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Excess Volumes of Some 1-Decanol–Cycloalkane Systems 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 1-decanol with cyclopentane, cyclohexane, and cyclooctane. The measurements were extended to high dilutions of 1-decanol. The excess volumes are positive except for 1-decanol–cyclopentane, which has a sigmoid-shaped excess volume curve. Partial molar excess volumes of the components were calculated for each mixture, and their values at infinite dilution were estimated.

Previous papers from our laboratory have investigated the effects of the sizes of the component molecules on the excess thermodynamic properties of cycloalkanol–cycloalkane mixtures (*1–4*) and of 1-alkanol–*n*-alkane mixtures (*5–8*). The present paper continues and extends these studies to include molecular shape effects through measurements of excess volumes for binary mixtures of 1-decanol with cyclopentane, cyclohexane, and cyclooctane.

Experimental Section

Cyclopentane from the J. T. Baker Chemical Co., cyclohexane (Spectro-grade) from the Fischer Scientific Co., and cyclooctane (Gold Label) from the Aldrich Chemical Co. were all purified by preparative GLC. In the course of the investigation, two samples (A and B) of 1-decanol were used. Sample A, BDH Pure Grade reagent further purified by GLC, was used for mixtures with cyclopentane. Sample B (marked 99%) from the Aldrich Chemical Co. was used as received, for mixtures with cyclohexane and cyclooctane. All of the components were stored over molecular sieves, as described previously (*5*). Densities, ρ, and refractive indexes, n_D, characterizing the pure liquids at 298.15 K are compared in Table I with data from the literature (*9*, *10*).

The changes in volume accompanying the mixing of the component liquids at constant pressure were measured in a successive dilution dilatometer (*11*), following the operational procedure described previously (*5*). 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 1-decanol was 2×10^{-5} for the high-dilution region ($x < 0.015$) and 8×10^{-5} for larger alkanol mole fractions. The experimental error of the molar excess volume, V^E, is estimated to be less than $(0.0003 + 0.001|V^E|)$ cm^3 mol^{-1}.

Results

The experimental results for the molar excess volumes of $xC_{10}H_{21}OH + (1 - x)C_nH_{2n}$ mixtures at 298.15 K are listed for $n = 5$, 6, and 8 in Table II. Each set of results was fitted with a polynomial in the square root of the mole fraction of 1-decanol

$$V^E = x(1 - x) \sum_{j=1}^{m} c_j x^{(j-1)/2} \tag{1}$$

Values of the coefficients c_j and standard deviations σ, determined by the method of least-squares with all points weighted equally, are given in Table III. The smoothed results are also presented graphically in Figure 1.

Table I. Physical Properties of Component Liquids at 298.15 K

	ρ/(g cm^{-3})		n_D	
	obsd	lit.	obsd	lit.
cyclopentane	0.740 42	0.740 45 (*9*)	1.403 63	1.403 63 (*9*)
cyclohexane	0.773 74	0.773 89 (*9*)	1.423 44	1.423 54 (*9*)
cyclooctane	0.831 95	0.832 0 (*9*)	1.456 22	1.456 3 (*9*)
1-decanol A	0.826 70	0.826 3 (*10*)		1.435 3 (*10*)
B	0.826 56		1.435 17	

The partial molar excess volumes, V_i^E, were derived for the most part from eq 1. However, for $x < 0.015$, values of V_i^E were obtained by smoothing the experimental results with cubic splines (*12*) since, as pointed out previously (*7*), eq 1 implies that V_1^E must have an infinite limiting slope at $x = 0$. These results are plotted in Figures 2 and 3. According to Euler's theorem for homogeneous functions, V_2^E should have zero slope at $x = 0$. However, this trend is not apparent on the scale of Figure 2 and for the present systems only becomes evident at very low mole fractions ($x < 0.002$). The values of V_1^E and of $V^E/[x(1 - x)]$ calculated from the splines in the dilute 1-decanol region are compared with the experimental results for $V^E/[x(1 - x)]$ in Figure 4. The limiting partial molar excess volumes, $V_1^{E,\infty}$, for 1-decanol at infinite dilution in the various cycloalkanes, and the limiting partial molar excess volumes, $V_2^{E,\infty}$, for the various cycloalkanes at infinite dilution in 1-decanol, are listed in Table IV.

