LITERATURE CITED

(1) Åkerlöf, G. C., Oshry, H. I., *J. Amer. Chem. Soc.*, **72**, 2844 (1950).
(2) Eigen, M., Wicke, E., *Z. Elektrochem.*, **55**, 354 (1951).
(3) Frazer, J. C. W., "The Direct Measurement of Osmotic Pressure. Contemporary Developments in Chemistry," Columbia University, New York, N.Y., 1927.
(4) Gardner, E. R., Jones, P. J., deNordwall, H. J., *Trans. Faraday Soc.*, **59**, 1994 (1963).
(5) Gibbard, H. F., Jr., *J. Phys. Chem.*, **73**, 2382 (1969).
(6) Gibbard, H. F., Jr., PhD Thesis, Massachusetts Institute of Technology, 1967.
(7) Gibbard, H. F., Jr., Gossmann, A. F., "Freezing Points of Aqueous Electrolyte Mixtures. The System $NaCl-MgCl_2$," Symposium on Electrolytes, 5th Middle Atlantic Regional Meeting, American Chemical Society, University of Delaware, April 1970.
(8) Harned, H. S., Owen, B. B., "The Physical Chemistry of Electrolytic Solutions," 3rd ed, p 491, Reinhold, New York, N.Y., 1958.
(9) Lietzke, M. H., Stoughton, R. W., *J. Phys. Chem.*, **65**, 508 (1961).
(10) Negus, S. S., PhD Thesis, Johns Hopkins University, 1922.
(11) Olynyk, P., Gordon, A. R., *J. Amer. Chem. Soc.*, **65**, 224 (1943).
(12) Owen, B. B., Miller, R. C., Milner, C. E., Cogan, H. L., *J. Phys. Chem.*, **65**, 2065 (1961).
(13) Patterson, C. S., Gilpatrick, L. O., Soldano, B. A., *J. Chem. Soc.*, **1960**, p 2730.
(14) Platford, R. F., *J. Phys. Chem.*, **72**, 4053 (1968).
(15) Robinson, R. A., Stokes, R. W., "Electrolyte Solutions," Academic Press, New York, N.Y., 1955.
(16) Rush, R. M., Johnson, J. S., *J. Chem. Eng. Data*, **11**, 590 (1966).
(17) Scatchard, G., *J. Amer. Chem. Soc.*, **83**, 2636 (1961).
(18) Scatchard, G., *ibid.*, **90**, 3124 (1968).
(19) Scatchard, G., *ibid.*, **91**, 2410 (1969).
(20) Scatchard, G., Gibbard, H. F., Jr., "The Osmotic Coefficients of Aqueous Lithium Chloride," presented to the Physical Chemistry Division, 156th National Meeting, American Chemical Society, Atlantic City, N.J., September 1968.
(21) Scatchard, G., Gibbard, H. F., Jr., Rousseau, R. A., *J. Chem. Thermodynam.*, in press, 1972.
(22) Scatchard, G., Prentiss, S. S., *J. Amer. Chem. Soc.*, **55**, 4355 (1933).
(23) Scatchard, G., Rush, R. M., Johnson, J. S., *J. Phys. Chem.*, **74**, 3786 (1970).
(24) Scatchard, G., Wilson, G. M., Satkiewicz, F. G., *J. Amer. Chem. Soc.*, **86**, 125 (1964).
(25) Soldano, B. A., Patterson, C. S., *J. Chem. Soc.*, **1962**, p 937.
(26) Spiegler, K. S., "Salt Water Purification," Wiley, New York, N.Y., 1962.
(27) Wu, Y. C., Rush, R. M., Scatchard, G., *J. Phys. Chem.*, **72**, 4048 (1968).

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Thermodynamic Properties of Some Cycloalkane–Cycloalkanol Systems at 25°C

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Molar excess enthalpies and volumes of the systems cyclopentane–cyclopentanol and cyclohexane–cyclohexanol at 25°C were determined by direct calorimetric and dilatometric measurements. Excess Gibbs free energies (also at 25°C) were obtained from studies of the vapor-liquid equilibria. Correlation of the results for the excess enthalpy and free energy by means of the NRTL theory was investigated.

There have been few previous investigations of the thermodynamic properties of binary mixtures formed from cycloalkanes and cycloalkanols. This paper reports measurements of excess enthalpies, excess volumes, and vapor-liquid equilibria for the systems cyclopentane–cyclopentanol and cyclohexane–cyclohexanol at 25°C.

