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

$c_1, c_2, ..., c_j$	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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Table I. Experimental Results for the Molar Excess Volume, V_m^E, of 2-Methyl-1-pentanol–Hexane Isomer Mixtures at Alcohol Mole Fraction, x, and 298.15 K

x	V_m^E/ ($cm^3 \cdot mol^{-1}$)	x	V_m^E/ ($cm^3 \cdot mol^{-1}$)	x	V_m^E/ ($cm^3 \cdot mol^{-1}$)	x	V_m^E/ ($cm^3 \cdot mol^{-1}$)
2-Methyl-1-pentanol–*n*-Hexane							
0.010 81	0.0367	0.151 47	0.0508	0.406 68	−0.0110	0.545 14	−0.0593
0.026 56	0.0525	0.179 84	0.0457	0.441 81	−0.0223	0.551 90	−0.0620
0.039 62	0.0570	0.184 74	0.0447	0.451 32	−0.0257	0.581 39	−0.0713
0.051 79	0.0591	0.214 95	0.0383	0.466 49	−0.0302	0.626 59	−0.0860
0.064 79	0.0608	0.231 71	0.0348	0.478 08	−0.0340	0.679 37	−0.0992
0.075 63	0.0601	0.247 24	0.0314	0.481 25	−0.0361	0.741 88	−0.1070
0.087 58	0.0599	0.290 80	0.0210	0.489 71	−0.0392	0.800 89	−0.1042
0.098 32	0.0585	0.291 40	0.0210	0.507 98	−0.0447	0.851 72	−0.0926
0.109 85	0.0575	0.341 65	0.0080	0.515 50	−0.0485	0.889 46	−0.0776
0.120 93	0.0556	0.354 14	0.0046	0.523 05	−0.0514	0.930 45	−0.0550
0.141 17	0.0527	0.395 83	−0.0075	0.542 22	−0.0572	0.963 87	−0.0317
2-Methyl-1-pentanol–2-Methylpentane							
0.005 39	0.0188	0.170 83	−0.0258	0.487 08	−0.1623	0.701 77	−0.2071
0.013 58	0.0323	0.206 92	−0.0439	0.514 20	−0.1725	0.733 15	−0.2036
0.024 23	0.0370	0.240 05	−0.0598	0.516 62	−0.1727	0.767 32	−0.1957
0.037 11	0.0362	0.284 80	−0.0802	0.544 32	−0.1824	0.804 73	−0.1813
0.052 09	0.0315	0.336 99	−0.1026	0.550 56	−0.1838	0.845 97	−0.1585
0.069 03	0.0248	0.392 35	−0.1258	0.589 15	−0.1946	0.891 74	−0.1240
0.087 73	0.0161	0.439 37	−0.1445	0.622 28	−0.2015	0.931 27	−0.0855
0.109 97	0.0051	0.472 21	−0.1570	0.646 65	−0.2053	0.964 83	−0.0476
0.141 41	−0.0111	0.479 48	−0.1599	0.673 17	−0.2072		
2-Methyl-1-pentanol–3-Methylpentane							
