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

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Excess enthalpies and volumes of the systems cycloheptane–cyclopentanol, cyclooctane–cyclopentanol, and cycloheptane–cycloheptanol at 298.15K were determined by direct calorimetric and dilatometric measurements. Excess Gibbs free energies were obtained from measurements of vapor pressure and carrier gas saturation. The thermodynamic properties of these systems are similar to those of the cycloalkane–cycloalkanol systems investigated previously in our laboratory and can be explained qualitatively as resulting from differences in the sizes of the component molecules and differences in the hydrogen bonding of the alcohols.

Excess enthalpies, excess volumes, and vapor-liquid equilibria of binary cycloalkane–cycloalkanol systems composed of compounds with either five- or six-membered carbon rings were reported in I and II of this series (*5, 9*). These studies of the dependence of the thermodynamic properties of cycloalkane–cycloalkanol systems on ring size have been extended by making similar measurements on the systems cycloheptane–cyclopentanol, cyclooctane–cyclopentanol, and cycloheptane–cycloheptanol at 298.15K.

Experimental

Materials. The primary liquids were obtained from the Aldrich Chemical Co. and were purified chromatographically with the exception of cycloheptanol. Since the primary cycloheptanol reacted slightly with mercury to form a scum, it was shaken with mercury and then distilled. Chromatographic analyses showed that the purities of all of the liquids used for the measurements exceeded 99.9 mol %. Densities, refractive indices, and vapor pressures of these materials are compared with values from the literature (*1, 8, 13*) in Table I.

Calorimetric and dilatometric studies. Excess enthalpies and excess volumes were both determined by successive dilution techniques. The calorimeter and dilatometer used for these measurements are described in previous publications (*10, 12*). All determinations were made at a nominal temperature of 298.15 ± 0.01K, which was controlled to 0.001K during a run. The accuracy of the results over most of the mole fraction range is estimated to be better than 1% for the excess enthalpies, and 1×10^{-3} cm^3 mol^{-1} for the excess volumes.

Vapor-liquid studies. The vapor-liquid equilibria reported in I and II were obtained from measurements of static vapor pressures for mixtures of known total composition (i.e., liquid + vapor phase). This method, which is described in I, becomes less appropriate as the vapor pressures of the components decrease and become more nearly equal to each other. It was used in the pres-

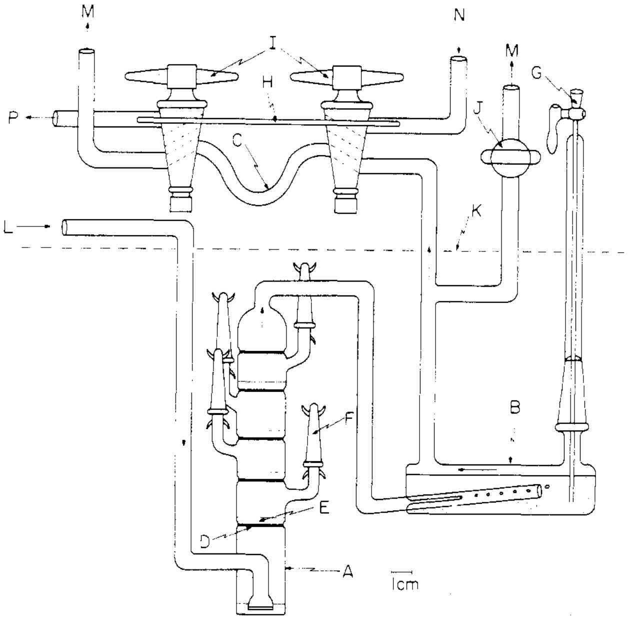

Figure 1. Apparatus for study of vapor-liquid equilibria by carrier gas saturation

A, presaturator containing more volatile component; B, saturator containing about 30 cm^3 of mixture; C, gas sampler; D, fine porosity fritted disc; E, thin layer of more volatile component; F, filling port (10/30 standard taper joint sealed with silicone grease); G, syringe adapter on tube used to sample liquid phase; H, capillary bypass for helium flow to column of chromatograph; I, two-way stopcock with Teflon plug; J, stopcock with Teflon plug, used to vent carrier gas during vapor sampling; K, level of water in thermostat; L, inlet for helium carrier gas; M, vent to atmosphere; N, helium supply for chromatograph; P, outlet to column of chromatograph