EXPERIMENTAL

Only a brief outline of the equipment and operational methods is given below. More detailed descriptions can be found in previous publications. Although the freezing temperature of cyclohexanol is about 25.4°C (*23*), it was possible to carry out the determinations of H^E and V^E at 25°C with this component in a supercooled liquid state.

Calorimetric Measurements. A modified form of Van Ness dilution calorimeter (*15*) was used to determine the excess enthalpies. In this calorimeter, successive measured portions of one component were added to a weighed amount of the other component in the absence of any vapor space. The cooling effect of the mixing process was compensated by Joule heating, and the electrical energy needed to maintain a set value of the temperature in the mixing vessel was determined. Generally, variations of the temperature from the set value were less than ±0.003°C, and there was close compensation between positive and negative deviations. At the completion of a dilution, the temperature was restored to within ±0.0003°C of the set value. The calorimeter was immersed in a water bath operated at 25.00 ± 0.01°C and controlled to ±0.001°C during a run. The error of the enthalpy results for the present systems is estimated to be less than ±1% over most of the concentration range.

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Table I. Physical Constants of Component Liquids at 25°C

Component	Refractive index n_D		Density, g cm^{-3}		Vapor pressure, torr	
	Measured	Lit.	Measured	Lit.	Measured	Lit.
Cyclopentane	1.40360	1.40363 (*1*)	0.74034	0.74045 (*1*)	317.49	317.46 (*1*)
Cyclopentanol	1.45159 (1.45527[c])	1.4505[a] (*23*) (1.45512[c]) (*23*)	0.94291	0.94298[b] (*23*)	2.20	...
Cyclohexane	1.42350	1.42354 (*1*)	0.77389	0.77389 (*1*)	97.52	97.58 (*1*)
Cyclohexanol	1.46445	1.46477 (*23*)	0.94504	0.94542[a] (*23*)	0.95	0.73 (*16*)

[a] Extrapolated value. [b] Interpolated value. [c] At 15°C.

Volumetric Measurements. Volumes of mixing at constant pressure were also measured by a successive dilution technique (*18*). The dilatometer initially contained about 40 grams of one component confined over mercury, and the changes in volume which occurred when known amounts of the second component were added were obtained from the changes in the level of mercury in a Tru-bore capillary tube (about 1-mm i.d.). All measurements were made at a nominal temperature of 25.00 ± 0.01°C controlled to ±0.001°C during a run. The values of the excess volumes are estimated to be accurate to better than $\pm 1 \times 10^{-3}$ cm^3 mol^{-1}.

Vapor-Liquid Studies. The equilibrium vapor pressures of mixtures of known total composition (i.e., liquid + vapor phases) were determined by the static method in a cell and vacuum system similar to that used by Singh and Benson (*22*). The total inner volume of the cell, together with those attached parts of the apparatus which contained vapor when the equilibrium was established, was known from prior calibration. The temperature of the cell and sample manifold was held constant at 25.000 ± 0.002°C; pressures were measured to ±0.005 torr with a quartz spiral gauge.

The distribution of material between the vapor and liquid phases was computed by a modified form of Barker's analysis (*2*). The excess chemical potentials can be related to the vapor-liquid equilibria by the equation

$$\mu_i^E = RT \ln (y_i p / x_i p_i^0) + (B_{ii} - V_i^0)(p - p_i^0) + \delta(1 - y_i)^2 p \quad (1)$$

where

$$\delta = 2\,B_{12} - B_{11} - B_{22} \quad (2)$$

and terms containing virial coefficients of order higher than the second are neglected. The Barker treatment assumes that, at constant temperature, the concentration dependence of the molar excess Gibbs free energy,

$$G^E = x_1 \mu_1^E + x_2 \mu_2^E \quad (3)$$

can be expressed by a suitable empirical form containing n adjustable coefficients. The best values of the coefficients were determined by an iterative calculation which minimized the sum of squares of the deviations between calculated and observed values of the pressure.

Since, in our application, only total compositions were known directly, it was necessary at each iteration to calculate the liquid composition by allowing for the material present in the vapor phase. This correction used the equation.

$$V^g = RT/p + y_1^2 B_{11} + 2\,y_1 y_2 B_{12} + y_2^2 B_{22} \quad (4)$$

to estimate the molar volume of the vapor.

