Thermodynamic Properties of Some Cycloalkane–Cycloalkanol Systems at 298.15K. II.

George C. Benson,[1] **Subhash C. Anand, and Osamu Kiyohara**[2]
Division of Chemistry, National Research Council of Canada, Ottawa, Ont., Canada K1A 0R6

The thermodynamic properties of mixtures of cyclopentane with cyclohexanol and of cyclohexane with cyclopentanol are investigated at 298.15K by calorimetric measurements of enthalpies of mixing, dilatometric measurements of volumes of mixing, and determinations of total vapor pressures. The method of Barker is used to calculate vapor-liquid equilibria and excess Gibbs free energies from the vapor-pressure results. The shapes of the curves for the excess enthalpies and for the excess Gibbs free energies of the present systems are quite similar to those of the cycloalkane–cycloalkanol systems studied previously. The values of H^E can be fitted well by the nonrandom two-liquid theory, and the assumption that the parameters are independent of temperature leads to estimates of G^E which agree approximately with the experimental values. The curves for the volumes of mixing show more variation in shape. This variation can be explained qualitatively as resulting from differences in the sizes of the component molecules and differences in the hydrogen bonding of the alcohols.

There have been a number of studies of the excess thermodynamic properties of hydrocarbon-alcohol systems. However, relatively little attention has been devoted to binary mixtures of cycloalkanes with cycloalkanols. Part I of this series (2) described measurements of molar excess enthalpies, molar excess volumes, and equilibrium vapor pressures for the systems cyclopentane–cyclopentanol and cyclohexane–cyclohexanol at 298.15K. In both of these systems, the ring sizes of the components are equal. Our investigation has now been broadened to include systems of unequal ring size, and this paper reports the results of similar measurements for cyclopentane–cyclohexanol and cyclohexane–cyclopentanol.

Experimental

The samples of the component cycloalkanes and cycloalkanols were the same as used previously. Values of their densities, refractive indices, and vapor pressures are given in Part I.

All of the experimental studies were carried out at a nominal temperature of 298.15K. Detailed descriptions of the equipment and techniques are available in previous publications.

A modified form of a Van Ness dilution calorimeter (*4*) was used to measure enthalpies of mixing in the absence of any vapor space. The accuracy of the results is estimated to be better than ±1% over most of the concentration range.

Volumes of mixing at constant pressure were determined dilatometrically, with a successive dilution technique (*7*). The results are estimated to be accurate to better than $\pm 1 \times 10^{-3}$ cm^3 mol^{-1}.

Static vapor pressures for mixtures of known total compositions (i.e., liquid + vapor phases) were measured to ±0.005 torr with a quartz spiral gauge. The equilibrium cell was similar to that used by Singh and Benson (*9*). The compositions of the vapor and liquid phases and the excess Gibbs free energy of the liquid phase were computed by the modified form of Barker's analysis described in Part I. Representation of the excess Gibbs free energy by a polynomial in the square root of the mole fraction of alcohol again provided a satisfactory basis for this analysis. Corrections for imperfection of the vapor phase were applied as described in Part I, and the same values were used for the second virial coefficients of the cycloalkanes.

Results

Table I summarizes the experimental results for the molar excess enthalpies and molar excess volumes. The equilibrium vapor-liquid mole fractions, vapor pressures, and molar excess Gibbs free energies are listed in Table II. In all cases, the subscript 1 indicates the cycloalkane component. The results for H^E, V^E, and G^E are also presented graphically in Figures 1–3.

The square-root relationship

$$X^E = x_1 (1 - x_1) \sum_{j=1}^{n} c_j (1 - x_1)^{(j-1)/2} \qquad (1)$$

which was used for representing G^E in the analysis of the vapor-liquid results, was also suitable for representing H^E and V^E. Values of the coefficients, c_j, obtained by the method of least squares, are given in Table III, along with the standard error of estimate for each representation. Smoothed values calculated from Equation 1 with the coefficients from Table III are shown as solid curves in Figures 1–3. Also shown are curves for the entropy contribution to G^E obtained from the relation

$$-TS^E = G^E - H^E \qquad (2)$$

Discussion

Values of excess properties of the present systems at 298.15K have not been reported previously. However, densities for both systems have been determined at 295.15K (*3*). Excess volumes calculated from these results show considerable scatter. For cyclopentane–cyclohexanol, the V^E curve agrees qualitatively in shape with our results, but the contractions at low values of x_1 are much larger than those we observed. The values of V^E for cyclohexane–cyclopentanol also are larger in magnitude than our results and are of opposite sign.