Table I. Physical Properties of Component Liquids at 298.15K

	d, g cm^{-3}		n_D		*p*, kPa	
	Measd	Lit	Measd	Lit	Measd	Lit
Cycloheptane	0.80656	0.8066 (*1*)	1.44236	1.4424 (*1*)	2.924	2.918 (*8*)
Cyclooctane	0.83202	0.8320 (*1*)	1.45620	1.4563 (*1*)	0.748	0.744 (*8*)
Cyclopentanol	0.94291	0.94298 (*13*)	1.45159	1.4505[a] (*13*)	0.293	. . .
Cycloheptanol	0.95484	. . .	1.47541	. . .	0.027	. . .

[a] Extrapolated value.

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Table II. Molar Excess Enthalpies of Mixtures at 298.15K

x_1	H^E, J mol^{-1}	x_1	H^E, J mol^{-1}
Cycloheptane(1)–cyclopentanol(2)			
0.0587	111.8	0.4874	674.3
0.0985	184.9	0.5117	683.1
0.1787	320.9	0.5206	689.3
0.2399	415.4	0.5627	699.7
0.3008	499.8	0.6075	697.7
0.3010	497.6	0.7115	660.6
0.3455	553.9	0.8103	578.7
0.3476	554.1	0.9125	437.0
0.4252	630.0	0.9684	293.4
0.4338	639.1	0.9947	106.0
Cyclooctane(1)–cyclopentanol(2)			
0.0583	110.7	0.4730	663.3
0.0603	115.9	0.4755	660.4
0.1317	241.9	0.5150	683.9
0.1401	257.8	0.5371	686.4
0.2170	377.9	0.5524	689.0
0.2385	413.6	0.6062	692.4
0.2696	459.4	0.6560	683.4
0.2961	494.1	0.6910	664.0
0.3036	499.3	0.7841	602.4
0.3306	538.1	0.7861	597.9
0.3359	541.0	0.8457	532.6
0.3445	552.6	0.8769	493.8
0.3567	566.2	0.9139	430.2
0.3940	599.3	0.9478	353.8
0.4160	624.5	0.9633	303.6
0.4202	626.7	0.9885	165.9
0.4284	630.6	0.9912	140.8
0.4593	654.4		
Cycloheptane(1)–cycloheptanol(2)			
0.0615	108.8	0.5639	692.5
0.0890	156.6	0.5712	692.2
0.1023	180.3	0.5875	691.0
0.1776	307.8	0.5896	693.3
0.2043	350.7	0.6184	691.9
0.2539	425.5	0.6192	693.4
0.3107	504.3	0.6534	686.6
0.3362	534.9	0.6619	681.7
0.4099	612.7	0.7016	668.6
0.4220	622.2	0.7943	608.1
0.4249	621.0	0.8254	579.6
0.4341	630.3	0.8812	512.8
0.4940	666.4	0.9115	464.6
0.4974	672.2	0.9640	332.6
0.4993	672.2	0.9700	308.2
0.5047	676.2		