Discussion

The excess volume curve is sigmoid-shaped only for the cyclopentane system, for which positive values of V^E are restricted to low mole fractions of 1-decanol ($x < 0.1$). For the two systems comprising the larger cycloalkane molecules, cyclohexane and cyclooctane, V^E is positive over the whole mole fraction range, and it is noteworthy that the values of V^E for corresponding mole fractions of 1-decanol differ by less than 0.04 cm^3 mol^{-1}.

Positive V^E values have also been reported for binary mixtures of cyclohexane with ethanol, 1-propanol, 1-butanol, 1-pentanol, and 1-octanol at 298.15 K (*13*). The results for equimolar mixtures decrease with increasing size of the 1-alkanol, and extrapolation to 1-decanol leads to a value of $V^E(0.5)$ ca. 0.15 cm^3 mol^{-1} lower than our result.

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Table II. Experimental Values of the Molar Excess Volumes of $xC_{10}H_{21}OH + (1 - x)C_nH_{2n}$ at 298.15 K

x	$V^E/(\mathrm{cm^3\ mol^{-1}})$	x	$V^E/(\mathrm{cm^2\ mol^{-1}})$	x	$V^E/(\mathrm{cm^3\ mol^{-1}})$	x	$V^E/(\mathrm{cm^3\ mol^{-1}})$
1-Decanol (1)–Cyclopentane (2)							
0.001 09	0.0045	0.052 13	0.0190	0.340 38	−0.0611	0.722 69	−0.0434
0.001 46	0.0059	0.058 15	0.0167	0.343 97	−0.0614	0.746 35	−0.0397
0.001 76	0.0071	0.067 24	0.0132	0.364 86	−0.0635	0.749 06	−0.0396
0.002 20	0.0087	0.075 90	0.0094	0.375 63	−0.0636	0.771 58	−0.0355
0.002 71	0.0106	0.087 41	0.0048	0.407 61	−0.0654	0.771 77	−0.0360
0.003 28	0.0123	0.094 46	0.0018	0.431 51	−0.0661	0.797 84	−0.0314
0.004 06	0.0146	0.096 47	0.0011	0.451 57	−0.0661	0.820 57	−0.0276
0.005 12	0.0172	0.098 44	0.0002	0.472 96	−0.0660	0.841 08	−0.0241
0.006 33	0.0195	0.099 72	−0.0002	0.500 82	−0.0653	0.861 45	−0.0205
0.007 52	0.0212	0.101 72	−0.0012	0.525 44	−0.0646	0.883 24	−0.0173
0.008 54	0.0225	0.103 53	−0.0020	0.545 47	−0.0638	0.897 40	−0.0150
0.009 61	0.0236	0.114 27	−0.0076	0.566 33	−0.0623	0.911 12	−0.0129
0.010 99	0.0246	0.129 75	−0.0133	0.571 31	−0.0614	0.920 58	−0.0114
0.012 92	0.0256	0.145 08	−0.0189	0.587 36	−0.0605	0.930 10	−0.0100
0.014 68	0.0262	0.164 75	−0.0252	0.601 61	−0.0589	0.939 84	−0.0087
0.016 91	0.0269	0.185 55	−0.0316	0.609 50	−0.0585	0.947 52	−0.0076
0.019 40	0.0271	0.206 38	−0.0372	0.634 61	−0.0555	0.956 64	−0.0063
0.021 74	0.0270	0.223 10	−0.0416	0.634 89	−0.0560	0.965 50	−0.0050
0.024 09	0.0269	0.240 20	−0.0454	0.660 11	−0.0526	0.975 80	−0.0039
0.026 37	0.0265	0.257 44	−0.0490	0.664 87	−0.0513	0.981 16	−0.0033