It is interesting to compare the results for the present systems with those obtained previously for cyclopentane–cyclopentanol and cyclohexane–cyclohexanol. From Figures 1 and 2 and from the corresponding illustrations in Part I, the behavior of each of the excess properties, H^E, G^E, and TS^E, is very similar in the four systems. All of the curves for H^E are skewed toward low alcohol mole fractions; the curves for G^E are similarly skewed, but to a lesser degree. In all cases, the values of TS^E are predominantly negative, but each system has a small region of positive values at dilute alcohol mole fractions.

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[1] To whom correspondence should be addressed.

[2] Present address, Department of Chemistry, Université de Sherbrooke, Sherbrooke, P.Q., Canada.

This general behavior is qualitatively attributable to the major role played by hydrogen bonding in determining the excess properties of these systems. The excess enthalpies of binary cycloalkane mixtures are fairly small in magnitude (<50 J mol^{-1}) at 298.15K (*1, 10*). When a cycloalkanol replaces one of the cycloalkanes, the values of H^E are increased substantially by the energy required to break the hydrogen bonds between the alcohol molecules. Positional and orientational order imposed by the hydrogen bonding remaining in the mixture leads to negative deviations of the entropy of mixing from the ideal (random mixing) value. However, at low alcohol mole fractions, there are few hydrogen bonds in the mixture, and positive excess entropies are possible as a result of the increasing orientational disorder.

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

x_1	H^E, J mol^{-1}	x_1	V^E, cm^3 mol^{-1}
	Cyclopentane(1)–cyclohexanol(2)		
0.1204	137.8	0.0287	−0.0319
0.2533	288.2	0.0699	−0.0721
0.3476	390.0	0.0873	−0.0880
0.4412	479.6	0.1293	−0.1205
0.4894	518.1	0.1897	−0.1588
0.5265	541.5	0.1988	−0.1636
0.5373	546.3	0.2620	−0.1891
0.5493	554.4	0.2850	−0.1973
0.6224	578.3	0.3495	−0.2044
0.6401	577.9	0.3714	−0.2063
0.6675	574.2	0.3882	−0.2056
0.7392	550.1	0.4439	−0.1958
0.7489	541.9	0.4757	−0.1875
0.8454	454.4	0.4870	−0.1852
0.8522	443.9	0.5127	−0.1759
0.9381	303.5	0.5546	−0.1586
0.9412	294.3	0.6041	−0.1353
		0.6543	−0.1075
		0.6604	−0.1053
		0.7187	−0.0734
		0.7801	−0.0403
		0.7952	−0.0309
		0.8368	−0.0108
		0.8930	0.0167
		0.9398	0.0352
		0.9687	0.0410
		0.9890	0.0325
	Cyclohexane(1)–cyclopentanol(2)		
0.0748	130.7	0.0166	0.0024
0.1475	248.7	0.0493	0.0088
0.1525	259.9	0.0936	0.0195
0.2222	364.8	0.1461	0.0363
0.2253	364.4	0.2121	0.0620
0.3072	471.7	0.2743	0.0899
0.3127	482.8	0.3282	0.1164
0.3664	544.3	0.3573	0.1303
0.3866	566.9	0.3801	0.1422
0.3933	569.6	0.3825	0.1432
0.3994	570.5	0.4104	0.1570
0.4201	594.0	0.4240	0.1641
0.4585	622.2	0.4407	0.1714
0.4627	628.5	0.4612	0.1821
0.4907	637.1	0.4763	0.1879
0.5238	656.7	0.4972	0.1976
0.5265	660.4	0.5100	0.2025
0.6546	659.6	0.5181	0.2052
0.6549	662.7	0.5681	0.2210
0.7487	612.3	0.6320	0.2339
0.7843	578.5	0.7080	0.2346
0.8295	536.4	0.7881	0.2167
0.9013	423.5	0.8574	0.1834
0.9190	402.1	0.9180	0.1409
0.9814	222.1	0.9663	0.0902

The curves for V^E show a wider variation in behavior than those for H^E, G^E, and TS^E. For both cyclopentane–cyclopentanol and cyclohexane–cyclohexanol (studied in Part I), the V^E curves are sigmoid shaped and have approximately equal positive and negative lobes. In Figure 3 the curve for cyclopentane–cyclohexanol is also sigmoid shaped, but the negative lobe is much larger than the positive lobe, and the minimum is approximately twice as deep as the minima observed in Part I. For cyclohexane–cyclopentanol mixtures, the V^E curve is no longer sigmoid shaped but is positive over the whole concentration range and skewed toward low alcohol mole fractions.