0.005 29	0.0204	0.145 12	0.0305	0.476 26	−0.0724	0.698 06	−0.1334
0.013 31	0.0369	0.173 62	0.0228	0.482 06	−0.0734	0.729 56	−0.1345
0.023 64	0.0454	0.208 77	0.0128	0.510 70	−0.0848	0.764 00	−0.1328
0.036 19	0.0485	0.241 10	0.0036	0.511 81	−0.0841	0.801 88	−0.1261
0.049 61	0.0491	0.284 91	−0.0094	0.540 55	−0.0955	0.843 65	−0.1125
0.060 63	0.0485	0.335 99	−0.0248	0.545 85	−0.0961	0.889 95	−0.0901
0.074 62	0.0466	0.390 41	−0.0424	0.585 81	−0.1093	0.930 91	−0.0624
0.091 50	0.0437	0.436 59	−0.0581	0.631 48	−0.1220	0.964 16	−0.0357
0.114 58	0.0385	0.463 35	−0.0668	0.669 21	−0.1296		
2-Methyl-1-pentanol–2,2-Dimethylbutane							
0.002 85	0.0073	0.069 60	−0.0266	0.484 54	−0.3326	0.674 52	−0.3547
0.005 55	0.0138	0.092 95	−0.0510	0.488 63	−0.3332	0.703 13	−0.3466
0.010 45	0.0187	0.121 57	−0.0806	0.518 38	−0.3434	0.734 31	−0.3336
0.013 67	0.0194	0.162 30	−0.1211	0.518 85	−0.3444	0.768 29	−0.3135
0.017 61	0.0186	0.216 66	−0.1699	0.548 50	−0.3523	0.805 66	−0.2842
0.021 77	0.0169	0.279 13	−0.2193	0.552 94	−0.3525	0.848 53	−0.2409
0.026 90	0.0141	0.344 51	−0.2630	0.592 45	−0.3588	0.892 35	−0.1855
0.032 13	0.0095	0.398 94	−0.2937	0.623 75	−0.3603	0.932 51	−0.1244
0.039 61	0.0032	0.445 02	−0.3162	0.648 08	−0.3588	0.965 17	−0.0681
0.052 37	−0.0090	0.470 49	−0.3264				
2-Methyl-1-pentanol–2,3-Dimethylbutane							
0.005 43	0.0186	0.150 89	−0.0145	0.485 43	−0.1561	0.699 47	−0.2014
0.013 44	0.0315	0.180 22	−0.0291	0.513 26	−0.1675	0.730 92	−0.1984
0.023 80	0.0359	0.213 98	−0.0451	0.515 03	−0.1666	0.765 13	−0.1907
0.033 68	0.0358	0.246 49	−0.0602	0.542 82	−0.1775	0.802 88	−0.1770
0.045 91	0.0328	0.289 36	−0.0789	0.549 14	−0.1778	0.846 32	−0.1536
0.060 83	0.0276	0.340 01	−0.1003	0.588 21	−0.1887	0.890 59	−0.1204
0.077 27	0.0210	0.393 95	−0.1223	0.619 65	−0.1954	0.931 38	−0.0827
0.097 63	0.0114	0.439 74	−0.1404	0.644 13	−0.1994	0.964 45	−0.0460
0.120 56	0.0000	0.479 06	−0.1553	0.670 69	−0.2015		