0.028 64	0.0264	0.271 67	−0.0516	0.683 29	−0.0496	0.987 07	−0.0025
0.032 13	0.0255	0.288 81	−0.0544	0.692 79	−0.0479	0.992 40	−0.0013
0.037 84	0.0241	0.302 94	−0.0566	0.702 20	−0.0469	0.995 25	−0.0007
0.043 42	0.0222	0.317 54	−0.0585	0.718 44	−0.0438		
1-Decanol (1)–Cyclohexane (2)							
0.000 66	0.0054	0.011 68	0.0670	0.050 10	0.1735	0.390 18	0.5005
0.001 14	0.0091	0.012 56	0.0703	0.050 85	0.1758	0.401 20	0.5004
0.001 21	0.0098	0.013 27	0.0735	0.053 89	0.1830	0.421 26	0.4990
0.001 79	0.0144	0.015 91	0.0827	0.068 48	0.2138	0.447 38	0.4954
0.001 91	0.0149	0.015 99	0.0823	0.072 97	0.2230	0.494 70	0.4824
0.002 57	0.0202	0.019 08	0.0931	0.086 99	0.2501	0.533 59	0.4660
0.002 79	0.0215	0.019 74	0.0943	0.109 06	0.2886	0.580 16	0.4399
0.003 56	0.0271	0.022 39	0.1030	0.132 13	0.3248	0.626 90	0.4083
0.003 60	0.0270	0.023 03	0.1049	0.156 86	0.3593	0.672 71	0.3733
0.004 07	0.0302	0.024 40	0.1082	0.184 56	0.3928	0.719 25	0.3321
0.004 32	0.0322	0.026 44	0.1146	0.214 43	0.4234	0.759 85	0.2927
0.005 36	0.0384	0.029 25	0.1216	0.248 25	0.4508	0.799 87	0.2514
0.005 42	0.0383	0.030 80	0.1265	0.284 42	0.4729	0.837 29	0.2094
0.006 84	0.0465	0.033 53	0.1338	0.317 30	0.4871	0.869 69	0.1713
0.007 16	0.0475	0.033 61	0.1332	0.325 02	0.4896	0.899 31	0.1345
0.008 53	0.0544	0.035 35	0.1383	0.356 25	0.4973	0.925 55	0.1006
0.009 67	0.0587	0.039 61	0.1487	0.358 95	0.4981	0.948 47	0.0704
0.010 69	0.0635	0.046 42	0.1660				
1-Decanol (1)–Cyclooctane (2)							
0.000 68	0.0056	0.040 86	0.1606	0.233 38	0.4684	0.519 09	0.5114
0.001 12	0.0092	0.047 69	0.1773	0.272 02	0.4974	0.549 91	0.4952
0.001 79	0.0143	0.053 16	0.1913	0.308 90	0.5169	0.599 44	0.4648
0.002 45	0.0194	0.057 65	0.2017	0.313 07	0.5192	0.645 84	0.4293
0.003 06	0.0237	0.060 52	0.2089	0.346 35	0.5293	0.694 48	0.3866
0.004 20	0.0314	0.076 64	0.2436	0.353 34	0.5322	0.737 46	0.3436
0.005 27	0.0383	0.080 46	0.2514	0.354 69	0.5321	0.776 43	0.3011
0.006 54	0.0455	0.082 80	0.2570	0.376 11	0.5354	0.814 32	0.2571
0.008 38	0.0550	0.103 61	0.2969	0.378 63	0.5354	0.849 28	0.2137
0.010 05	0.0628	0.106 95	0.3035	0.395 55	0.5370	0.880 28	0.1737
0.012 39	0.0728	0.109 09	0.3062	0.400 27	0.5368	0.907 65	0.1367
0.013 26	0.0752	0.133 06	0.3472	0.410 99	0.5373	0.931 78	0.1027
0.014 60	0.0814	0.133 72	0.3484	0.435 27	0.5347	0.951 53	0.0739
0.017 54	0.0923	0.161 26	0.3889	0.454 15	0.5324	0.967 28	0.0505
0.020 77	0.1032	0.164 87	0.3934	0.485 91	0.5240	0.979 42	0.0321
0.024 60	0.1145	0.192 38	0.4284	0.500 69	0.5183	0.990 73	0.0146
0.032 47	0.1377	0.195 83	0.4314	0.513 49	0.5134	0.995 19	0.0077

