Table IX. Phase Boundary Data of All Systems Investigated Expressed in Mole Ratio of Water to Acid

	mol of water/mol of acid[a]							
no.	I	II	III	IV	V	VI	VII	VIII
2	36.60	46.16	22.88	20.61	29.38	12.96	11.21	8.23
3	33.54	31.45	20.73	18.50	21.75	11.87	10.21	7.72
4	27.13	25.15	18.43	16.41	18.95	11.65	9.88	6.40
5	24.18	25.40	15.08	15.24	16.48	11.03	9.55	6.67
6	26.06	22.02	14.28	14.55	15.43	10.87	9.24	6.75
7	24.50	21.10	13.66	13.72	14.42	10.61	9.19	6.56
8	24.14	20.50	13.19	13.41	14.01	10.15	8.94	6.55
9	23.50	20.41	12.77	13.27	13.51	10.29	8.47	6.82
10	22.85	19.66	12.42	13.11	13.28	9.73	8.31	6.14
11	22.75	19.47	12.27	12.92	13.09	9.83	8.48	6.41
12	22.51	19.61	12.46	12.95	13.02	9.80	8.16	5.72
13	21.25	18.73	11.73	12.56	12.59	9.79	8.33	6.23
14	20.97	17.13	11.31	12.56	12.39	9.13	8.12	5.46
15	20.77	17.71	11.20	12.44	12.33	9.50	8.41	5.47
16	20.66	18.25	11.37	12.38	12.34	9.75	8.12	5.13
17	21.08	17.05	11.12	12.16	12.08	9.18	7.46	5.30
18	20.47	17.03	10.61	12.08	12.03	10.06	7.92	5.21
19	20.93	16.52	10.00	11.83	11.79	9.98	7.80	5.19
20	20.94	16.28	11.40	11.53	11.52	10.38	8.04	5.33
21	21.39	17.33	12.03	11.27	11.33	11.87	7.84	5.48
22	25.43	21.78	14.78	11.12	11.00	14.68	8.80	6.69
23	25.47	24.08	13.64	11.41	10.75	19.26	10.66	9.55
24	36.80	33.75	11.26	11.75	10.64	23.79	11.25	21.20
av[b]	21.43	18.12	11.45	12.50	12.49	9.68	8.11	5.63
SD[c]	0.91	1.20	0.80	0.41	0.50	0.31	0.32	0.47
CV[d]	4.3	6.6	7.0	3.3	4.0	3.2	3.8	8.4
	(20.7)[e]	(23.5)	(23.4)	(14.0)	(14.0)	(36.0)	(40.2)	(49.2)

[a] Ratios calculated from Tables I-VIII. [b] Average of measurement no. 10-19. [c] Standard deviation calculated according to the instructions of: *Anal. Chem.* **1983**, *55*, 173. [d] Coefficient of variation calculated according to the instructions of: *Anal. Chem.* **1983**, *55*, 173. [e] In parentheses: acid content of the aqueous solution in weight percent; calculated from the mean value (av) of mole ratios (water/acid) of the given system.

addition to the rapid preparation for gas-chromatographic analysis, they may also be of some technological importance.

The synergetic effect of *n*-butyl and isobutyl alcohols in extraction is well-known. Our results may help support the use of butyl alcohol as an auxiliary material in extractants.

On the basis of our results, the use of butyl alcohol as an extractant from concentrated aqueous solutions of mineral acids is limited: As is shown (data in parentheses in Table IX), one can extract neither with *n*-butyl alcohol nor with isobutyl alcohol from mixtures containing more than about 14 wt % of hydrochloric acid solutions. But, for example, *n*-butyl alcohol is a good extractant up to about 50 wt % of phosphoric acid content.

Registry No. Butyl alcohol, 71-36-3; isobutyl alcohol, 78-83-1; hydrochloric acid, 7647-01-0; perchloric acid, 7601-90-3; nitric acid, 7697-37-2; sulfuric acid, 7664-93-9; phosphoric acid, 7664-38-2.

