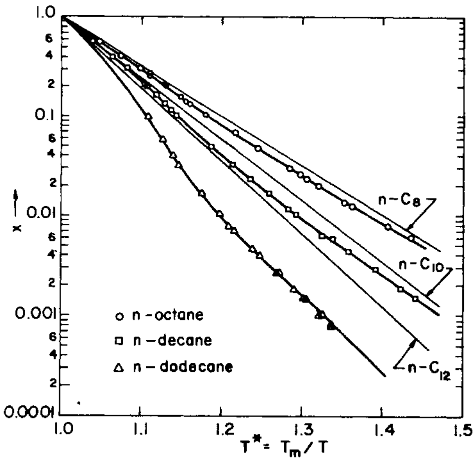

Figure 1. A comparison of the solute mole fraction vs. reciprocal temperature experimental data with ideal predictions. The heavy lines are the smoothed data presentations of Tables I–III, while the light lines are the ideal loci for the three systems studied.

the solute. Thus extrapolation of the data into even more dilute regions would be likely to be reasonably accurate.

Nomenclature

R = universal gas law constant = 1.987 cal/(g mol K)
T = temperature, K
T_{FUS} = freezing temperature (triple point temperature), K
x_i = ideal solubility, mole fraction
ΔH_{FUS} = enthalpy of fusion of pure solute component, cal/(g mol)

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Supplementary Material Available: Vapor–liquid–solid three-phase raw data (3 pages). Ordering information is given on any current masthead page.

Thermodynamic Properties of Some Cycloalkane–Cycloalkanol Systems at 298.15 K. 4. Excess Volumes

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Measurements of excess volumes at 298.15 K are reported for the systems cycloheptane–cyclohexanol, cyclooctane–cyclohexanol, cyclopentane–cycloheptanol, cyclohexane–cycloheptanol, and cyclooctane–cycloheptanol. The results are compared with the excess volumes of other cycloalkane–cycloalkanol systems investigated previously in our laboratory. The volume behavior of cycloalkane–cycloalkanol systems can be attributed qualitatively to the effects of hydrogen bonding and to differences in the sizes of the component molecules.

Previous investigations (*1–3*) of binary cycloalkane–cycloalkanol systems have shown that the shapes of the excess volume curves vary considerably when the ring sizes of the component species are changed. This is in marked contrast to the curves for both the excess enthalpy and excess Gibbs free energy, the shapes of which are relatively insensitive to changes of component ring size.

As an extension of our earlier studies, we have measured excess volumes at 298.15 K for binary mixtures of cyclohexanol with cycloheptane and cyclooctane, and of cycloheptanol with cyclopentane, cyclohexane, and cyclooctane.

Experimental Section

The component liquids were the same as used in our earlier studies. Reference can be made to those publications (*1, 3*) for the methods of purification and for values of the densities, refractive indices, and vapor pressures characterizing the final samples.

The changes in volume which occurred on mixing the component liquids at 298.15 K were measured in a successive dilution dilatometer. A description of the equipment and operating technique is available in the literature (*4*). The results are estimated to be accurate to better than ±1 × 10^{-3} cm^3 mol^{-1}.

Results

Experimental values of the molar excess volume V^E measured for the five cycloalkane–cycloalkanol systems are summarized in Table I. In each case, x_1 is the mole fraction of the cycloalkane. The results are also presented graphically in Figures 1 and 2, where each figure refers to systems containing a common cycloalkanol.

Polynomial forms

$$V^E = x_1(1 - x_1) \sum_{k=1}^{n} c_k(1 - x_1)^{(k-1)/2} \qquad (1)$$

in the square root of the cycloalkanol mole fraction were used to smooth the resuls. Least-squares analyses led to the coefficients and standard error of estimate

$$\sigma = \left\{ \sum_{1}^{m} [V^E(\text{exptl}) - V^E(\text{eq 1})]^2/(m - n) \right\}^{1/2} \qquad (2)$$

given in Table II for each system.