Table III. Molar Excess Volumes of Mixtures at 298.15K

x_1	V^E, cm^3 mol^{-1}	x_1	V^E, cm^3 mol^{-1}
Cycloheptane(1)–cyclopentanol(2)			
0.0282	0.0144	0.4518	0.2747
0.0532	0.0297	0.5008	0.2949
0.0807	0.0454	0.5503	0.3099
0.1151	0.0674	0.6061	0.3184
0.1637	0.0984	0.6647	0.3166
0.2110	0.1291	0.7240	0.3025
0.2597	0.1608	0.7890	0.2733
0.2991	0.1881	0.8478	0.2329
0.3091	0.1924	0.8982	0.1877
0.3295	0.2071	0.9422	0.1373
0.3659	0.2290	0.9779	0.0799
0.4067	0.2520		
Cyclooctane(1)–cyclopentanol(2)			
0.0084	0.0045	0.3989	0.2595
0.0245	0.0148	0.4145	0.2682
0.0453	0.0297	0.4385	0.2794
0.0782	0.0515	0.4567	0.2880
0.1066	0.0700	0.4852	0.2988
0.1207	0.0803	0.4930	0.3023
0.1707	0.1141	0.5377	0.3147
0.1990	0.1317	0.5966	0.3229
0.2197	0.1471	0.6561	0.3208
0.2724	0.1823	0.7213	0.3068
0.2740	0.1840	0.7947	0.2683
0.3213	0.2145	0.8582	0.2224
0.3317	0.2204	0.9187	0.1635
0.3638	0.2399	0.9598	0.1094
0.3681	0.2428	0.9836	0.0634
Cycloheptane(1)–cycloheptanol(2)			
0.0155	−0.0008	0.4710	0.0983
0.0437	−0.0016	0.4984	0.1069
0.0801	−0.0012	0.5053	0.1092
0.1197	0.0005	0.5524	0.1214
0.1615	0.0052	0.5567	0.1217
0.2131	0.0159	0.6029	0.1314
0.2673	0.0310	0.6579	0.1380
0.3185	0.0478	0.7177	0.1420
0.3581	0.0612	0.7801	0.1400
0.3693	0.0650	0.8337	0.1333
0.3881	0.0717	0.8797	0.1230
0.4211	0.0827	0.9264	0.1059
0.4224	0.0827	0.9585	0.0856
0.4570	0.0947	0.9847	0.0533
0.4577	0.0947		

ent work only to study cycloheptane–cycloheptanol mixtures.

Investigations of the isothermal vapor-liquid equilibria of cycloheptane–cyclopentanol and cyclooctane–cyclopentanol mixtures were based on direct determinations of the compositions of the liquid and vapor phases by gas chromatography, with carrier gas saturation to sample the vapor phase. This approach is similar in principle to techniques described by Wichterle and Hála (*14*) and by Arnikar et al. (*2*).

Our apparatus, which is shown schematically in Figure 1, consists of a presaturator connected in series with a saturator cell. These units were mounted in a water thermostat controlled to ±0.001K at the nominal operating temperature of 298.15K. The presaturator contained the more volatile component held as a series of thin layers over fritted glass discs. Helium carrier gas at a low flow rate (<0.01 cm^3 sec^{-1}) passed through the presaturator and was loaded with the more volatile component at a somewhat higher partial pressure than the equilibrium value for the mixture contained in the saturator cell. The latter was designed, not only to provide good contact between the carrier gas and the liquid mixture with only a small pressure drop across the cell, but also to use the motion of the bubbles to stir the liquid (*6, 11*). Samples of the carrier gas after leaving the cell could be isolated between the valves of the gas sampler and introduced into the stream of helium being supplied to the column of an analytical chromatograph. The gas sampler was wrapped with a heating tape and maintained at a temperature high enough to avoid any condensation of the vapor. After values steady within 0.002 mole were obtained for the vapor composition, a sample of the liquid phase was removed from the cell with a syringe.

All analyses were carried out with a Hewlett-Packard Model 700 chromatograph equipped with a flame ionization detector. A column containing Apiezon L on Chromosorb P at 423K gave good separations of the present components, and peak areas were measured with a Hewlett-Packard Model 3370A electronic integrator. Response factors were obtained from measurements made on mixtures with known compositions. Values of the compositions of the vapor and liquid phases are estimated to be accurate within 0.002 mole.