Table II. Coefficients v_j and Standard Deviations s for Least-Squares Representations of V_m^E for 2-Methyl-1-pentanol–Hexane Isomer Mixtures at 298.15 K by Eq 1 in the Range $0 < x < 1$

	n-C6	2-MP	3-MP	2,2-DMB	2,3-DMB
v_1	9.1760	7.7718	8.2162	6.2595	7.6340
v_2	−87.9496	−75.8297	−77.4192	−68.0697	−74.8509
v_3	414.3717	341.0347	352.4236	303.8581	338.0180
v_4	−1154.217	−912.608	−955.427	−806.924	−905.580
v_5	1961.555	1502.707	1593.297	1320.603	1489.072
v_6	−1986.318	−1484.520	−1593.095	−1297.849	−1466.316
v_7	1093.123	799.387	868.104	694.470	785.929
v_8	−250.706	−179.374	−197.166	−154.395	−175.276
s	0.0003	0.0003	0.0005	0.0006	0.0005

Table III. Coefficients v_j and Standard Deviations s for Least-Squares Representations of V_m^E for 2-Methyl-1-pentanol–Hexane Isomer Mixtures at 298.15 K by Eq 2 in the Range $0 < x < 0.2$

	n-C6	2-MP	3-MP	2,2-DMB	2,3-DMB
v_1	5.2858	4.4492	4.7847	3.3789	4.4516
$10^{-2} v_2$	−2.2820	−2.1089	−2.0655	−2.0236	−2.2186
$10^{-3} v_3$	5.7049	5.3290	5.0576	5.2700	6.0326
$10^{-4} v_4$	−8.5248	−8.1634	−7.4864	−8.0038	−10.0883
$10^{-5} v_5$	7.6722	7.5867	6.7181	6.9255	10.3613
$10^{-6} v_6$	−4.0718	−4.1581	−3.5597	−3.1380	−6.3401
$10^{-7} v_7$	1.1723	1.2308	1.0208	0.5740	2.1119
$10^{-7} v_8$	−1.4107	−1.5120	−1.2177		−2.9367
s	0.0003	0.0003	0.0002	0.0004	0.0002

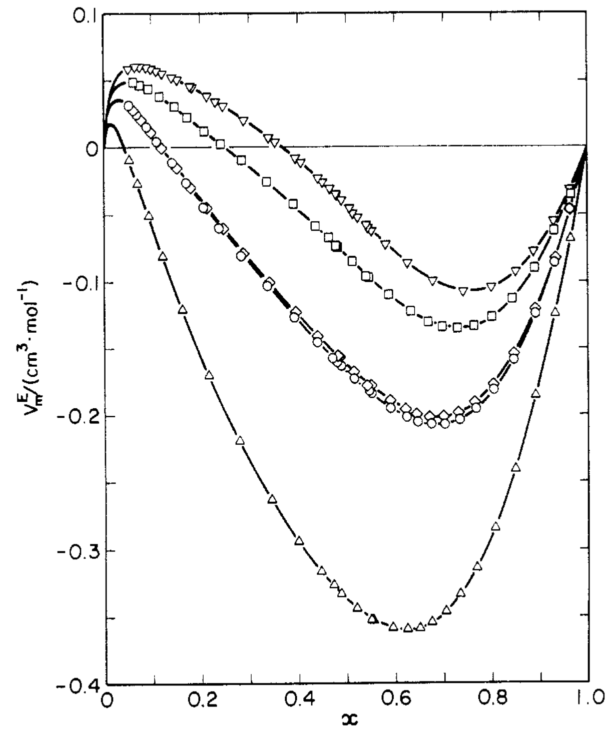

Figure 1. Excess molar volume, V_m^E, of 2-methyl-1-pentanol–hexane isomer mixtures at mole fraction, x, of 2-methyl-1-pentanol and 298.15 K: (▽) n-C_6, (○) 2-MP, (□) 3-MP, (△) 2,2-DMB, (◇) 2,3-DMB. Points for $x < 0.05$ are shown in Figure 2. Curves are least-squares representations of the results by eq 1.

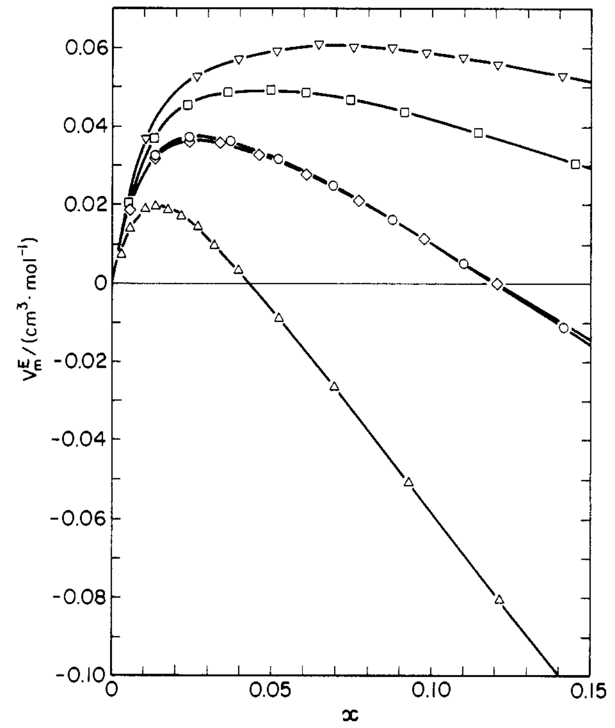

Figure 2. Excess molar volume, V_m^E, of 2-methyl-1-pentanol–hexane isomer mixtures at low mole fraction, x, of 2-methyl-1-pentanol and 298.15 K: (▽) n-C6, (○) 2-MP, (□) 3-MP, (△) 2,2-DMB, (◇) 2,3-DMB. Curves calculated from combination of eq 1 and 2.