No abrupt changes in volume behavior were observed in our previous studies of 1-alkanol–*n*-alkane systems (*5–8*) or of cycloalkanol–cycloalkane systems (*1–4*). The V^E curves for both of these sets of systems change more systematically from negative to positive values over the whole mole fraction range as the ratio of molecular sizes, alcohol/hydrocarbon, decreases. This behavior was interpreted as a balance between positive and negative effects. Positive contributions to V^E arise from the chemical effect of H-bond breaking and from nonspecific interactions between the real species in the mixture (alkanol monomers and multimers, and hydrocarbon molecules). Negative contributions result from interstitial accommodation and changes of free volume (*8*).

Several factors may contribute to the somewhat different behavior of 1-decanol–cycloalkane systems. The packing of the molecules in these systems is less efficient since interstitial accommodation of the cycloalkane within the branched structure of alkanol multimers is hindered. A comparison of excess enthalpy data for mixtures of 1-alkanols with *n*-alkanes and with cycloalkanes (*14*, *15*) suggests that the breaking of H bonds may also play a more important role in the latter systems. The excess volumes of cyclohexane + *n*-alkane systems (*16*),

Table III. Coefficients and Standard Deviations for Representations of the Molar Excess Volumes of 1-Decanol (1)–Cycloalkane (2) Mixtures at 298.15 K by Eq 1

	component 2		
	cyclopentane	cyclohexane	cyclooctane
c_1	7.2348	11.8690	11.7373
c_2	−76.9690	−91.2461	−83.8514
c_3	365.3765	427.7322	370.4190
c_4	−1007.658	−1170.328	−949.618
c_5	1694.031	1931.881	1454.543
c_6	−1704.554	−1903.439	−1316.546
c_7	941.501	1030.622	648.655
c_8	−219.126	−235.714	−133.756
σ	0.0004	0.0006	0.0005

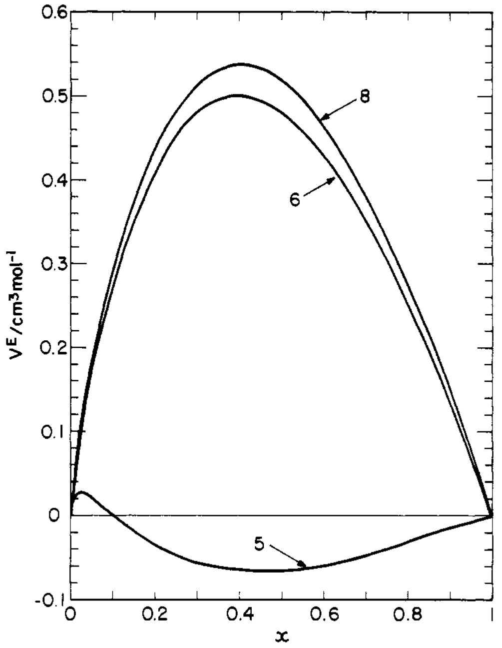

Figure 1. Molar excess volumes V^E for $xC_{10}H_{21}OH + (1 - x)C_nH_{2n}$ at 298.15 K. Curves calculated from eq 1. Labels indicate n.