Table I. Experimental Values of Molar Excess Volume at 298.15 K

x_1	V^E, cm^3 mol^{-1}	x_1	V^E, cm^3 mol^{-1}	x_1	V^E, cm^3 mol^{-1}
		Cyclopentane (1)–Cycloheptanol (2)			
0.0203	−0.0260	0.6550	−0.2676	0.9239	−0.0372
0.0516	−0.0668	0.6749	−0.2563	0.9314	−0.0267
0.0917	−0.1150	0.6971	−0.2438	0.9318	−0.0278
0.1412	−0.1688	0.7050	−0.2382	0.9483	−0.0097
0.1944	−0.2182	0.7164	−0.2321	0.9532	−0.0050
0.2510	−0.2606	0.7547	−0.2027	0.9555	−0.0016
0.3065	−0.2908	0.8038	−0.1597	0.9606	0.0027
0.3615	−0.3106	0.8200	−0.1429	0.9704	0.0114
0.4148	−0.3201	0.8465	−0.1201	0.9753	0.0156
0.4662	−0.3190	0.8619	−0.1013	0.9785	0.0175
0.5114	−0.3140	0.8634	−0.1012	0.9804	0.0191
0.5520	−0.3053	0.8882	−0.0767	0.9863	0.0203
0.5888	−0.2945	0.8993	−0.0618	0.9908	0.0191
0.6206	−0.2826	0.9049	−0.0573	0.9943	0.0152
0.6492	−0.2698				
		Cyclohexane (1)–Cycloheptanol (2)			
0.0160	−0.0134	0.4428	−0.1111	0.8063	0.0086
0.0367	−0.0272	0.4755	−0.1035	0.8375	0.0200
0.0666	−0.0477	0.5074	−0.0954	0.8399	0.0204
0.0996	−0.0667	0.5295	−0.0868	0.8716	0.0313
0.1223	−0.0783	0.5380	−0.0862	0.8733	0.0325
0.1484	−0.0908	0.5582	−0.0780	0.9013	0.0408
0.1732	−0.0999	0.5843	−0.0694	0.9066	0.0429
0.1983	−0.1079	0.6368	−0.0518	0.9273	0.0477
0.2192	−0.1138	0.6592	−0.0423	0.9365	0.0498
0.2518	−0.1205	0.6960	−0.0300	0.9508	0.0511
0.2662	−0.1224	0.7030	−0.0291	0.9607	0.0516
0.3024	−0.1255	0.7338	−0.0168	0.9710	0.0495
0.3115	−0.1252	0.7533	−0.0099	0.9800	0.0451
0.3495	−0.1242	0.7712	−0.0038	0.9905	0.0325
0.3807	−0.1216	0.7844	0.0005	0.9931	0.0262
0.4115	−0.1170	0.7968	0.0058		
		Cycloheptane (1)–Cyclohexanol (2)			
0.0225	0.0009	0.3429	0.0895	0.5665	0.1794
0.0559	0.0038	0.3487	0.0923	0.6198	0.1938
0.0948	0.0090	0.3958	0.1125	0.6741	0.2029
0.1078	0.0102	0.4004	0.1154	0.7300	0.2037
0.1390	0.0192	0.4316	0.1273	0.7824	0.1969
0.1907	0.0332	0.4469	0.1355	0.8353	0.1806
0.1976	0.0335	0.4723	0.1450	0.8865	0.1556
0.2483	0.0532	0.4879	0.1529	0.9291	0.1267
0.2759	0.0620	0.5180	0.1624	0.9612	0.0950
0.3169	0.0795	0.5263	0.1681	0.9868	0.0528
		Cyclooctane (1)–Cyclohexanol (2)			
0.0110	0.0030	0.3269	0.1525	0.6490	0.2699
0.0241	0.0076	0.3704	0.1751	0.7106	0.2668
0.0429	0.0163	0.4106	0.1948	0.7729	0.2514
0.0695	0.0252	0.4300	0.2042	0.8328	0.2226
0.1051	0.0408	0.4483	0.2121	0.8852	0.1866
0.1412	0.0572	0.4817	0.2268	0.9301	0.1455
0.1827	0.0774	0.4882	0.2302	0.9622	0.1051
0.2301	0.1010	0.5355	0.2471	0.9857	0.0601
0.2801	0.1274	0.5903	0.2622		
		Cyclooctane (1)–Cycloheptanol (2)			
0.0131	0.0045	0.2835	0.1298	0.5845	0.2303
0.0360	0.0130	0.2999	0.1358	0.6494	0.2314
0.0723	0.0268	0.3698	0.1682	0.7131	0.2235
0.0797	0.0293	0.3765	0.1726	0.7835	0.2056
0.1207	0.0485	0.4197	0.1922	0.8490	0.1772
0.1592	0.0664	0.4304	0.1961	0.9020	0.1457
0.1689	0.0704	0.4679	0.2075	0.9544	0.1013
0.2257	0.0983	0.5221	0.2217	0.9841	0.0552
0.2288	0.1016				

