.009
0.398	0.666	0.83756	-0.003	-0.005
0.299	0.564	0.84498	0.002	0.003
0.199	0.428	0.85257	0.012	0.014
0.101	0.253	0.85993	0.023	0.023
0.000	0.000	0.86780	0	0

TABLE I
(Continued)

φ_1	x_1	$\rho, \text{g cm}^{-3}$	$V^E, \text{cm}^3 \text{mol}^{-1}$	$\Delta V \cdot 10^2$
Methanol(1)- <i>p</i> -xylene(2)				
1.000	1.000	0.79161	0	0
0.898	0.964	0.79906	-0.017	-0.039
0.792	0.921	0.80667	-0.032	-0.069
0.695	0.874	0.81363	-0.044	-0.085
0.595	0.817	0.82065	-0.053	-0.095
0.492	0.746	0.82787	-0.057	-0.093
0.396	0.666	0.83450	-0.057	-0.084
0.299	0.565	0.84110	-0.048	-0.063
0.192	0.420	0.84832	-0.034	-0.039
0.090	0.231	0.85519	-0.007	-0.007
0.000	0.000	0.86142	0	0
Ethanol(1)-benzene(2)				
1.000	1.000	0.78988	0	0
0.893	0.927	0.79986	-0.031	-0.052
0.804	0.862	0.80800	-0.047	-0.076
0.706	0.786	0.81677	-0.049	-0.076
0.589	0.686	0.82711	-0.038	-0.056
0.491	0.595	0.83561	-0.016	-0.023
0.376	0.479	0.84550	0.014	0.019
0.302	0.397	0.85192	0.035	0.046
0.201	0.277	0.86065	0.061	0.076
0.099	0.144	0.86967	0.073	0.087
0.000	0.000	0.87931	0	0
Ethanol(1)-toluene(2)				
1.000	1.000	0.78987	0	0
0.899	0.942	0.79843	-0.057	-0.093
0.801	0.880	0.80646	-0.096	-0.150
0.703	0.812	0.81428	-0.120	-0.178
0.603	0.734	0.82203	-0.126	-0.178
0.496	0.642	0.83009	-0.119	-0.157
0.395	0.543	0.83768	-0.101	-0.125
0.296	0.434	0.84483	-0.061	-0.071
0.196	0.308	0.85211	-0.016	-0.017
0.098	0.165	0.85935	0.026	0.027
0.000	0.000	0.86714	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)–ethylbenzene(2)				
1.000	1.000	0.78990	0	0
0.899	0.949	0.79802	-0.027	-0.043
0.801	0.894	0.80585	-0.048	-0.074
0.705	0.834	0.81336	-0.061	-0.088
0.598	0.757	0.82155	-0.060	-0.082
0.499	0.677	0.82900	-0.052	-0.066
0.395	0.578	0.83683	-0.033	-0.038
0.305	0.480	0.84345	-0.007	-0.007
0.194	0.336	0.85167	0.030	0.030
0.099	0.188	0.85874	0.062	0.056
0.000	0.000	0.86688	0	0
Ethanol(1)– <i>p</i> -xylene(2)				
1.000	1.000	0.79003	0	0
0.899	0.950	0.79783	-0.047	-0.077
0.801	0.895	0.80513	-0.074	-0.113
0.703	0.834	0.81233	-0.095	-0.137
0.606	0.764	0.81932	-0.101	-0.137
0.498	0.677	0.82692	-0.098	-0.123
0.405	0.590	0.83327	-0.077	-0.090
0.293	0.467	0.84090	-0.040	-0.043
0.191	0.333	0.84785	-0.007	-0.007
0.099	0.188	0.85409	0.038	0.034
0.000	0.000	0.86144	0	0
1-Propanol(1)–benzene(2)				
1.000	1.000	0.80397	0	0
0.906	0.920	0.81117	-0.010	-0.014
0.805	0.830	0.81877	-0.006	-0.008
0.699	0.734	0.82658	0.010	0.012
0.598	0.639	0.83392	0.033	0.041
0.499	0.542	0.84111	0.061	0.075
0.402	0.444	0.84817	0.089	0.108