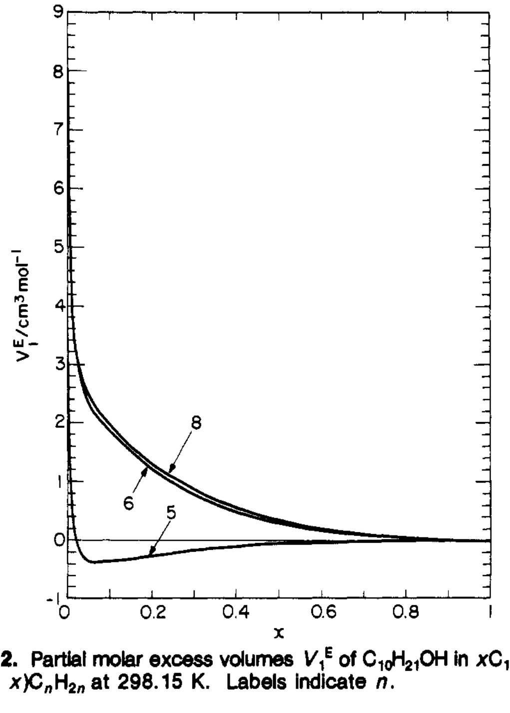

Figure 2. Partial molar excess volumes V_1^E of $C_{10}H_{21}OH$ in $xC_{10}H_{21}OH + (1 - x)C_nH_{2n}$ at 298.15 K. Labels indicate n.

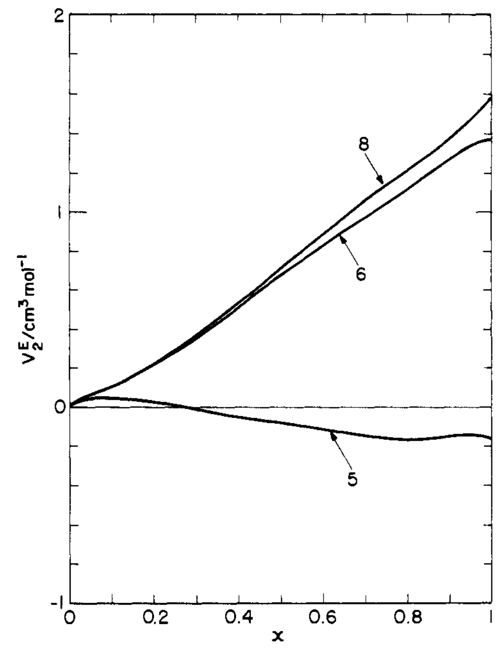

Figure 3. Partial molar excess volumes V_2^E of C_nH_{2n} in $xC_{10}H_{21}OH + (1 - x)C_nH_{2n}$ at 298.15 K. Labels indicate n.

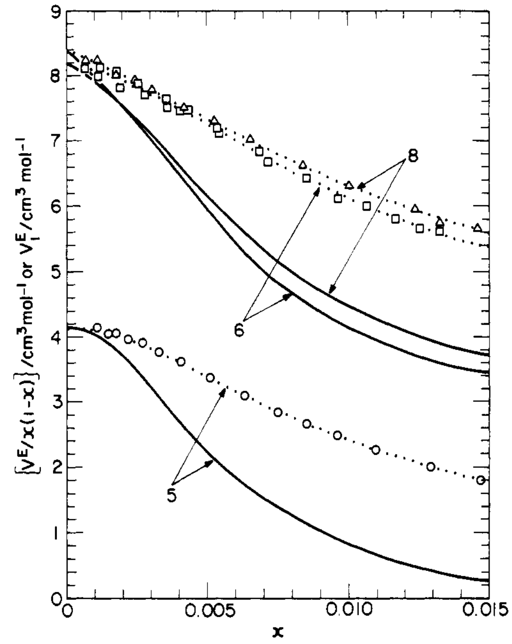

Figure 4. Plots of $V^E/[x(1 - x)]$ and V_1^E for $xC_{10}H_{21}OH + (1 - x)C_nH_{2n}$ at 298.15 K and low values of x. Our results for $V^E/[x(1 - x)]$: (○) cyclopentane; (□) cyclohexane; (△) cyclooctane. Curves calculated from splines: (···) $V^E/[x(1 - x)]$; (—) V_1^E. Labels indicate n.

Table IV. Partial Molar Excess Volumes at Infinite Dilution, $V_i^{E,\infty}$, for 1-Decanol (1)–Cycloalkane (2) Mixtures at 298.15 K

component 2	$V_1^{E,\infty}$/(cm^3 mol^{-1})	$V_2^{E,\infty}$/(cm^3 mol^{-1})
cyclopentane	4.14	−0.16
cyclohexane	8.19	1.38
cyclooctane	8.40	1.58

which, in contrast to those of binary *n*-alkane systems, are positive and increase with increasing *n*-alkane chain length, have been attributed to the disruption of orientational order in the larger *n*-alkanes by cyclohexane (*17*). The hydrocarbon tails of long 1-alkanols may participate to some extent in a similar ordering, but cycloalkane molecules will disrupt the structure more than *n*-alkane molecules.