For both of the present systems at 25°C, the cycloalkane is much more volatile than the cycloalkanol, and only the second virial coefficient of the cycloalkane was considered in allowing for imperfection of the vapor phase. Values of B_{11} equal to -1054 and -1650 cm^3 mol^{-1} were used for cyclopentane (*12*) and cyclohexane (*10*), respectively; B_{22} and δ were set equal to zero. Several different empirical forms for G^E were investigated, and for each the value of n was identified with the minimum number of coefficients which provided an adequate representation of the vapor pressure results. To confirm that setting B_{22} and δ equal to zero did not introduce any serious error, the analysis was repeated with rough estimates of B_{22} and δ included. These calculations led to values of y_1 and G^E which did not differ significantly from those obtained previously.

Materials. All of the components were purified chromatographically. Refractive indices, densities, and vapor pressures typical of the liquids at 25°C are summarized in Table I. In most cases, these values agree well with data from the literature (*1, 16, 23*).

RESULTS

Experimental values of the molar excess enthalpies and of the molar excess volumes of cyclopentane–cyclopentanol mixtures and of cyclohexane–cyclohexanol mixtures at 25.00°C are listed in Table II. In both instances, x_1 indicates the mole

Table II. Experimental Values of Molar Excess Enthalpy and Molar Excess Volume at 25°C

x_1	H^E, J mol^{-1}	x_1	V^E, cm^3 mol^{-1}
Cyclopentane(1)–Cyclopentanol(2) Mixtures			
0.0579	84.3	0.0324	−0.0229
0.0680	97.0	0.0564	−0.0378
0.0811	118.7	0.0767	−0.0484
0.1350	192.6	0.1080	−0.0639
0.1583	221.3	0.1208	−0.0677
0.2060	289.2	0.1564	−0.0810
0.2788	375.9	0.1701	−0.0825
0.3250	431.8	0.2018	−0.0908
0.3396	443.2	0.2373	−0.0910
0.4089	508.2	0.2556	−0.0941
0.4421	535.5	0.3124	−0.0872
0.4464	543.4	0.3160	−0.0895
0.4834	564.7	0.3653	−0.0766
0.5001	570.6	0.3876	−0.0732
0.5245	588.6	0.4320	−0.0565
0.5319	587.1	0.4460	−0.0529
0.5402	591.6	0.4564	−0.0509
0.6056	602.7	0.4643	−0.0477
0.6187	607.7	0.4848	−0.0356
0.6285	604.4	0.4956	−0.0343
0.6372	599.9	0.5015	−0.0320
0.7331	570.8	0.5290	−0.0174
0.7438	560.6	0.5394	−0.0152
0.8275	498.3	0.5462	−0.0122
0.8431	477.9	0.5915	0.0075
0.9053	403.7	0.6005	0.0112
0.9212	372.4	0.6557	0.0327
0.9646	274.9	0.6621	0.0347
0.9682	268.3	0.7146	0.0507
		0.7194	0.0524
		0.7668	0.0638
		0.7697	0.0638
		0.8212	0.0720
		0.8218	0.0721

(*Continued on next page*)

Table II. *(Continued)*

x_1	H^E, J mol $^{-1}$	x_1	V^E, cm^3 mol^{-1}
Cyclopentane(1)–Cyclopentanol(2) Mixtures *(Contd.)*			
		0.8721	0.0746
		0.8734	0.0754
		0.9137	0.0731
		0.9160	0.0739
		0.9594	0.0625
		0.9629	0.0620
Cyclohexane(1)–Cyclohexanol(2) Mixtures			
0.0324	41.5	0.0359	−0.0232
0.0557	72.5	0.0503	−0.0307
0.0835	108.3	0.0821	−0.0485
0.0856	110.7	0.0896	−0.0506
0.1258	166.6	0.1415	−0.0710
0.1304	170.5	0.1697	−0.0768
0.1449	190.0	0.2084	−0.0843
0.2077	277.3	0.2731	−0.0872
0.2137	282.0	0.2794	−0.0844
0.2299	303.4	0.3363	−0.0804
0.3030	398.1	0.3702	−0.0715
0.3180	417.0	0.4051	−0.0632
0.3875	497.4	0.4415	−0.0494
0.4058	518.1	0.4612	−0.0430
0.4735	581.1	0.4992	−0.0267
0.4880	595.4	0.5176	−0.0208
0.5532	633.0	0.5270	−0.0176
0.5595	637.2	0.5570	−0.0035
0.5616	642.2	0.6189	0.0234
0.5626	636.3	0.6941	0.0519
0.6203	660.4	0.7313	0.0635
0.6265	651.4	0.7809	0.0759
0.6528	657.7	0.7943	0.0778
0.6679	650.1	0.8344	0.0839
0.7409	630.0	0.8622	0.0862
0.7694	604.8	0.8803	0.0862
0.8309	553.1	0.9115	0.0838
0.8463	530.1	0.9240	0.0829
0.8684	503.6	0.9513	0.0734
0.9030	452.3	0.9521	0.0745
0.9287	398.8		
0.9460	361.3		