0.300	0.337	0.85566	0.111	0.132
0.203	0.233	0.86284	0.119	0.139
0.099	0.116	0.87092	0.097	0.111
0.000	0.000	0.87937	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)-toluene(2)				
1.000	1.000	0.80398	0	0
0.911	0.936	0.81012	-0.051	-0.067
0.798	0.849	0.81754	-0.077	-0.096
0.694	0.763	0.82427	-0.092	-0.111
0.599	0.680	0.83018	-0.083	-0.098
0.493	0.581	0.83673	-0.074	-0.084
0.398	0.484	0.84240	-0.034	-0.037
0.303	0.382	0.84804	0.002	0.002
0.197	0.259	0.85445	0.036	0.037
0.101	0.138	0.86038	0.053	0.052
0.000	0.000	0.86724	0	0
1-Propanol(1)-ethylbenzene(2)				
1.000	1.000	0.80437	0	0
0.899	0.936	0.81097	-0.028	-0.035
0.797	0.866	0.81752	-0.049	-0.060
0.703	0.795	0.82334	-0.040	-0.048
0.600	0.711	0.82962	-0.030	-0.034
0.503	0.624	0.83553	-0.012	-0.013
0.404	0.526	0.84147	0.015	0.015
0.300	0.413	0.84770	0.046	0.045
0.200	0.290	0.85378	0.072	0.066
0.102	0.157	0.85985	0.080	0.070
0.000	0.000	0.86682	0	0
1-Propanol(1)- <i>p</i> -xylene(2)				
1.000	1.000	0.80432	0	0
0.910	0.943	0.80980	-0.032	-0.041
0.806	0.873	0.81604	-0.065	-0.080
0.704	0.797	0.82178	-0.056	-0.067
0.607	0.718	0.82735	-0.062	-0.070
0.510	0.632	0.83274	-0.049	-0.053
0.397	0.521	0.83889	-0.017	-0.018
0.301	0.416	0.84397	0.030	0.029
0.198	0.290	0.84957	0.066	0.060
0.101	0.156	0.85509	0.077	0.067
0.000	0.000	0.86141	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)–benzene(2)				
1.000	1.000	0.81004	0	0
0.899	0.897	0.81677	0.027	0.030
0.796	0.791	0.82359	0.064	0.070
0.694	0.687	0.83026	0.106	0.117
0.593	0.586	0.83690	0.139	0.154
0.497	0.490	0.84323	0.170	0.188
0.394	0.387	0.85018	0.187	0.208
0.298	0.292	0.85685	0.187	0.209
0.199	0.195	0.86388	0.163	0.183
0.100	0.098	0.87125	0.109	0.122
0.000	0.000	0.87925	0	0
1-Butanol(1)–toluene(2)				
1.000	1.000	0.81003	0	0
0.901	0.913	0.81597	-0.029	-0.031
0.800	0.823	0.82183	-0.039	-0.041
0.703	0.734	0.82730	-0.035	-0.036
0.603	0.638	0.83289	-0.016	-0.017
0.493	0.530	0.83891	0.018	0.018
0.403	0.439	0.84386	0.042	0.042
0.295	0.327	0.84978	0.068	0.067
0.198	0.223	0.85526	0.076	0.073
0.093	0.107	0.86138	0.064	0.061
0.000	0.000	0.86724	0	0
1-Butanol(1)–ethylbenzene(2)				
1.000	1.000	0.81039	0	0
0.898	0.922	0.81628	-0.012	-0.013
0.800	0.843	0.82175	-0.007	-0.008
0.694	0.752	0.82766	0.004	0.004
0.603	0.670	0.83262	0.024	0.024
0.495	0.567	0.83850	0.052	0.050
0.398	0.469	0.84379	0.079	0.073
0.299	0.363	0.84923	0.100	0.090
0.201	0.252	0.85470	0.106	0.093
0.101	0.131	0.86050	0.090	0.076
0.000	0.000	0.86686	0	0