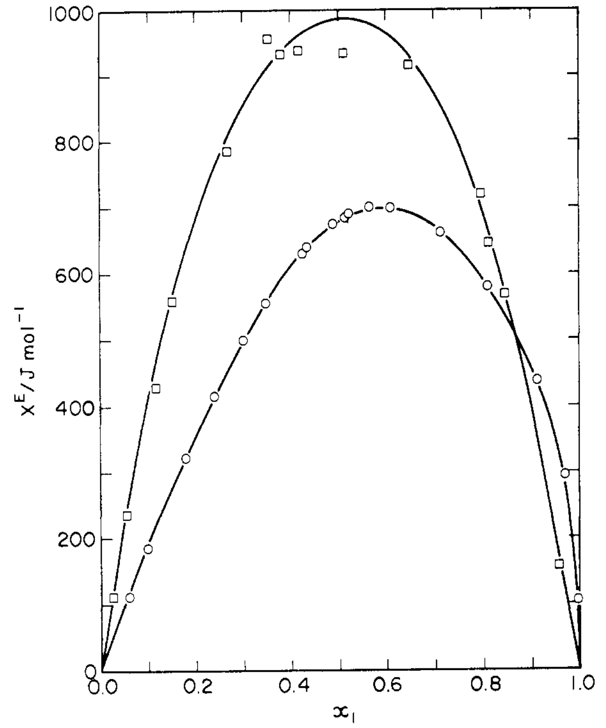

Figure 2. Molar excess enthalpies and Gibbs free energies for cycloheptane-cyclopentanol mixtures at 298.15K
Experimental results: H^E, O; G^E, □. Solid curves are representations by Equation 1

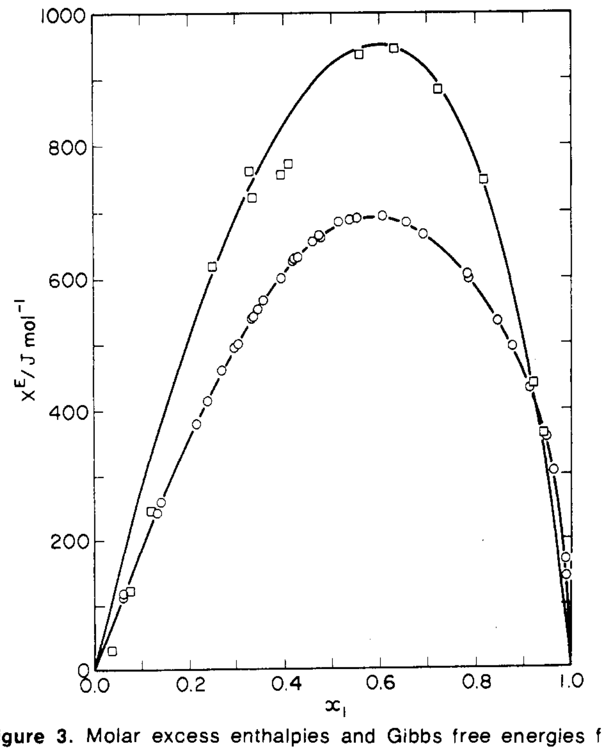

Figure 3. Molar excess enthalpies and Gibbs free energies for cyclooctane-cyclopentanol mixtures at 298.15K
Experimental results: H^E, O; G^E, □. Solid curves are representations by Equation 1

Results

The experimental values of the excess enthalpies and excess volumes are listed in Tables II and III, respectively. Graphical presentations of these results are given in Figures 2-5, where x_1 represents the mole fraction of cy-

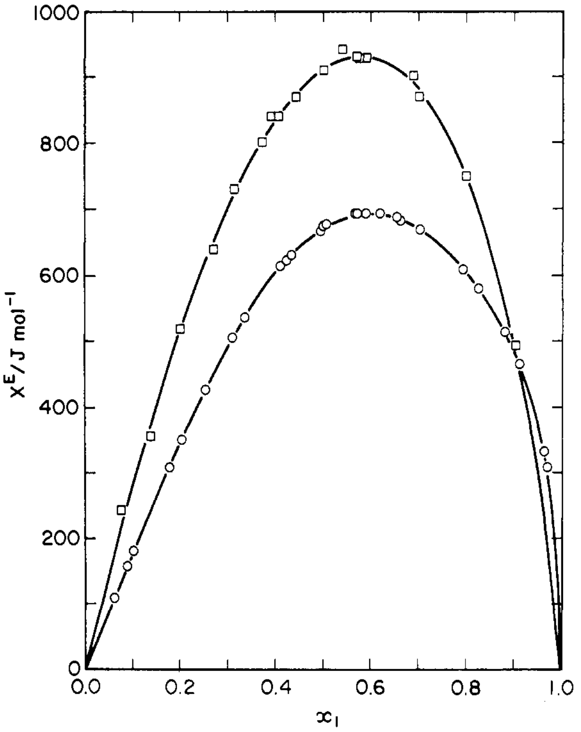

Figure 4. Molar excess enthalpies and Gibbs free energies for cycloheptane-cycloheptanol mixtures at 298.15K
Experimental results: H^E, O; G^E, □. Solid curves are representations by Equation 1