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Excess Volumes for Mixtures of Benzene with Some Cycloalkanes at 293.15, 298.15, and 303.15 K

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Excess volumes were determined from density measurements for binary mixtures of benzene with cyclopentane, methylcyclohexane, and cyclooctane at 293.15, 298.15, and 303.15 K.

This paper reports excess volumes for binary mixtures of benzene with cyclopentane, methylcyclohexane, and cyclooctane at 293.15, 298.15, and 303.15 K. The measurements were undertaken to provide information about thermodynamic properties of benzene-cycloalkane systems; determinations for the mixture of benzene-cyclohexane which were carried out as a part of the present series have been published previously (*1*).

Experimental Section

Excess volumes were determined from densities measured by use of a vibrating densimeter (Model 01D, Sodev Inc.,

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Table I. Density Values (in g cm^{-3}) of Component Liquids

	293.15 K		298.15 K		303.15 K	
	obsd	lit.[a]	obsd	lit.[a]	obsd	lit.[a]
C_6H_6	0.878 99	0.879 01	0.873 65	0.873 70	0.868 31	0.868 37
C_5H_{10}	0.745 02	0.745 38	0.740 07	0.740 45	0.735 08	0.735 49
$C_6H_{11}CH_3$	0.769 30	0.769 39	0.764 97	0.765 06	0.760 64	0.760 72
C_8H_{16}	0.836 07		0.831 98		0.827 90	

[a] Reference 2.

Table II. Molar Excess Volumes[a] of Benzene (1)-Cycloalkane (2) Mixtures

component 2					
cyclopentane		methylcyclohexane		cyclooctane	
x_1	V^E	x_1	V^E	x_1	V^E
		293.15 K			
0.053 40	0.0746	0.047 32	0.0991	0.047 63	0.1085
0.145 98	0.1804	0.160 23	0.2962	0.168 33	0.3360
0.265 55	0.2790	0.240 87	0.4040	0.222 32	0.4157
0.364 85	0.3293	0.341 72	0.5000	0.302 77	0.5089
0.447 16	0.3493	0.422 82	0.5453	0.402 48	0.5831
0.556 14	0.3467	0.494 05	0.5622	0.462 67	0.6058
0.634 61	0.3251	0.560 18	0.5578	0.562 64	0.6059
0.732 92	0.2745	0.626 12	0.5346	0.651 05	0.5666
0.826 85	0.2013	0.688 20	0.4944	0.720 37	0.5093
0.929 54	0.0925	0.789 35	0.3887	0.796 79	0.4165
		0.865 13	0.2767	0.859 28	0.3164
		0.917 17	0.1827	0.931 62	0.1708
		298.15 K			
0.056 92	0.0787	0.027 69	0.0594	0.034 12	0.0780
0.160 21	0.1937	0.155 49	0.2909	0.155 96	0.3129
0.240 44	0.2604	0.245 68	0.4128	0.237 13	0.4315
0.362 69	0.3265	0.342 95	0.5052	0.304 28	0.5064
0.449 42	0.3467	0.405 79	0.5430	0.392 91	0.5741
0.551 42	0.3447	0.473 78	0.5644	0.458 83	0.6013
0.636 23	0.3209	0.560 24	0.5626	0.564 27	0.6029
0.746 83	0.2617	0.637 82	0.5331	0.644 15	0.5694
0.846 04	0.1799	0.736 31	0.4549	0.719 02	0.5096
0.927 09	0.0935	0.793 08	0.3878	0.802 12	0.4088
		0.853 30	0.2993	0.854 65	0.3247
		0.913 25	0.1925	0.933 91	0.1658
		303.15 K			
0.068 90	0.0938	0.044 35	0.0941	0.039 24	0.0885
0.137 62	0.1714	0.172 60	0.3194	0.158 66	0.3144
0.257 32	0.2707	0.241 06	0.4111	0.227 68	0.4159
0.359 10	0.3229	0.346 23	0.5123	0.308 82	0.5069
0.450 36	0.3445	0.431 90	0.5591	0.404 04	0.5765
0.554 71	0.3404	0.492 65	0.5729	0.464 55	0.5995
0.642 96	0.3149	0.560 12	0.5687	0.567 87	0.6002
0.724 90	0.2728	0.641 71	0.5366	0.641 13	0.5704
0.833 05	0.1895	0.707 54	0.4877	0.722 72	0.5056
0.913 31	0.1079	0.798 36	0.3845	0.806 46	0.4022
		0.866 33	0.2804	0.859 91	0.3158
		0.913 88	0.1929	0.933 51	0.1670