TABLE I
(Continued)

ψ_1	x_1	ρ , g cm ⁻³	V^E , cm ³ mol ⁻¹	$\Delta V \cdot 10^2$
1-Butanol(1)- <i>p</i> -xylene(2)				
1.000	1.000	0.80998	0	0
0.896	0.921	0.81562	-0.032	-0.034
0.806	0.848	0.82023	-0.032	-0.033
0.700	0.758	0.82557	-0.018	-0.018
0.601	0.669	0.83060	-0.010	-0.009
0.392	0.465	0.84081	0.058	0.053
0.294	0.359	0.84573	0.073	0.065
0.197	0.249	0.85042	0.115	0.100
0.100	0.130	0.85554	0.104	0.087
0.000	0.000	0.86140	0	0
1-Pentanol(1)-benzene(2)				
1.000	1.000	0.81506	0	0
0.906	0.888	0.82062	0.065	0.061
0.794	0.760	0.82725	0.132	0.127
0.697	0.653	0.83304	0.188	0.185
0.594	0.546	0.83917	0.235	0.237
0.493	0.444	0.84543	0.262	0.269
0.400	0.354	0.85128	0.269	0.281
0.302	0.262	0.85770	0.252	0.268
0.195	0.166	0.86499	0.201	0.218
0.124	0.104	0.86993	0.154	0.170
0.000	0.000	0.87941	0	0
1-Pentanol(1)-toluene(2)				
1.000	1.000	0.81509	0	0
0.898	0.897	0.82049	-0.012	-0.011
0.800	0.798	0.82559	-0.012	-0.011
0.701	0.698	0.83064	0.004	0.004
0.599	0.595	0.83581	0.025	0.023
0.497	0.492	0.84090	0.055	0.052
0.396	0.392	0.84602	0.073	0.068
0.295	0.291	0.85116	0.089	0.083
0.198	0.195	0.85621	0.088	0.083
0.097	0.095	0.86164	0.068	0.064
0.000	0.000	0.86724	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)–ethylbenzene(2)				
1.000	1.000	0.81489	0	0
0.898	0.908	0.82022	-0.003	-0.002
0.801	0.820	0.82514	0.008	0.007
0.702	0.728	0.83015	0.027	0.024
0.604	0.633	0.83509	0.051	0.045
0.495	0.526	0.84049	0.082	0.071
0.398	0.428	0.84539	0.102	0.087
0.300	0.326	0.85042	0.115	0.097
0.199	0.220	0.85568	0.109	0.091
0.101	0.113	0.86094	0.087	0.072
0.000	0.000	0.86681	0	0
1-Pentanol(1)– <i>p</i> -xylene(2)				
1.000	1.000	0.81510	0	0
0.797	0.817	0.82482	-0.043	-0.039
0.695	0.722	0.82951	-0.039	-0.035
0.594	0.626	0.83402	-0.020	-0.018
0.493	0.526	0.83851	0.005	0.004
0.399	0.431	0.84267	0.030	0.026
0.290	0.318	0.84756	0.055	0.046
0.201	0.223	0.85163	0.063	0.053
0.120	0.135	0.85537	0.062	0.051
0.000	0.000	0.86138	0	0

Literature values for excess volumes of alkanol–aromatic hydrocarbon mixtures are scarce, we were able to find good quality data only for methanol–benzene⁶, ethanol–benzene^{4–7}, ethanol–toluene⁵, and four alkanol–*p*-xylene^{4,5,8} mixtures. All these mixtures exhibit a sharp increase of the $\Delta V/\varphi_1 \varphi_2$ values in the region of the lowest concentrations of the alkanols. In Fig. 1, we have plotted the $\Delta V/\varphi_1 \varphi_2$ values for the ethanol–benzene mixtures as reported by Marsh et al.⁴ (curve 1) together with our experimental values and with the correlated dependence (data from Table II, curve 2). It is apparent, that there is a good agreement within our experimental region (the small differences are apparently a result of different temperatures in the two experiments, the higher temperature leading to more positive values) but that it is not possible to extrapolate the smoothed curve beyond our last experimental point ($\varphi_1 = 0.1$).