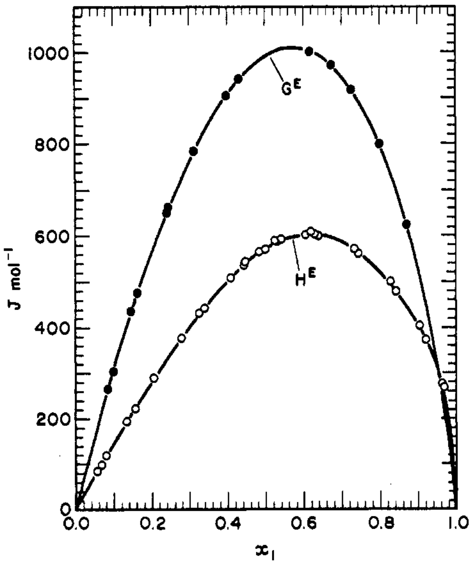

Figure 1. Molar excess enthalpies and Gibbs free energies of cyclopentane–cyclopentanol mixtures at 25°C

Experimental results H^E, ○; G^E, ●
Curves are least-squares representations by Equation 6

fraction of the cycloalkane. Figures 1-4 provide graphical presentations of these results.

The empirical form

$$X^E = x_1 x_2 \sum_{k=1}^{n} c_k (x_2 - x_1)^{k-1} \tag{5}$$

has frequently been used for the representation and smoothing of experimental values of the excess properties of mixtures. However, Equation 5 is ill-suited for representing the values of H^E for the present systems, since unrealistically large numbers of coefficients are required and there is a tendency for such representations to exhibit questionable points of inflection. The difficulty appears to stem from the asymmetry of the H^E results and from the fairly abrupt decrease of H^E at high values

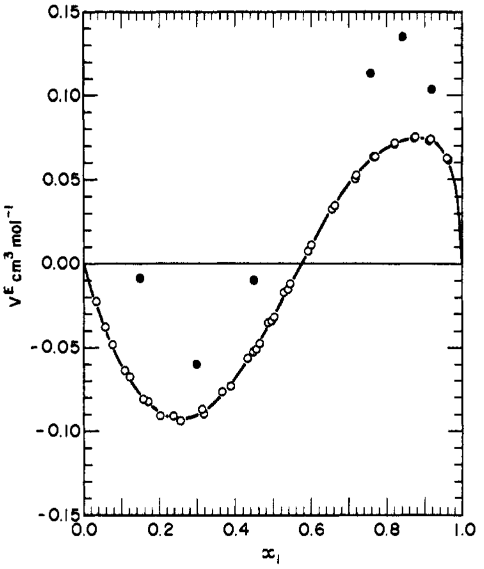

Figure 2. Molar excess volumes of cyclopentane–cyclopentanol mixtures

○ Present work 25°C. ● Klapproth (13) 22°C
Curve is least-squares representation of our results by Equation 6

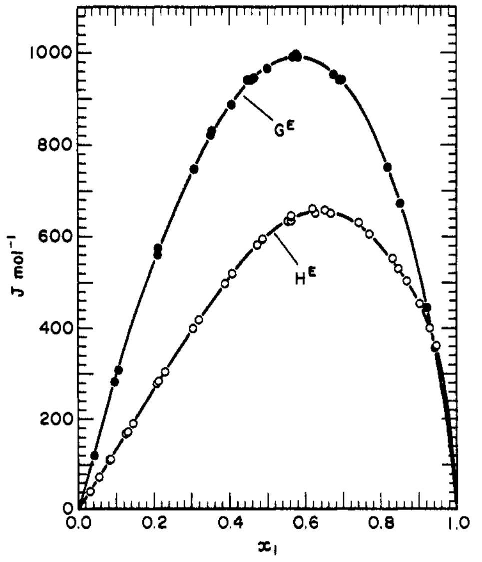

Figure 3. Molar excess enthalpies and Gibbs free energies of cyclohexane–cyclohexanol mixtures at 25°C

Experimental results H^E, ○; G^E, ●
Curves are least-squares representations by Equation 6

Table III. Coefficients and Standard Errors for Representations of the Excess Functions by Equation 6