[a] Units: cm^3 mol^{-1}.

Sherbrooke, Canada). Details of equipment and operating procedures will be found in the previous paper (*1*).

The mixtures were prepared with specially devised vessels so that the error yielded in composition x due to the vapor over the liquid phase was eliminated (*1*), and x was accurate to 2 × 10^{-5}. The imprecision in density measurements was less than 3 × 10^{-6} g cm^{-3}. The total uncertainty in excess volumes was estimated to be a maximum of 1.2 × 10^{-3} cm^3 mol^{-1}.

Benzene, cyclopentane, and methylcyclohexane were distilled after shaking with sulfuric acid. Cyclooctane was treated with sulfuric acid and potassium permanganate and distilled. According to GLC analysis the purity of cyclopentane was 99.7 mol %. No impurities were detected for the other liquids. Densities of used liquids are listed in Table I with literature values for comparison.

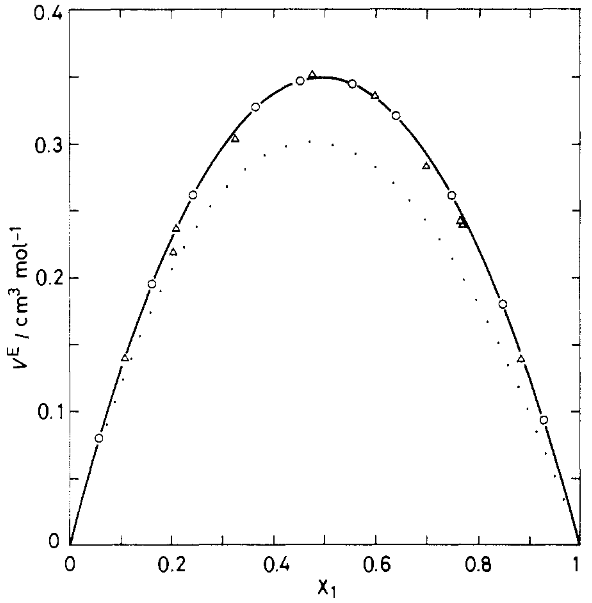

Figure 1. Molar excess volumes at 298.15 K. Benzene (1)-cyclopentane (2): (O) present work; (Δ) Stookey et al. (*4*). Dotted curve is smoothed function given by Watson et al. (*3*). Solid curve is least-squares representation of our results by eq 1.

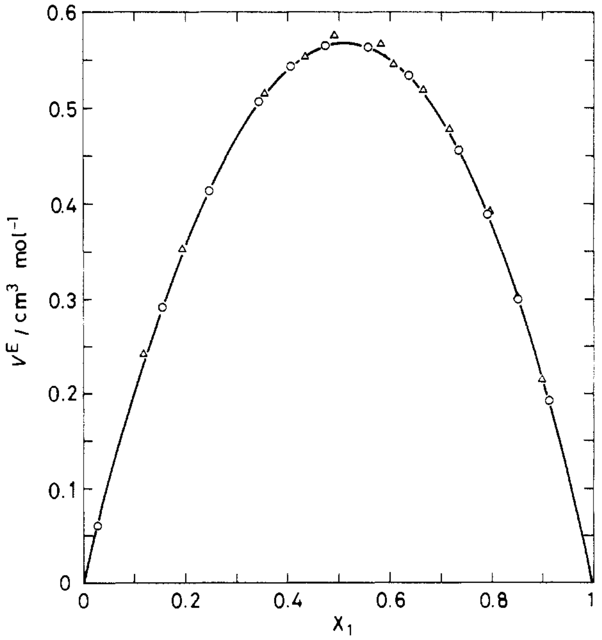

Figure 2. Molar excess volumes at 298.15 K. Benzene (1)-methylcyclohexane (2): (O) present work; (Δ) Letcher (*5*). Solid curve is least-squares representation of our results by eq 1.