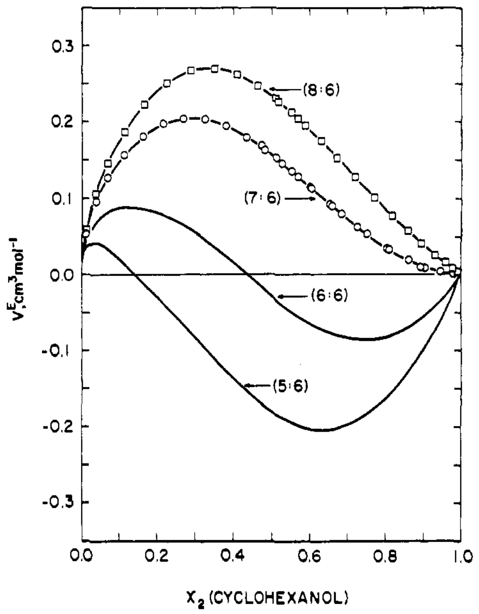

Figure 1. Molar excess volumes of cyclohexanol systems at 298.15 K. Experimental results: cycloheptane–cyclohexanol, O; cyclooctane–cyclohexanol, □. Curves are least-squares representations by eq 1: (5:6) from ref 2, (6:6) from ref 3.

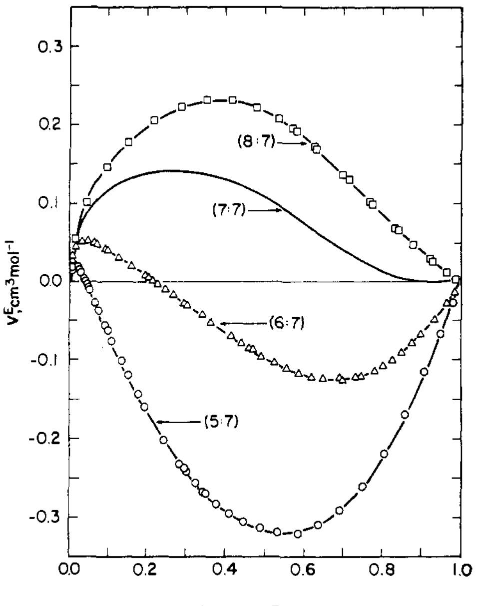

Figure 2. Molar excess volumes of cycloheptanol systems at 298.15 K. Experimental results: cyclopentane–cycloheptanol, O; cyclohexane–cycloheptanol, Δ; cyclooctane–cycloheptanol, □. Curves are least-squares representations by eq 1, (7:7) from ref 1.

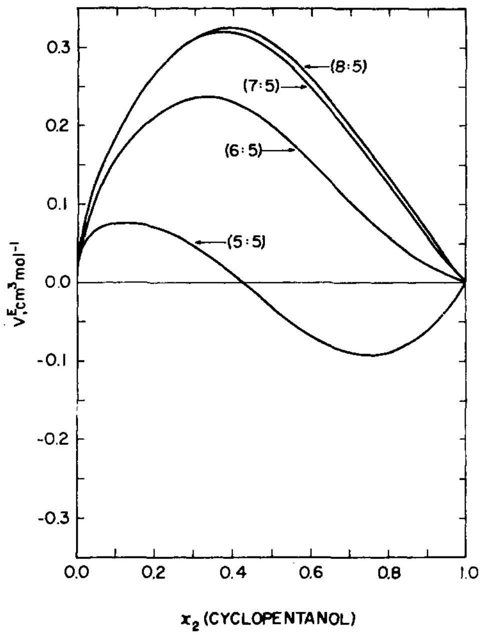

Figure 3. Molar excess volumes of cyclopentanol systems at 298.15 K: (5:5) from ref 3, (6:5) from ref 2, (7:5) and (8:5) from ref 1.

Discussion

Curves for the cycloalkane–cyclohexanol and cycloalkane–cycloheptanol systems studied previously (*1–3*)† have been added to Figures 1 and 2, and curves for cycloalkane–cyclopentanol systems (*1–3*) are shown in Figure 3 for comparison.

It can be seen from Figures 1–3 that V^E curves for cycloalkane–cycloalkanol systems tend to be sigmoid shaped with expansions and contractions occurring respectively at low and high mole fractions of cycloalkanol. Furthermore, there is a tendency for the magnitudes of the deviations from ideality to increase with increasing difference of the ring sizes of the components.