It has been suggested that sigmoid-shaped V^E curves for mixtures containing alcohols result from two opposing effects (*5, 6*). A contraction results when a nonpolar molecule can be accommodated interstitially within the hydrogen-bonded alcohol structure; on the other hand, an expansion results when there is a breakup of the hydrogen-bonded structure. Other factors being equal, the relative contributions of these effects will depend on the rel-

Table II. Vapor-Liquid Equilibria at 298.15K

x_1	y_1	p, torr	G^E, J mol^{-1}
	Cyclopentane(1)–cyclohexanol(2)		
0.0836	0.9893	75.45	225.4
0.1872	0.9950	145.75	472.5
0.1935	0.9951	150.44	503.8
0.2935	0.9966	197.62	677.8
0.3985	0.9974	234.44	840.3
0.4048	0.9974	235.40	839.3
0.5003	0.9978	257.49	921.2
0.5026	0.9978	258.98	932.4
0.5750	0.9980	269.56	939.2
0.6064	0.9981	274.96	945.8
0.6102	0.9981	276.91	957.7
0.6590	0.9982	281.19	922.6
0.7074	0.9983	287.93	896.1
0.7286	0.9984	290.26	874.3
0.7811	0.9985	295.99	803.7
0.8237	0.9986	298.79	712.3
0.8619	0.9987	303.12	627.1
0.9317	0.9989	309.27	396.2
0.9376	0.9989	309.48	368.7
	Cyclohexane(1)–cyclopentanol(2)		
0.0517	0.9010	21.13	177.0
0.0891	0.9368	32.00	293.9
0.1374	0.9554	43.64	442.3
0.1445	0.9571	44.99	454.3
0.1940	0.9657	54.38	592.6
0.2159	0.9683	57.70	637.9
0.2199	0.9687	58.32	648.1
0.3029	0.9749	68.62	812.9
0.4305	0.9799	78.78	979.4
0.5901	0.9834	86.83	1054.3
0.6738	0.9849	89.39	1002.7
0.6750	0.9849	89.89	1014.3
0.7452	0.9861	91.29	912.4
0.7713	0.9866	93.01	896.0
0.8213	0.9876	93.37	768.1
0.8232	0.9876	93.82	774.0
0.8911	0.9891	95.91	593.1
0.9088	0.9895	95.40	506.8
0.9288	0.9901	96.51	443.9
0.9617	0.9914	96.96	277.5

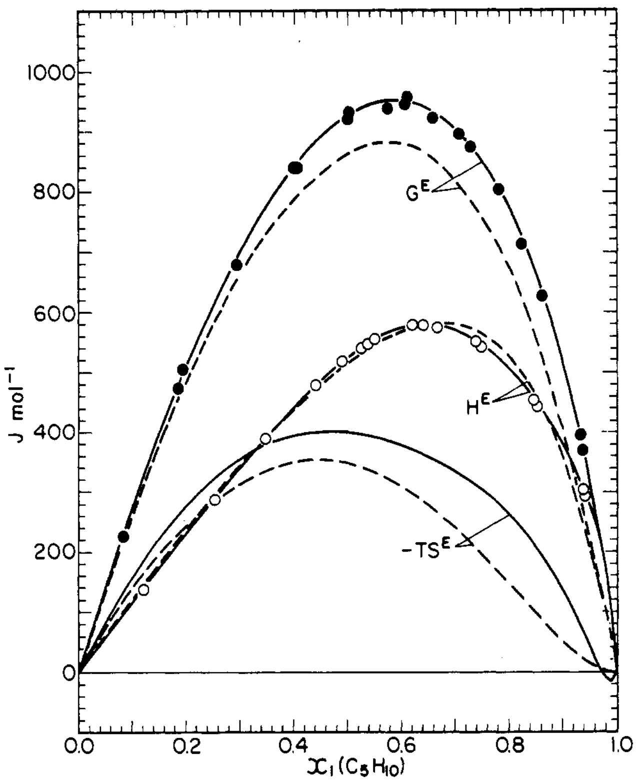

Figure 1. Molar excess enthalpies, Gibbs free energies, and entropies for cyclopentane–cyclohexanol mixtures at 298.15K
Experimental results H^E, ○; G^E, ●
Solid curves for H^E and G^E are least-squares representations by Equation 1; curve for $-TS^E$ obtained from Equation 2
Broken curves NRTL theory, assuming NRTL parameters are independent of temperature.