Results and Discussion

Experimental values of V^E are listed in Table II. The smoothing function

$$V^E = x_1(1 - x_1)\sum c_j(1 - 2x_1)^{j-1} \qquad (1)$$

Table III. Coefficients c_j and Standard Deviations σ for Representations of Excess Volumes V^E of Benzene (1)-Cycloalkane (2) Mixtures by Eq 1

component 2	T/K	c_1	c_2	c_3	c_4	σ/cm^3 mol^{-1}
cyclopentane	293.15	1.4083	0.0326	0.0396	-0.0051	0.0003
	298.15	1.3970	0.0424	0.0306	0.0018	0.0003
	303.15	1.3845	0.0527	0.0348	0.0058	0.0003
methylcyclohexane	293.15	2.2505	-0.1103	0.0682	-0.0154	0.0003
	298.15	2.2702	-0.1109	0.0684	-0.0306	0.0003
	303.15	2.2940	-0.1179	0.0621	-0.0226	0.0003
cyclooctane	293.15	2.4446	-0.1235	0.1221	-0.0565	0.0001
	298.15	2.4318	-0.1409	0.1264	-0.0543	0.0001
	303.15	2.4212	-0.1626	0.1285	-0.0433	0.0002

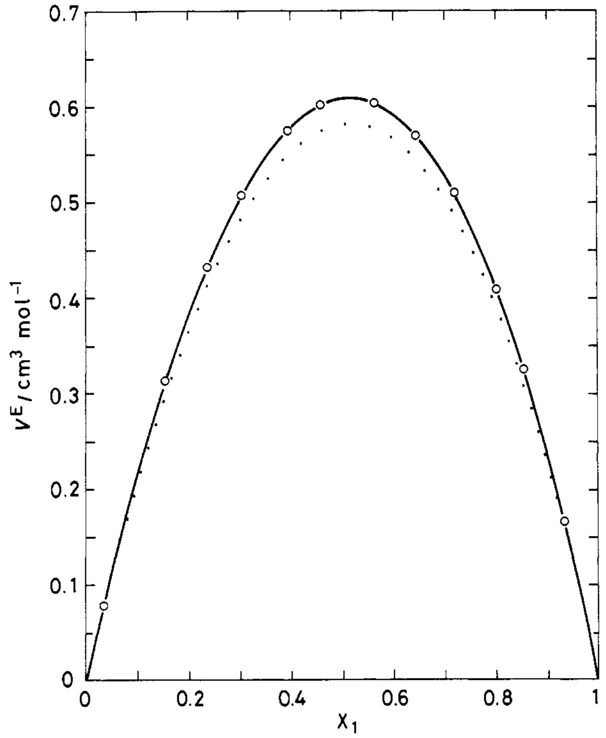

Figure 3. Molar excess volumes at 298.15 K. Benzene (1)-cyclooctane (2) at 298.15 K: (○) present work. Dotted curve is smoothed function given by Watson et al. (*3*). Solid curve is least-squares representation of our results by eq 1.

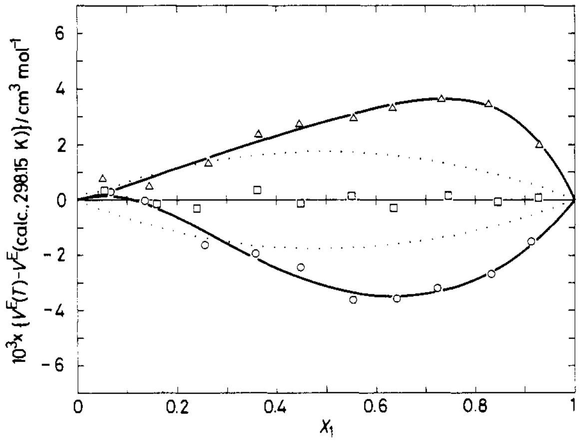

Figure 4. Variations of molar excess volumes $\Delta V^E(T)$ expressed by eq 2. Benzene (1)-cyclopentane (2): at (△) 293.15, (□) 298.15, and (○) 303.15 K. Dotted curves represent ±0.5% deviations from V^E(calcd, 298.15 K).