	Cyclopentane(1)–cyclopentanol(2)			Cyclohexane(1)–cyclohexanol(2)		
	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	26917.0	5.83667	10182.9	22669.8	5.97216	10110.6
c_2	−180221.0	−36.0986	−20604.3	−120212.0	−35.2211	−20545.5
c_3	597347.0	100.260	27703.9	308209.0	95.2462	27888.1
c_4	−1101810.0	−142.766	−19394.1	−405441.0	−135.584	−19991.9
c_5	1167810.0	98.0566	5429.16	263978.0	92.6156	5695.60
c_6	−670192.0	−26.0535		−67948.9	−24.7329	
c_7	161659.0					
σ	2.8	0.0011	1.7	2.5	0.0008	4.2

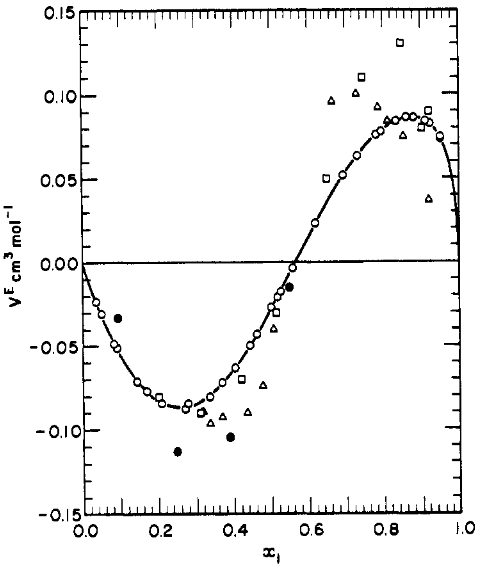

Figure 4. Molar excess volumes of cyclohexane–cyclohexanol mixtures

○ Present work 25°C □ Chevalley (6) 27°C
● Klapproth (13) 30°C △ Díaz Peña and Haya (9) 30°C
Curve is least-squares representation of our results by Equation 6

of x_1 (i.e., low alcohol mole fractions), which cannot be fitted properly by Equation 5. A number of previous authors (*3, 4, 8, 14, 24*) have encountered similar difficulties in fitting the excess properties of alcohol–nonpolar solvent systems, and have recommended a variety of other empirical forms in place of Equation 5. We investigated several of these and compared the variation of their standard errors with increasing numbers of coefficients. We also investigated the significance of the improvement in fit achieved by each succeeding coefficient (F-test). Each representation was also checked for points of inflection by examining the sign of the second derivative over the whole concentration range.

Both the reciprocal polynomial form of Mrazek and Van Ness (*14*) and the square-root relationship of Missen and coworkers (*3, 4*) give much better representations of our results for H^E than does Equation 5. The square-root relationship

$$X^E = x_1x_2 \sum_{k=1}^{n} c_k x_2^{(k-1)/2} \qquad (6)$$

also provides a good basis for the analysis of the results of the vapor-liquid studies and leads to better fits of the sigmoid-shaped concentration dependence of V^E for which the polynomial form cannot be used. We have therefore adopted Equation 6 for representing all of the excess functions of the present systems.

Equation 6 was fitted to the results for H^E and V^E by the method of least squares. Values of the coefficients are given in Table III, along with the standard error of estimate for each representation. We used these coefficients to calculate the solid curves in Figures 1–4 from the square-root relationship.

Table IV. Experimental Values of Vapor Pressure of Cyclopentanol

Temp, °C	p, torr	Δp,[a] torr
10.150	0.67	−0.003
14.982	1.00	0.001
18.945	1.38	−0.001
25.000	2.20	0.008
29.494	3.09	−0.003
34.818	4.53	−0.007
39.523	6.25	0.008
44.248	8.58	−0.005
47.600	10.65	0.001

[a] $\Delta p = p$ (Equation 7) $- p$ (experimental).

In the course of our vapor-liquid studies, vapor pressures of cyclopentanol were measured at a number of temperatures between 10° and 50°C. Since there is very little previous information about the vapor pressure of cyclopentanol in this temperature range, a list of our results is given in Table IV. The Antoine form

$$\log_{10} p(\text{torr}) = 8.64856 - 2093.02/[227.03 + t(°\text{C})] \qquad (7)$$

represents our results, with a standard error of estimate of 0.01 torr.

The results of the vapor-liquid experiments are summarized in Table V where equilibrium pressures are listed against the corrected mole fractions of cycloalkane in the liquid phase. Also listed are values of y_1 obtained from the Barker analysis using Equation 6 to represent G^E. The last column of each table contains "experimental" values of G^E computed from the first three columns using Equations 1 to 3. The coefficients and standard errors for the representations of G^E by Equation 6 are included in Table III. The experimental values of G^E and the smoothed curves are shown in Figures 1 and 3.