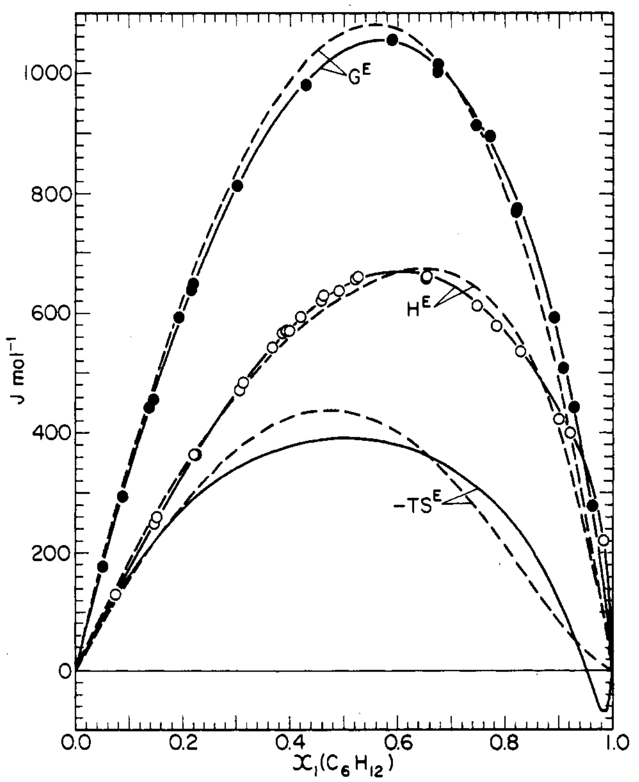

Figure 2. Molar excess enthalpies, Gibbs free energies, and entropies for cyclohexane–cyclopentanol mixtures at 298.15K
Experimental results H^E, ○; G^E, ●
Solid curves for H^E and G^E are least-squares representations by Equation 1; curve for $-TS^E$ obtained from Equation 2
Broken curves NRTL theory, assuming NRTL parameters are independent of temperature

ative molecular sizes of the two components. In each of the systems studied in Part I, the two components are of approximately equal molecular size, and sigmoid-shaped curves with approximately equal lobes were observed. When cyclopentane–cyclohexanol mixtures are formed, the small cycloalkane molecule can be accommodated more readily (i.e., to a higher concentration) within the hydrogen-bonded structure of the large cycloalkanol. Thus, the negative lobe is accentuated, and the positive lobe decreased. For cyclohexane–cyclopentanol, accommodation of the larger cycloalkane molecule within the alcohol structure becomes difficult, and it appears that the contribution from the breakup of the alcohol structure predominates at all concentrations.

The nonrandom two-liquid (NRTL) theory (*8*) was moderately successful in providing an empirical correlation between the results for H^E and G^E in Part I. The treatment assumed that the NRTL parameters (i.e., free energies g_{ij} and measure of nonrandomness α_{12}) were independent of temperature. A similar analysis was carried out for the present systems. Values of NRTL parameters obtained by fitting the smoothed curves for H^E are given in Table IV. The broken curves shown for H^E, G^E, and $-TS^E$ in Figures 1 and 2 were calculated with these values. Standard deviations of the NRTL curves from the experimental curves are listed in Table IV. As in Part I, the NRTL theory provides a useful way of estimating G^E for cycloalkane–cycloalkanol mixtures from experimental results for H^E.