From Table I, it can be found that the excess volumes of mixtures of alkanols and aromatic hydrocarbons are rather small in comparison with those of mixtures of alkanes and aromatic hydrocarbons. In many systems the excess volumes are negative.

The dependencies of the $\Delta V/\varphi_1 \varphi_2$ values on compositions for systems alkanol-toluene and 1-propanol-aromatic hydrocarbons are plotted in Figs 2 and 3, respectively. The other systems have similar trends. The $\Delta V/\varphi_1 \varphi_2$ values have a strong compositional dependence through the whole concentration range. As the concentration of alcohol increases in the mixture, the $\Delta V/\varphi_1 \varphi_2$ value decreases sharply. This phenomenon is probably caused by the nonregular nature of mixtures of alkanols with aromatic hydrocarbons. Alkanols have strong self-interaction due to the presence of hydrogen bonds. As long as the concentration of the alkanol is not too small, strong interaction among their molecules prevails; this causes only a small volume change upon mixing. In the

TABLE II
Coefficients in Eqs (4) and (5) and standard deviations

System	c	a_0	a_1	$\sigma(V^E/x_1x_2)$ $\text{cm}^3 \text{ mol}^{-1}$	d	$b_0 \cdot 10^2$	$b_1 \cdot 10^2$	$[\sigma(\Delta V/\varphi_1\varphi_2)] \cdot 10^2$
ML-BE	-0.086	-0.030	0.217	0.004	-0.772	-0.161	0.318	0.004
ML-TO	0.183	-0.296	0.199	0.008	-0.994	-0.562	0.614	0.012
ML-EB	-0.717	0.022	0.116	0.006	-1.085	-0.028	0.076	0.016
ML-PX	0.285	-0.164	0.203	0.007	-0.873	-0.375	0.429	0.006
EL-BE	-0.210	0.026	0.646	0.025	-0.584	-0.138	0.804	0.029
EL-TO	0.045	-0.323	0.731	0.027	-0.589	-0.661	1.012	0.025
EL-EB	-0.143	-0.046	0.640	0.021	-0.775	-0.277	0.640	0.016
EL-PX	0.196	-0.185	0.649	0.043	-0.617	-0.504	0.853	0.043
PL-BE	-0.346	0.285	0.521	0.018	-0.479	0.287	0.589	0.019
PL-TO	-0.040	-0.151	0.758	0.046	-0.417	-0.315	0.854	0.045
PL-EB	-0.065	0.097	0.663	0.033	-0.537	-0.065	0.618	0.029
PL-PX	-0.161	-0.012	0.764	0.040	-0.608	-0.189	0.712	0.035
BL-BE	-0.280	0.660	0.360	0.014	-0.254	0.741	0.410	0.016
BL-TO	-0.169	0.090	0.600	0.016	-0.310	0.045	0.588	0.016
BL-EB	-0.183	0.280	0.525	0.020	-0.439	0.186	0.437	0.017
BL-PX	-0.256	0.185	0.724	0.064	-0.523	0.069	0.612	0.056
AL-BE	-0.383	0.984	0.187	0.021	-0.260	1.057	0.236	0.021
AL-TO	-0.359	0.189	0.442	0.016	-0.344	0.181	0.416	0.015
AL-EB	-0.268	0.336	0.428	0.022	-0.374	0.263	0.347	0.019
AL-PX	-0.191	0.039	0.556	0.014	-0.316	0.002	0.470	0.012