DISCUSSION

Excess properties of the present systems at 25°C have not been investigated previously. However, excess volumes of cyclopentane–cyclopentanol mixtures have been measured at 22°C (*13*), and those of cyclohexane–cyclohexanol mixtures at 27°C (*6*), 30°C (*9, 13, 19, 20*), and higher temperatures (*6*). Several of these sets of data are plotted in Figures 2 and 4. In comparison with our results, they are more scattered but the agreement is reasonable. Values of V^E for cyclohexane–cyclohexanol at 30°C reported by Rastogi and Varma (*19, 20*) appear to be erroneously large and have not been included in Figure 4.

Sigmoid-shaped V^E curves have also been observed for mixtures of alcohols with carbon tetrachloride (*17*). It has been suggested that this shape results from two opposing effects.

Table V. Vapor-Liquid Equilibria at 25°C

x_1	y_1[a]	p, torr	G^E, J mol^{-1}[a]
Cyclopentane(1)-Cyclopentanol(2) Mixtures			
0.0862	0.9773	89.03	265.5
0.0989	0.9799	99.64	303.5
0.1462	0.9857	134.81	435.3
0.1648	0.9871	146.54	475.9
0.2410	0.9905	187.77	650.9
0.2444	0.9906	189.58	661.1
0.3128	0.9922	216.46	783.4
0.3970	0.9934	241.47	905.4
0.4301	0.9938	249.28	941.5
0.6182	0.9951	279.56	1001.4
0.6725	0.9954	285.96	971.5
0.7266	0.9957	291.81	917.5
0.7998	0.9961	298.93	799.0
0.8712	0.9966	305.18	622.8
Cyclohexane(1)-Cyclohexanol(2) Mixtures			
0.0429	0.9379	14.61	120.2
0.0944	0.9698	28.73	281.6
0.1057	0.9727	31.43	307.7
0.2104	0.9850	52.24	561.7
0.2119	0.9851	52.68	574.4
0.3063	0.9889	65.35	746.6
0.3514	0.9900	70.17	822.1
0.3546	0.9901	70.56	829.9
0.4065	0.9910	74.69	886.7
0.4480	0.9916	78.03	941.0
0.4546	0.9917	78.26	940.5
0.4646	0.9918	78.81	946.2
0.5009	0.9922	80.77	966.0
0.5669	0.9928	84.10	991.0
0.5755	0.9929	84.66	997.0
0.5811	0.9929	84.66	990.1
0.6750	0.9937	88.12	954.0
0.6909	0.9938	88.68	942.1
0.6967	0.9938	89.07	942.3
0.8177	0.9948	92.40	751.6
0.8509	0.9951	93.31	672.8
0.9210	0.9958	95.06	445.7
0.9429	0.9962	95.75	355.6

[a] Calculated from the Barker analysis.

At high alcohol concentrations, the nonpolar solvent is accommodated interstitially within the hydrogen-bonded alcohol structure, and a contraction results. In more dilute alcohol mixtures, breakup of the hydrogen-bonded structure leads to expansion.

The maxima of our G^E curves are 991.9 J mol^{-1} at $x_1 = 0.578$ for the cyclopentane system, and 1009.8 J mol^{-1} at $x_1 = 0.572$ for the cyclohexane system. The latter value may be compared with 975 ± 28 J mol^{-1} at $x_1 = 0.6$ obtained by Chevalley (*5*, *7*) from vapor-liquid studies at 35, 45, and 50°C. The experimental technique of this earlier investigation was not sensitive enough to detect the variation of G^E with temperature, and it was concluded that the entropy term

$$TS^E = H^E - G^E \tag{8}$$

made only a minor contribution to the free energy. However, it can be seen from our results (Figures 5 and 6) that the contribution of the entropy may be of the same order as that of the enthalpy. The predominantly negative deviations of the entropy of mixing from the ideal (random mixing) value are probably due to the positional and orientational order imposed by hydrogen bonding. However, at low alcohol concentrations, there are few hydrogen bonds in the mixture and the decreasing orientational order leads to positive excess entropies.

Recently the nonrandom two-liquid (NRTL) theory of Renon and Prausnitz (*21*) has been used to predict isothermal vapor-liquid equilibria from excess enthalpy data (*11*). This approach proved to be moderately successful in correlating G^E and H^E for the present systems. Since there appear to be several misprints in the equations of the NRTL theory given in ref. *11*, the equations used for our calculations are summarized in the next paragraph.