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Glossary

c_1, c_2, ..., c_j	coefficients in representation of V^E by eq 1, cm^3 mol^{-1}
m	numer of coefficients used in eq 1
n_D	refractive index for sodium light
V^E	molar excess volume, cm^3 mol^{-1}
V_i^E	partial molar excess volume of component i, cm^3 mol^{-1}
$V_i^{E,\infty}$	limiting value of V_i^E at infinite dilution of component i, cm^3 mol^{-1}
x	mole fraction of 1-decanol

Greek Letters

ρ	density, g cm^{-3}
σ	standard deviation for fit of V^E, cm^3 mol^{-1}

Subscripts

1	1-decanol component
2	cycloalkane component

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Surface Tension of Mercury between 15 and 50 °C by the Sessile Drop Method

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The surface tension of mercury has been determined by the sessile drop method in vacuo at 15, 20, 25, and 50 °C. Ca. 50 measurements were made at each of the four temperatures, extending over a period of 2 yr. The greatest attention was paid to the purification of the mercury and the estimation of all possible errors in the determination of the surface tension. The surface tension varied linearly with temperature according to the equation $\gamma = 490.8 - 0.2155t$ with a correlation coefficient of 0.9998, where γ = surface tension in mN m^{-1} at t °C. This relation is in excellent agreement with the results obtained previously by one of the authors and with that postulated by Jasper from the large number of determinations of the surface tension of mercury, $\gamma = 490.6 - 0.2049t$. The temperature coefficient obtained in this study is in slightly better agreement with the average of all previous experimental measurements, −0.224 mN m^{-1} K^{-1}, than with the value recommended by Jasper, 0.2049 mN m^{-1} K^{-1}.

Introduction

The surface tension of mercury is an important quantity, as indicated in the lengthy review on the surface properties of mercury by Wilkinson (*1*). Even so there is still some uncertainty about its value. Wilkinson (*1*) reports that the range of values obtained during the three decades preceding his review (1942–1972) is still exceptionally large. The average of all of these values is 469.7 ± 34.3 mN m^{-1}. Jasper (*2*) has carefully analyzed the wide range of values and selected the results of one of the present authors (N.K.R.) (*3*), Kemball (*4*), and Bosworth (*5*) as reference data for the National Bureau of Standards. He proposes a linear relation between the surface tension and temperature of the following form:

$$\gamma = 490.6 - 0.2049t \qquad (1)$$

where γ = surface tension in mN m^{-1} at temperature t °C.

The original results of Roberts (*3*) were over a limited temperature range, 16.5–25.0 °C. In this paper we present results from 15 to 50 °C using the sessile drop method in vacuo and involving over 50 measurements at each of the following temperatures: 15, 20, 25, and 50 °C. The sessile drop method avoids a contact angle and therefore has advantages over other methods for measuring surface tension. Furthermore the measurements for all four temperatures extended over a period of 2 yr.

Before proceeding it is necessary to correct a serious error in Wilkinson's otherwise excellent review. On p 582 of the review, referring to the surface tension obtained by Roberts (*3*), he says, "Some recent workers have just added 1 dyne cm^{-1} to a value calculated by means of the Worthington equation [to obtain the surface tension]. It is clear that accurate values cannot be obtained unless recourse is made to equation 2", i.e.

$$\gamma = h^2\rho g/2 - \gamma \int_0^h \sin\phi/x \, dz + 2\gamma h/b \qquad (2)$$

where h = height of the apex of the drop above the maximum cross-sectional area, ρ = density of the liquid (Hg), g = acceleration due to gravity, x = horizontal radius of a given section above the maximum cross-sectional diameter, z = distance between the apex and this horizontal section, ϕ = angle of