BE benzene; TO toluene; EB ethylbenzene; PX *p*-xylene; ML methanol; EL ethanol; PL 1-propanol; BL 1-butanol; AL 1-pentanol.

region of lowest concentrations of alkanols, the strong interaction among pairs of alkanols are finally replaced by weak interactions between alkanols and aromatic hydrocarbons, resulting in a big increase of excess volume. For mixtures of alkanols and alkanes, which, similarly to mixtures of alkanols with aromatic hydrocarbons, have strong interaction within one component and weak interaction between two components, the same trends were observed. From literature data, the compositional dependence of $\Delta V/\varphi_1 \varphi_2$ value for 1-propanol with hexane, heptane, octane, and cyclohexane¹⁰⁻¹³ is presented for comparison in Fig. 4.

From Fig. 2, it can also be seen that as the length of the alkanols increases from ethanol to 1-pentanol, the dependence of $\Delta V/\varphi_1 \varphi_2$ value on composition becomes less obvious. This reflects the decrease of the number of hydrogen bonds per unit volume of the alkanol within this series.

For systems of a given aromatic hydrocarbon (Fig. 2), the $\Delta V/\varphi_1 \varphi_2$ value is correlated to the length of the alkyl group of the alcohol. It gradually increases as the length of the alkyl group increases. For systems with a given alkanol (Fig. 3), the $\Delta V/\varphi_1 \varphi_2$ value increases with increasing aliphatic content of the aromatic hydrocarbon: from toluene to *p*-xylene to ethylbenzene; this is similar to behavior observed in mixtures of alkyl esters with aromatic hydrocarbons³.

Two other observations are worth mentioning: (i) mixtures with benzene exhibit $\Delta V/\varphi_1 \varphi_2$ values noticeably higher than those mixture with the other aromatic hydrocarbons; the longer is the alkyl group of the alcohol, the larger is the difference between

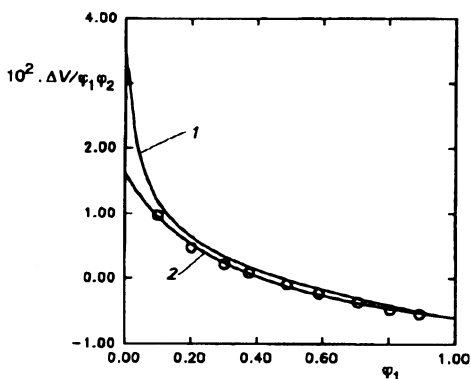


FIG. 1
Variation of $\Delta V/\varphi_1 \varphi_2$ with volume fraction φ_1 of ethanol for ethanol(1)-benzene(2) mixtures. 1 spline curve from the experimental data of Marsh et al.⁴ at 25 °C; 2 data from Table II (at 20 °C)

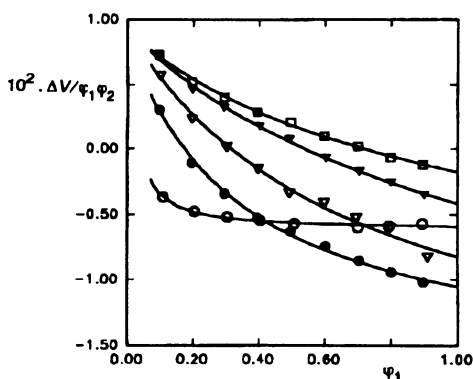


FIG. 2
Variation of $\Delta V/\varphi_1 \varphi_2$ with volume fraction φ_1 of alkanol for alkanol(1)-toluene(2) mixtures at 20 °C. ○ methanol; ● ethanol; ▽ 1-propanol; ▼ 1-butanol; □ 1-pentanol

the $\Delta V/\varphi_1 \varphi_2$ values of mixtures with benzene and mixtures with other aromatic hydrocarbons; (ii) mixtures with methanol exhibit $\Delta V/\varphi_1 \varphi_2$ values that decrease first with increasing methanol content, but they level off quickly and become much less composition dependent. Similar phenomena were also observed for mixtures of benzene with alkanes² and with carbonyl compounds³. Methyl acetate (an ester of methanol) exhibited in its mixtures with alkanes¹ and with aromatic hydrocarbons³ a behaviour similar to that of methanol.