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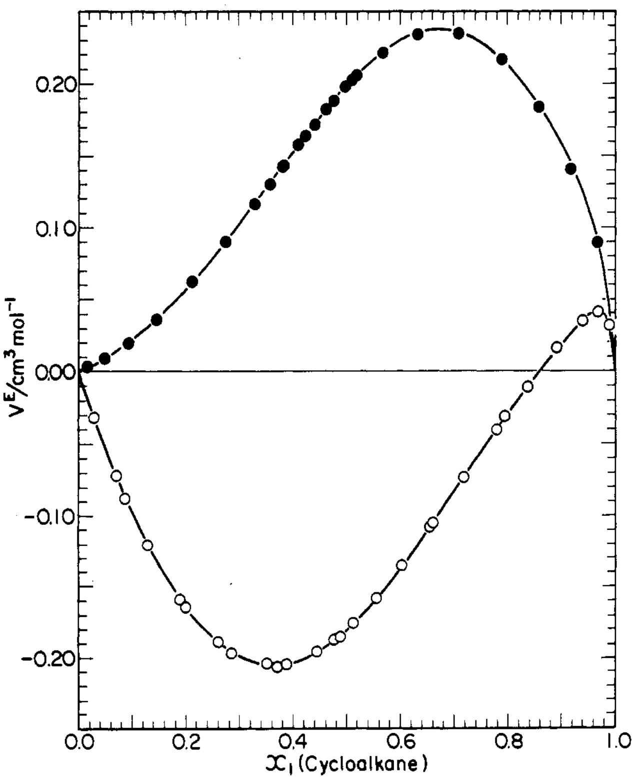

Figure 3. Molar excess volumes at 298.15K
Experimental results cyclopentane–cyclohexanol, ○; cyclohexane–cyclopentanol, ●
Curves are least-squares representations by Equation 1

Table III. Coefficients and Standard Errors for Representations of Excess Functions by Equation 1

	Cyclopentane–cyclohexanol			Cyclohexane–cyclopentanol		
	H^E, J mol^{-1}	V^E, cm^3 mol^{-1}	G^E, J mol^{-1}	H^E, J mol^{-1}	V^E, cm^3 mol^{-1}	G^E, J mol^{-1}
c_1	16762.0	7.1719	10128.0	32991.0	6.8650	11071.0
c_2	−86763.0	−58.966	−21561.0	−246797.0	−36.388	−24565.0
c_3	225410.0	206.02	30366.0	902334.0	98.133	35968.0
c_4	−299490.0	−390.07	−22840.0	−1819600.0	−134.68	−27397.0
c_5	193870.0	406.81	6822.0	2086500.0	88.82	8568.0
c_6	−48635.0	−221.90		−1278200.0	−22.61	
c_7		49.80		324700.0		
σ^a	1.2	0.0009	6.0[b]	3.5	0.0005	7.3[c]

[a] $\sigma^2 = \Sigma[X^E(\text{Equation 1}) - X^E(\text{experimental})]^2/(\text{number of degrees of freedom})$ where the sum is taken over the experimental points, and the number of degrees of freedom is equal to the difference between the number of points and the number of adjustable coefficients. [b] Corresponding standard error in fit of vapor pressures = 0.66 torr. [c] Corresponding standard error in fit of vapor pressures = 0.30 torr.

Table IV. Comparison of NRTL and Experimental Curves for Excess Thermodynamic Functions

	NRTL parameters			σ^a		
System	$g_{12} - g_{11}$, J mol^{-1}	$g_{12} - g_{22}$, J mol^{-1}	α_{12}	H^E, J mol^{-1}	G^E, J mol^{-1}	TS^E, J mol^{-1}
C_5H_{10}–$C_6H_{11}OH$	620	4330	0.405	19.6	66.9	65.5
C_6H_{12}–C_5H_9OH	1600	4560	0.421	32.7	32.6	35.0

[a] $\sigma^2 = \int_0^1 [X^E(\text{Equation 1}) - X^E(\text{NRTL})]^2 dx_1$.

Nomenclature

$c_1, c_2, \ldots c_j$ = coefficients in representations of excess properties by Equation 1
g_{ij} = Gibbs energy parameter (in NRTL theory) for interaction between an i–j pair of molecules, J mol^{-1}
G^E = molar excess Gibbs free energy, J mol^{-1}
H^E = molar excess enthalpy, J mol^{-1}
n = number of coefficients in Equation 1
p = vapor pressure, torr
S^E = molar excess entropy, J mol^{-1} K^{-1}
T = absolute temperature, K
V^E = molar excess volume, cm^3 mol^{-1}
X^E = typical molar excess property
x_i = mole fraction of component i in liquid phase
y_i = mole fraction of component i in vapor phase

Greek Letters

α_{12} = nonrandomness parameter (in NRTL theory)
σ = standard error

Subscripts

1 = cycloalkane component
2 = cycloalkanol component

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