in Figure 1, where, for clarity of presentation, points in the region $x < 0.05$ have been omitted. The latter are plotted on an expanded scale in Figure 2.

The polynomial equation

$$V_m^E = x(1 - x) \sum_{j=1}^{n} v_j x^{(j-1)/2} \qquad (1)$$

in the square root of x was fitted to each set of results by the method of least squares with all points assigned unit weight. The coefficients v_j and standard deviations s for these representations are given in Table II, and the curves calculated from eq 1 are shown in Figure 1. Although eq 1 can be used to smooth the results over most of the mole fraction range, it does not represent the experimental values for $x < 0.05$ as well as for larger x, and it is unsuitable for estimating the limiting excess partial molar volumes of 2-methyl-1-pentanol at infinite dilution in the various hexane isomers. Better representations of V_m^E in the dilute alcohol regions are obtained by fitting the polynomial

$$V_m^E = \sum_{j=1}^{n} v_j x^j \qquad (2)$$

to the data for $x < 0.2$. Table III summarizes the results of the least-squares analysis. The curves in Figure 2 were calculated from eq 2 at low x ($x < 0.13$ for n-C6, and $x < 0.07$ for the other isomers) and from eq 1 at higher x.

The excess volume curves for the present systems are all sigmoid, as were those for mixtures of 1-hexanol with the hexane isomers (*4*). A comparison of Figures 1 and 2 with the corresponding plots in ref *4* reveals several other similarities. Thus, over most of the mole fraction range, the curves fall in the same order

n-C6 > 3-MP > 2,3-DMB > 2-MP > 2,2-DMB

for the two sets of systems, and also the curves for 2,3-DMB and 2-MP cross at low x. However, the positive lobes of the present curves are increased and the negative lobes are decreased in relation to those obtained previously for 1-hexanol, indicating a net positive contribution to V_m^E when 2-methyl-1-pentanol replaces 1-hexanol in mixtures with the hexane isomers. In the dilute alcohol region, it is reasonable to attribute this effect to a greater expansion accompanying the dissociation of H bonds between 2-methyl-1-pentanol molecules as compared to 1-hexanol. At higher alcohol mole fractions where the dissociation of the alcohol is relatively unimportant, 2-methyl-1-pentanol is less able than 1-hexanol to accommodate the hexane isomers interstitially.

Previously (*4*) we noted that the excess molar volumes

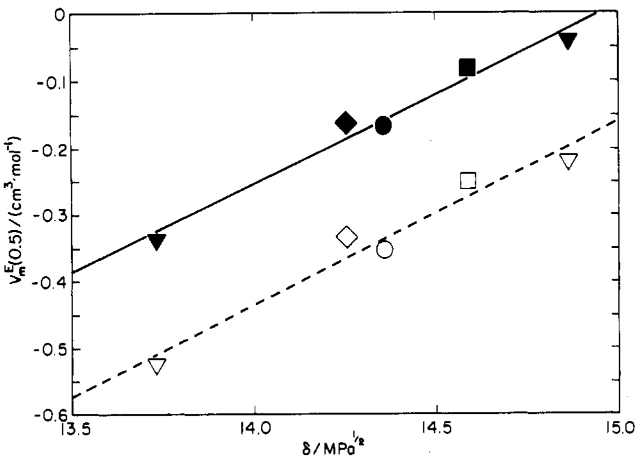

Figure 3. Plot of $V_m^E(0.5)$, the exces molar volume of an equimolar C_6-alcohol–hexane isomer mixture against δ, the solubility parameter of the isomer. Present results for 2-methyl-1-pentanol mixtures: (▼) n-C6, (●) 2-MP, (■) 3-MP, (▲) 2,2-DMB, (◆) 2,3-DMB; (—) least-squares line ($r = 0.99$). Results for 1-hexanol mixtures (taken from ref *4*) are represented by the corresponding open symbols and the broken line ($r = 0.98$).