In order to examine the volume changes more closely, excess partial molar volumes

$$V_i^E(x_1) = \bar{V}_i(x_1) - \bar{V}_i^0 \qquad (3)$$

were calculated from eq 1 using the coefficients in Table II and the corresponding results from our previous work (*1–3*). Limiting values of $V_2^E(1)$ for cycloalkanols at infinite dilution in cycloalkanes, and of $V_1^E(0)$ for cycloalkanes at infinite dilution in cycloalkanols are summarized in Tables III and IV. The values of $V_2^E(1)$ in Table III are subject to relatively large errors since the

Table II. Coefficients and Standard Errors for Representations of V^E (cm^3 mol^{-1}) by Equation 1

	System $(p:q)^a$				
	(5:7)	(6:7)	(7:6)	(8:6)	(8:7)
c_1	6.204 04	7.278 99	8.350 57	8.536 97	5.706 90
c_2	−63.565 7	−56.181 4	−55.536 4	−53.274 7	−24.472 2
c_3	251.838	191.927	191.244	176.742	50.129 0
c_4	−560.558	−365.491	−364.594	−322.252	−46.779 5
c_5	714.282	398.401	390.126	327.767	15.763 5
c_6	−485.660	−235.530	−222.286	−176.915	
c_7	136.225	58.829 4	52.719 6	39.731 0	
σ	0.001 2	0.000 7	0.000 8	0.000 5	0.001 3

$^a p$ and q are ring sizes of cycloalkane and cycloalkanol, respectively.

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† There is an error in Table III of ref 3. The value of the coefficient c_4 for V^E of cyclohexane–cyclohexanol should be −134.584 (instead of −135.584).

Table III. Values of $V_2^E(1)$, the Excess Partial Molar Volume of Cycloalkanol at Infinite Dilution in Cycloalkane

Cycloalkane	$V_2^E(1)$ (cm^3 mol^{-1}) for cycloalkanol q		
p	$q = 5$	$q = 6$	$q = 7$
5	5.8	7.2	6.2
6	6.9	6.0	7.3
7	7.5	8.4	8.3
8	7.1	8.5	5.7

Table IV. Values of $V_1^E(0)$, the Excess Partial Molar Volume of Cycloalkane at Infinite Dilution in Cycloalkanol

Cycloalkanol	$V_1^E(0)$ (cm^3 mol^{-1}) for cycloalkane p			
q	$p = 5$	$p = 6$	$p = 7$	$p = 8$
5	−0.76	0.14	0.51	0.63
6	−1.13	−0.70	0.02	0.34
7	−1.23	−0.77	−0.04	0.35

V^E curves have a steep slope at $x_1 = 1$; thus the differences between the results for different systems are probably not reliable. It is clear, however, that a significant increase in volume (roughly 7 cm^3 mol^{-1}) accompanies the initial addition of a cycloalkanol to a cycloalkane.

The slopes of the V^E curves at $x_1 = 0$ are smaller and better defined by eq 1. Table IV shows that in a given cycloalkanol, $V_1^E(0)$ is negative for cyclopentane and becomes increasingly more positive as the ring size of the cycloalkane is increased. It can also be seen that the initial addition of a given cycloalkane to cycloalkanols of increasing ring size leads to increasing volume contractions or decreasing expansions.

The above observations indicate that the volume behavior of cycloalkane–cycloalkanol systems is the resultant of contributions from two opposing effects. A contraction occurs when the cycloalkane can be accommodated interstitially within the hydrogen bonded alcohol structure. On the other hand, an expansion occurs when there is a breakup of the alcohol structure. Other factors being equal, the relative contributions of these effects depend on the relative molecular sizes of the components.

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Nomenclature

$c_1, c_2, \ldots, c_k$ = coefficients in representation of V^E by eq 1, cm^3 mol^{-1}
m = number of experimental results for a system
n = number of coefficients used in eq 1
p = number of carbon atoms in cycloalkane molecule
q = number of carbon atoms in cycloalkanol molecule
$\bar{V}_i^0$ = partial molar volume of pure component i, cm^3 mol^{-1}
$\bar{V}_i(x_1)$ = partial molar volume of component i in mixture with mole fraction x_1, cm^3 mol^{-1}
V^E = molar excess volume, cm^3 mol^{-1}
$V_i^E(x_1)$ = excess partial molar volume of component i in mixture with mole fraction x_1, cm^3 mol^{-1}
x_i = mole fraction of component i

Greek Letters

σ = standard error for fit of V^E, cm^3 mol^{-1}

Subscripts

1 = cycloalkane component
2 = cycloalkanol component

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