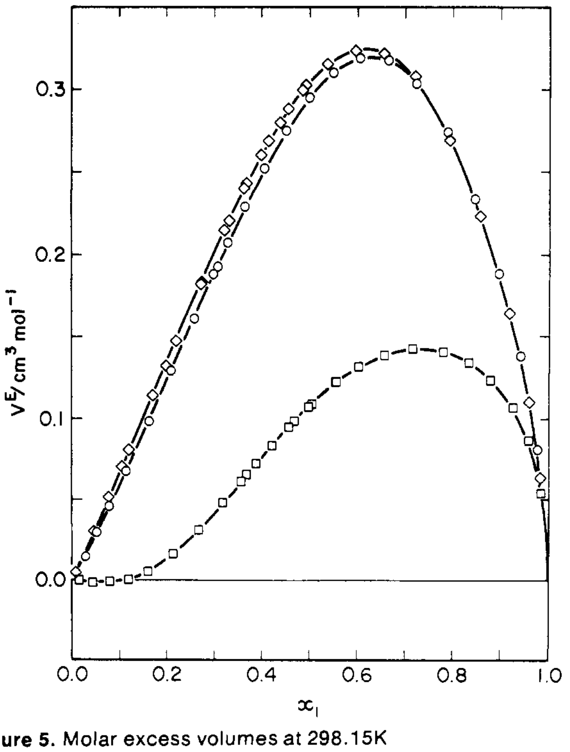

Figure 5. Molar excess volumes at 298.15K
Experimental results: cycloheptane-cyclopentanol, O; cyclooctane-cyclopentanol, ◇; cycloheptane-cycloheptanol, □. Solid curves are representations by Equation 1

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

	H^E, J mol^{-1}	V^E, cm^3 mol^{-1}	G^E, J mol^{-1}
Cycloheptane(1)–cyclopentanol(2)			
c_1	32505.1	7.50522	3162.23
c_2	−233388.0	−38.9234	9551.89
c_3	831205.0	106.333	−21780.2
c_4	−1651710.0	−148.016	13924.3
c_5	1883400.0	100.349	
c_6	−1154040.0	−26.7375	
c_7	294121.0		
σ	2.5	0.0008	28.3
Cyclooctane(1)–cyclopentanol(2)			
c_1	32975.3	7.05631	8323.18
c_2	−262864.0	−35.3446	−9599.89
c_3	1108820.0	94.1936	4289.34
c_4	−2778000.0	−127.165	
c_5	4285670.0	82.9742	
c_6	−3976750.0	−21.0891	
c_7	2027060.0		
c_8	−434963.0		
σ	2.0	0.0008	53.5
Cycloheptane(1)–cycloheptanol(2)			
c_1	31834.6	8.28496	9127.30
c_2	−213053.0	−59.2066	−15510.7
c_3	715420.0	213.753	14901.9
c_4	−1360180.0	−439.845	−5543.09
c_5	1500620.0	524.235	
c_6	−895462.0	−338.161	
c_7	222647.0	90.9007	
σ	1.6	0.0004	12.6

cloalkane. In agreement with previous findings for other cycloalkane(1)-cycloalkanol(2) systems (*4*, *5*, *9*), a polynomial form in $x_2^{1/2}$

$$X^E = x_1 x_2 \sum_{j=1}^{n} c_j x_2^{(j-1)/2} \qquad (1)$$

proved to be more suitable for representing the results than the corresponding form in $(x_2 - x_1)$. Equation 1 was fitted to each set of results by the method of least squares with all points assigned the same statistical weight. The minimum number of coefficients required for an adequate fit of the m experimental points in a set was determined from an examination of the variation of the standard error of the estimate

$$\sigma = \{\sum_{1}^{m}[X^E(\text{Experimental}) - X^E(\text{Equation 1})]^2/(m-n)\}^{1/2} \qquad (2)$$

for representations with increasing values of n. Values of the coefficients and standard errors are summarized in Table IV. The curves in Figures 2–5 were calculated from Equation 1 with these coefficients.