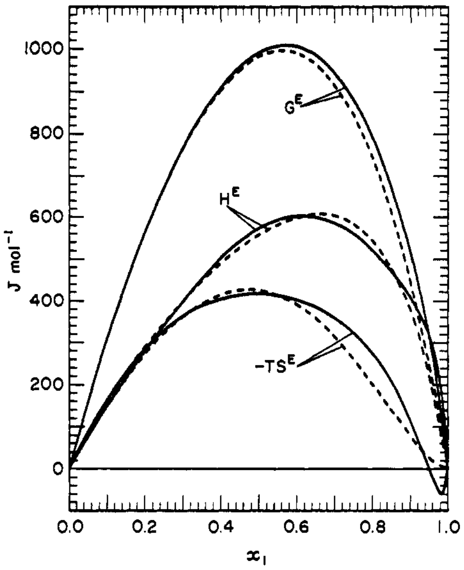

Figure 5. Comparison of calculated and experimental values of H^E, G^E, and $-TS^E$ for cyclopentane–cyclopentanol mixtures at 25°C

Solid-curves representations of experimental results by Equation 6
Broken-curves NRTL theory, assuming NRTL parameters are independent of temperature

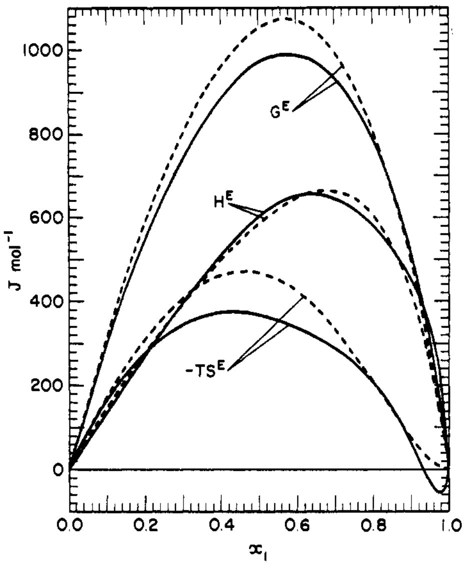

Figure 6. Comparison of calculated and experimental values of H^E, G^E, and $-TS^E$ for cyclohexane–cyclohexanol mixtures at 25°C

Solid-curves representations of experimental results by Equation 6
Broken-curves NRTL theory, assuming NRTL parameters are independent of temperature

The basic relationship for the molar excess Gibbs free energy, proposed by Renon and Prausnitz (*21*), can be written in the form

$$G^E = x_1x_2RT(F_{12}G_{12} + F_{21}G_{21}) \tag{9}$$

where

$$G_{ij} = \exp(-\alpha_{12}\tau_{ij}) \tag{10}$$

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

System	NRTL parameters			σ^a		
	$g_{12} - g_{11}$, 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}
Cyclopentane–cyclopentanol	1350	4470	0.449	30.0	31.7	33.7
Cyclohexane–cyclohexanol	1060	5520	0.379	29.0	56.3	58.6

[a] $\sigma^2 = \int_0^1 [X^E \text{ (Equation 6)} - X^E \text{ (NRTL)}]^2 dx_1$.

$$\tau_{ij} = (g_{12} - g_{jj})/RT \qquad (11)$$

and

$$F_{ij} = \tau_{ij}/(x_i G_{ij} + x_j) \qquad (12)$$

The parameters g_{ij} are free energies characterizing the interactions between molecules of species i and j, and α_{12} is related to the nonrandomness of the mixture. If α_{12} and the differences $g_{12} - g_{11}$ and $g_{12} - g_{22}$ are assumed to be independent of temperature, it can be shown that

$$H^E = x_1 x_2 RT[F_{12}G_{12}(1 - \alpha_{12}F_{12}x_2) + F_{21}G_{21}(1 - \alpha_{12}F_{21}x_1)] \qquad (13)$$

In applying the NRTL formulas, the three parameters (α_{12}, and the free energy differences $g_{12} - g_{11}$, and $g_{12} - g_{22}$) were adjusted to give a least-squares fit of Equation 13 to smoothed values of H^E calculated from Equation 6 at 0.1 mol-fraction intervals and weighted equally in the least-squares analysis. The resulting values of the parameters are listed in Table VI. These values were used in calculating the broken curves for G^E, H^E, and $-TS^E$ in Figures 5 and 6. Standard deviations between the NRTL and experimental curves are also given in Table VI. The NRTL equations give a good correlation of the excess functions for cyclopentane–cyclopentanol mixtures, except in the dilute alcohol range. If the NRTL parameters are readjusted to improve the fit for $x_1 > 0.9$, the fit at lower values of x_1 deteriorates. Although the deviations between the NRTL and experimental curves are larger for cyclohexane–cyclohexanol, it is clear for both systems that the NRTL theory provides a useful way of estimating G^E from experimental results for H^E.