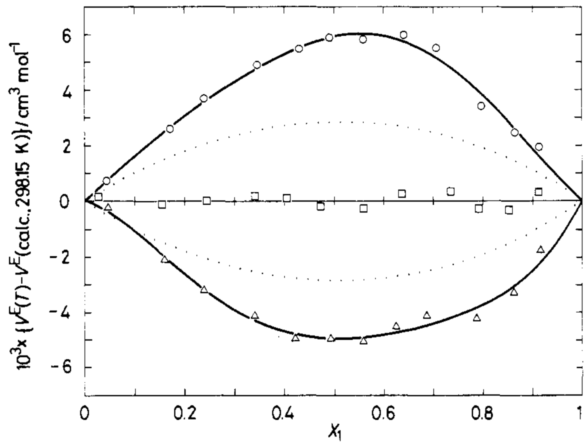

Figure 5. Variations of molar excess volumes $\Delta V^E(T)$ expressed by eq 2. Benzene (1)-methylcyclohexane (2): at (△) 293.15, (□) 298.15, and (○) 303.15 K. Dotted curves represent ±0.5% deviations from V^E(calcd, 298.15 K).

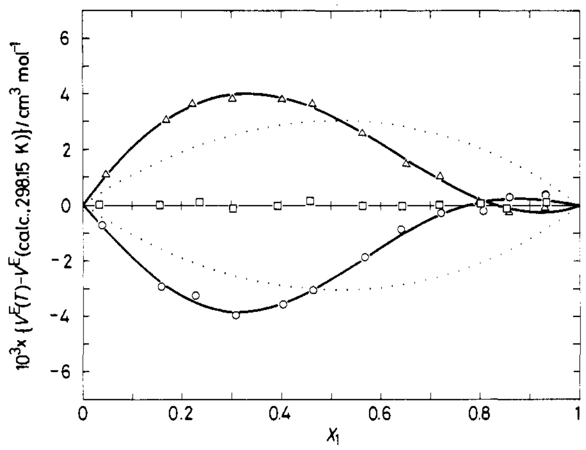

Figure 6. Variations of molar excess volumes $\Delta V^E(T)$ expressed by eq 2. Benzene (1)-cyclooctane (2): at (△) 293.15, (□) 298.15, and (○) 303.15 K. Dotted curves represent ±0.5% deviations from V^E(calcd, 298.15 K).

was fitted to each set of results by the least-squares method. Values of the coefficients c_j and the standard deviations σ are summarized in Table III. The results and the smoothed curves for 298.15 K are represented graphically in Figures 1-3, along with literature values. The results at the other temperatures are expressed as deviations $\Delta V^E(T)$

$$\Delta V^E(T) = V^E(T) - V^E(\text{calcd, } 298.15\text{ K}) \qquad (2)$$

and are shown in Figures 4-6. In all cases x_1 is the mole fraction of benzene.

***Benzene-Cyclopentane*.** Watson et al. (*3*) have determined V^E using a dilution dilatometer at 298.15 K. Disagreement between the present results and their results exceeds the estimates for experimental error. Stookey et al. (*4*) have reported the results made by use of a batch dilatometer between 283.15 and 313.15 K, and values at 298.15 K can be compared with ours. Though their scattering is much larger than that of the present work, those results agree reasonably well with ours. The variation of V^E with temperature is negative and linear within the uncertainty of determinations, and the maximum value of $\partial V^E/\partial T$ is about -0.0007 cm^3 K^{-1} mol^{-1}. The variations of V^E with T and x, obtained from the report by Stookey et al., are irregular and strange.