Results of the vapor-liquid studies at 298.15K are listed in Table V. The primary quantities for cycloheptane-cycloheptanol are x_1 and p. For the other two systems, they are x_1 and y_1. Although vapor pressures of the pure components are needed only at 298.15K for analyses of these data, pressure measurements were made on our samples over the temperature range 285–320K approximately, with a calibrated quartz spiral gauge. The results for cyclopentanol were reported previously (*9*); vapor pressures for the other components are listed in Table VI, along with values of the coefficients for their representations by the Antoine equation

$$\log_{10}(p/\text{kPa}) = A - B[C + (T/\text{K})]^{-1} \qquad (3)$$

Table V. Vapor-Liquid Equilibria of Mixtures at 298.15K

x_1	y_1	p, kPa	G^E, J mol^{-1}
Cycloheptane(1)–cyclopentanol(2)			
0.0242	0.5974	0.712	112.5
0.0542	0.7397	1.075	235.9
0.1163	0.8243	1.512	429.7
0.1521	0.8414	1.665	559.1
0.2680	0.8750	1.979	784.0
0.3528	0.8856	2.153	955.6
0.3787	0.8934	2.202	931.4
0.4162	0.9007	2.273	938.0
0.5112	0.9166	2.437	933.4
0.6458	0.9287	2.612	914.0
0.7959	0.9369	2.726	718.0
0.8118	0.9443	2.736	645.2
0.8443	0.9472	2.758	567.2
0.9575	0.9832	2.865	156.8
Cyclooctane(1)–cyclopentanol(2)			
0.0365	0.2596	0.368	30.3
0.0751	0.4032	0.437	122.6
0.1191	0.5015	0.504	244.8
0.2501	0.6386	0.651	618.6
0.3291	0.6895	0.713	760.5
0.3330	0.7023	0.716	720.8
0.3929	0.7423	0.753	755.3
0.4099	0.7505	0.763	771.3
0.5587	0.7861	0.821	935.7
0.6316	0.8005	0.837	945.5
0.7228	0.8224	0.848	881.5
0.8169	0.8361	0.852	745.8
0.9215	0.8554	0.847	437.6
0.9422	0.8744	0.840	359.9
Cycloheptane(1)–cycloheptanol(2)			
0.0753	0.9633	0.684	243.0
0.1381	0.9789	1.099	356.5
0.2000	0.9847	1.448	518.4
0.2713	0.9881	1.741	638.8
0.3133	0.9894	1.903	729.5
0.3715	0.9907	2.064	799.5
0.3911	0.9910	2.126	837.2
0.4058	0.9913	2.149	838.1
0.4423	0.9918	2.228	868.9
0.4993	0.9925	2.341	908.4
0.5380	0.9930	2.426	941.3
0.5692	0.9933	2.461	930.5
0.5733	0.9933	2.464	927.1
0.5911	0.9935	2.492	927.8
0.6885	0.9944	2.637	900.6
0.6999	0.9945	2.626	868.4
0.7983	0.9953	2.738	747.9
0.9037	0.9962	2.834	492.6

Calculation of the excess Gibbs free energies from the primary results of the vapor-liquid studies uses the thermodynamic relations:

$$G^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \qquad (4)$$

$$\gamma_i = y_i p / x_i p_i^\circ \, \Phi_i \qquad (5)$$

$$RT \ln \Phi_i = (p - p_i^\circ)(V_i^\circ - B_{ii}) - p\delta(1 - y_i)^2 \qquad (6)$$

and

$$RT \ln \gamma_i = G^E + (1 - x_i)\frac{dG^E}{dx_i} \qquad (7)$$

The method of Barker (*3*) assumes that the concentration dependence of G^E at constant temperature can be expressed by a suitable empirical form containing a number of adjustable parameters and uses Equation 7 to derive activity coefficients. In the case of (x_1, p) data, the best values of the parameters are determined, as outlined previously (*9*), by an iterative calculation which minimizes the weighted sum of squares of the deviations between observed pressures and values calculated from