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NOMENCLATURE

B_{ii} = second virial coefficient of pure component i, cm^3 mol^{-1}
B_{12} = cross virial coefficient, cm^3 mol^{-1}
$c_1, c_2, \ldots c_k$ = coefficients in representations of excess properties by Equations 5 or 6
F_{ij} = coefficient defined in Equation 12
g_{ij} = Gibbs energy parameter for interaction between an i-j pair of molecules, J mol^{-1}
G^E = molar excess Gibbs free energy, J mol^{-1}
G_{ij} = coefficient defined in Equation 10
H^E = molar excess enthalpy, J mol^{-1}
n = number of coefficients in Equations 5 or 6
p = total vapor pressure, torr
p_i^0 = vapor pressure of pure component i, torr
R = gas constant
S^E = molar excess entropy, J mol^{-1} K^{-1}
t = temperature on centigrade scale, °C
T = absolute temperature, K
V^E = molar excess volume, cm^3 mol^{-1}
V^G = molar volume of vapor phase, cm^3 mol^{-1}
V_i^0 = molar volume of pure liquid component i, 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
δ = difference of virial coefficients defined in Equation 2, cm^3 mol^{-1}
μ_i^E = excess chemical potential of component i
σ = standard error
τ_{ij} = parameter defined in Equation 11

SUBSCRIPTS

1 = cycloalkane component
2 = cycloalkanol component

LITERATURE CITED

(1) American Petroleum Institute, Research Project 44, "Selected Values of Properties of Hydrocarbons and Related Compounds," College Station, Tex (sheets dated 1949 to 1952).
(2) Barker, J. A., *Aust. J. Chem.*, **6**, 207 (1953).
(3) Brandreth, D. A., *J. Chem. Ed.*, **45**, 657 (1968).
(4) Brandreth, D. A., O'Neill, S. P., Missen, R. W., *Trans. Faraday Soc.*, **62**, 2355 (1966).
(5) Chevalley, J., *Bull. Soc. Chim. Fr.*, 510 (1961).
(6) Chevalley, J., *C. R. Acad. Sci.* **249**, 1672 (1959).
(7) Chevalley, J., *ibid.*, **250**, 3326 (1960).
(8) Díaz Peña, M., *Ann. Fis.*, **66**, 377 (1970).
(9) Díaz Peña, M., Haya, M., *An. Real. Soc. Espan. Fis. Quim. Ser.*, B **60**, 423 (1964).
(10) Dymond, J. H., Smith, E. B., "The Virial Coefficients of Gases," Oxford University Press, Oxford, 1969.
(11) Hanks, R. W., Gupta, A. C., Christensen, J. J., *Ind. Eng. Chem. Fundam.*, **10**, 504 (1971).
(12) Hermsen, R. W., Prausnitz, J. M., *Chem. Eng. Sci.*, **18**, 485 (1963).
(13) Klapproth, H., *Nova Acta Leopold.*, **9**, 305 (1940).
(14) Mrazek, R. V., Van Ness, H. C., *AIChE J.*, **7**, 190 (1961).
(15) Murakami, S., Benson, G. C., *J. Chem. Thermodynam.*, **1**, 559 (1969).
(16) Nitta, I., Seki, S., *J. Chem. Soc. Japan Pure Chem. Sect.* **69**, 141 (1948).
(17) Paraskevopoulos, G. C., Missen, R. W., *Trans. Faraday Soc.*, **58**, 869 (1962).
(18) Pflug, H. D., Benson, G. C., *Can. J. Chem.*, **46**, 287 (1968).
(19) Rastogi, R. P., Varma, K. T. R., *J. Chem. Phys.*, **25**, 1077 (1956).
(20) Rastogi, R. P., Varma, K. T. R., *J. Chem. Soc.*, **1957**, p 2257.
(21) Renon, H., Prausnitz, J. M., *AIChE J.*, **14**, 135 (1968).
(22) Singh, J., Benson, G. C., *Can. J. Chem.*, **46**, 1249 (1968).
(23) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds," Vol. I, Elsevier, New York, N.Y., 1950.
(24) Voňka, P., Svoboda, V., Strubl, K., Holub, R., *Collect. Czech. Chem. Commun.*, **36**, 18 (1971).

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