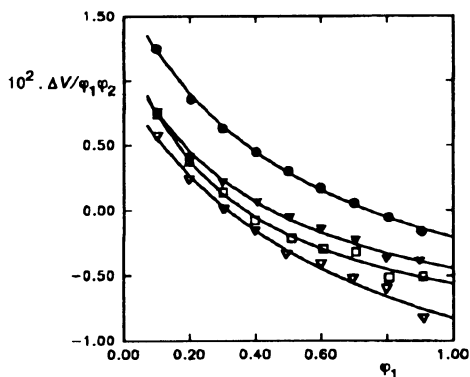


FIG. 3

Variation of $\Delta V/\varphi_1 \varphi_2$ with volume fraction φ_1 of 1-propanol for 1-propanol(1)-aromatic hydrocarbon(2) mixtures at 20 °C. ● benzene; ▽ toluene; ▼ ethylbenzene; □ *p*-xylene

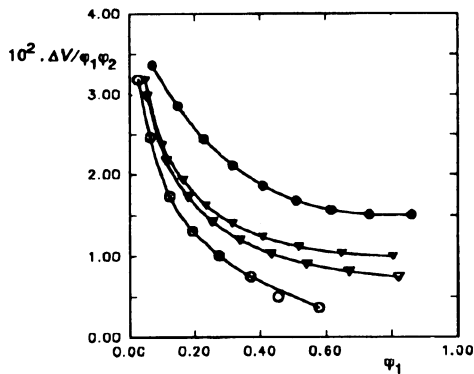


FIG. 4

Variation of $\Delta V/\varphi_1 \varphi_2$ with volume fraction φ_1 of 1-propanol for 1-propanol(1)-alkane(2) mixtures at 25 °C. ○ hexane⁹; ▽ heptane¹⁰; ▼ octane¹¹; ● cyclohexane¹²

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REFERENCES

1. Qin A., Hoffman D. E., Munk P.: *J. Chem. Eng. Data* **37**, 55 (1992).
2. Qin A., Hoffman D. E., Munk P.: *J. Chem. Eng. Data* **37**, 61 (1992).
3. Qin A., Hoffman D. E., Munk P.: *J. Chem. Eng. Data* **37**, 66 (1992).
4. Marsh K. N., Burfitt C.: *J. Chem. Thermodyn.* **7**, 955 (1975).
5. Pardo F., van Ness H.: *J. Chem. Eng. Data* **10**, 163 (1965).
6. Cibulka I., Hynek V., Holub R., Pick J.: *Collect. Czech. Chem. Commun.* **44**, 295 (1979).
7. Kato M.: *Bull. Chem. Soc. Jpn.* **53**, 1937 (1980).
8. Rodriguez-Nunez E., Paz-Andrade M. I., Ortega J.: *J. Chem. Thermodyn.* **18**, 303 (1986).

9. Qin A., Hoffman D. E., Munk P.: *Collect. Czech. Chem. Commun.* **58**, 2625 (1993).
10. Brown I., Fock W., Smith F.: *J. Chem. Thermodyn.* **1**, 273 (1969).
11. Treszczanowicz A. J., Benson G. C.: *J. Chem. Thermodyn.* **9**, 1189 (1977).
12. Berro C.: *Int. DATA Ser., Sel. Data Mixtures, A* **1987**, 64.
13. Janssens J-M., Ruel M.: *Can. J. Chem. Eng.* **50**, 591 (1972).