$V_m^E(0.5)$ for equimolar mixtures of 1-hexanol with hexane isomers varied nearly linearly with the solubility parameter δ of the isomer. Figure 3 shows that this is also true for the 2-methyl-1-pentanol mixtures. The least-squares line, which corresponds to a coefficient of correlation $r = 0.99$, provides further evidence of the behavioral similarity of the two sets of systems.

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We are indebted to Dr. M. K. Kumaran for helpful discussions and to Mr. P. J. D'Arcy and Mr. C. J. Halpin for technical assistance.

Glossary

n	number of coefficients in eq 1 or 2
n_D	refractive index for sodium light
r	coefficient of correlation
s	standard deviation
$v_1, v_2, ..., v_j$	coefficients in representation of excess molar volume by eq 1 or 2
V_m^E	excess molar volume, $cm^3 \cdot mol^{-1}$
x	mole fraction of 2-methyl-1-pentanol

Greek Letters

δ	solubility parameter, $MPa^{-1/2}$

Registry No. 2-Methyl-1-pentanol hexane, 110-54-3; 2-methylpentane, 107-83-5; 3-methylpentane, 96-14-0; 2,2-dimethylbutane, 75-83-2; 2,3-dimethylbutane, 79-29-8.

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Molar Volume Contraction for Alcohols in Acetic Acid

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The densities of binary mixtures containing acetic acid and a series of alcohols (methyl, ethyl, propyl, and butyl alcohols) are measured at 25 °C. The molar volume contraction and the degree of association of alcohols are calculated. It is found that the molar volume contraction exhibits a maximum value at $m \simeq 0.5$ mole fraction of acetic acid; this indicates that complex formation occurs at a molar ratio of 1:1 of the acid and the alcohol. Furthermore, it is found that the degree of association decreases in the sequence MeOH > EtOH > PrOH > *n*-BuOH. The effect of various factors such as the hydrocarbon length, the solubility, and the degree of association are discussed.

The change in molar volume for binary mixtures is considered as an important tool for studying solute–solvent interactions. I (*1*) previously studied the molar volume change for binary mixtures containing glycerol with a series of carboxylic acids. It was found that there is a maximum molar volume contraction at 0.34 mole fraction of glycerol. This behavior was attributed to complex formation between glycerol and each of the carboxylic acids at a molar ratio of 1:2, respectively.

The present investigation aims to study the effect of the chain length and the structure of alcohols and acetic acid in their binary mixtures.

Experimental Section

The methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, and isobutyl alcohols and acetic acid used were of AnalaR grade. The materials were further purified according to the recommended methods (*2*). The purity of each substance was checked by measuring the density, *d*, the refractive index, *n*, the dielectric constant, ϵ, and the difference between the boiling and condensation points, Δt. The density was measured by the usual Sprengel-Ostwald pycnometer to an accuracy of ±0.0001 g·mL^{-1} (*3*). The refractive index was measured for the sodium D line with an Abbe refractometer. The refractive index could be directly read to 0.0001 unit. The dielectric constant was measured by a multi-Dekameter type DK06 which has a frequency band from 0.2 to 10 MHz. The measurements were based on the superheterodyne principle; the beat frequencies were indicated on a cathode ray tube. The tuning condenser, which had 4500 uniform divisions, permitted fine adjustments and allowed a sensitivity of order 10^{-5}. The difference between

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