Benzene-Methylcyclohexane. The results of Letcher (*5*), determined by pycnometer at 298.15 K, agree well with ours. The variation of V^E with T is linear and symmetrical for composition. The value of $\partial V^E/\partial T$ is 0.0011 cm^3 K^{-1} mol^{-1} at the maximum. Stookey et al. (*4*) have measured V^E for this mixture between 283.15 and 343.15 K. Their V^E values change nonlinearly with T, and the variation is asymmetrical for x.

Benzene-Cyclooctane. The results obtained by Watson et al. (*3*) at 298.15 K are systematically smaller than ours, and the disagreement exceeds the estimates of experimental error. The variation of V^E with T is linear but asymmetrical on x, with a value $\partial V^E/\partial T$ of -0.0008 cm^3 K^{-1} mol^{-1} at the maximum. It is quite interesting to see that $\partial V^E/\partial T$ comes to zero at mole fractions nearly equal to 0.8; namely V^E is kept constant for temperature change in this region.

Glossary

$c_1, c_2, \ldots, c_j$	coefficients in representations of excess volumes by eq 1
T	thermodynamic temperature, K
V^E	molar excess volume, cm^3 mol^{-1}
x_1	mole fraction of benzene

Greek Letters

σ	standard deviation calculated from eq 1

Subscripts

1	benzene
2	cycloalkane

Registry No. Benzene, 71-43-2; cyclopentane, 287-92-3; methylcyclohexane, 108-87-2; cyclooctene, 292-64-8.

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Excess Volumes of Binary Mixtures of 2-Methyl-1-pentanol with Hexane Isomers at 298.15 K[†]

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Excess volumes, measured at 298.15 K in a successive dilution dilatometer, are reported for binary mixtures of 2-methyl-1-pentanol with the five isomeric hexanes.

In the course of our studies of the effect of molecular shape on the thermodynamic properties of alcohol-hydrocarbon systems, we have reported excess enthalpies for binary mixtures of 2-methyl-1-pentanol with the five isomeric hexanes (*1*). As an extension of that work, we have determined excess volumes for the same five systems, namely, binary mixtures of 2-methyl-1-pentanol with *n*-hexane (n-C6), 2-methylpentane (2-MP), 3-methylpentane (3-MP), 2,2-dimethylbutane (2,2-DMB), and 2,3-dimethylbutane (2,3-DMB).

Experimental Section

The 2-methyl-1-pentanol (Aldrich Chemical Co.) was purified chromatographically in a column containing 20% (by mass) Apiezon L on Chromosorb W (60/80 mesh). The density and refractive index (n_D) of the final product at 298.15 K were 818.34 kg·m^{-3} and 1.416 23, respectively. These values are somewhat higher than those for the sample used in our previous investigation (*1*) but are still lower than the literature values, 820.6 kg·m^{-3} and 1.4172 (*2*). The hexane isomers were Phillips Petroleum Co. Research Grade reagents with purities of 99.88 mol % or greater. They were used without further purification. The densities and refractive indices of these materials did not differ significantly from those of samples used in our previous studies (*1*, *3*, *4*).

A successive dilution dilatometer (*5*) was used to determine the changes in volume resulting from mixing the component liquids at constant temperature and pressure. Details of the operational procedure have been described previously (*5*, *6*). The temperature was controlled within ±0.0015 K at a value of 298.15 ± 0.01 K (IPTS-68). The imprecision of the mole fraction x of alcohol is estimated to be about 2×10^{-5} for $x < 0.02$, and to be less than 8×10^{-5} for larger x. The imprecision in the determination of the excess molar volume, V_m^E, is estimated to be less than $0.0003 + 0.001|V_m^E|$ cm^3·mol^{-1}.

Results and Discussion

The experimental values of V_m^E are listed in Table I. In all cases, x is the mole fraction of 2-methyl-1-pentanol. A graphical comparison of the results for the five mixtures is given

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