$$p = x_1 p_1^\circ \Phi_1 \gamma_1 + x_2 p_2^\circ \Phi_2 \gamma_2 \tag{8}$$

Table VI. Experimental Values of Vapor Pressure

	T, K	p, kPa
Cycloheptane	283.048	1.272
	288.237	1.711
	292.906	2.218
$A = 6.19317$	298.150	2.924
$B = 1450.17$	301.924	3.550
$C = -44.91$	309.193	5.080
$\sigma = 0.0036$	312.723	6.006
	317.813	7.573
	323.551	9.741
Cyclooctane	290.961	0.488
	294.376	0.601
	298.150	0.748
$A = 5.97188$	302.060	0.944
$B = 1447.45$	306.922	1.244
$C = -60.67$	311.678	1.605
$\sigma = 0.0029$	316.472	2.056
	323.326	2.890
Cycloheptanol	284.842	0.008
	290.382	0.013
	294.769	0.021
$A = 11.5518$	298.150	0.027
$B = 4543.44$	303.574	0.044
$C = 48.37$	307.695	0.063
$\sigma = 0.0007$	313.106	0.096
	317.661	0.137
	323.083	0.209

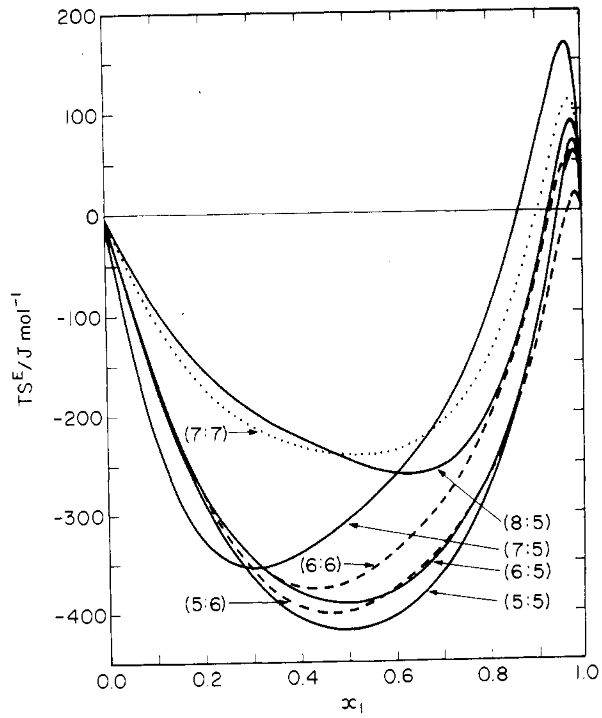

Figure 6. Molar excess entropies of cycloalkane–cycloalkanol mixtures at 298.15K

Curves of TS^E calculated from Equation 9. In labels (M:N), M and N indicate ring sizes of cycloalkane and cycloalkanol, respectively. Present work: (7:5), (8:5), (7:7). Other curves from refs. *5* and *9*

The treatment of (x_1, y_1) data is similar, but the quantity $\ln(\gamma_1/\gamma_2)$ instead of p is used in the minimization. Values of the pressure are also calculated iteratively from Equations 5–8, using $x_1 p_1^\circ + x_2 p_2^\circ$ as a first approximation.

In treating the present vapor-liquid results, values of −2700 and −4200 cm^3 mol^{-1} (*7*) were adopted for the virial coefficients of cycloheptane and cyclooctane, respectively. The values of B_{22} for the less volatile cycloalkanols were put equal to zero, and the second term in Equation 6 was assumed to be negligible. Equation 1 was used to represent G^E, and the statistical weights in the minimization were assigned to each point according to the estimated errors of the primary experimental quantities. Coefficients and standard errors for the representations of G^E are included in Table IV. In Table V, the values of G^E listed for cycloheptane–cycloheptanol were calculated from Equations 4–6, by use of the observed (x_1, p) values and y_1 obtained from the Barker analysis; for the other two systems, the observed (x_1, y_1) values and calculated p were used. The results for G^E and their smoothed representations are plotted in Figures 2–4.

Discussion

The curves for the excess enthalpies of the three present systems are very similar to one another and are noticeably skewed to high cycloalkane mole fractions. The excess Gibbs free energies show more variation but are skewed to a lesser degree. In all cases, the relative behavior of H^E and G^E is the same as found for the cycloalkane–cycloalkanol systems studied previously (*5*, *9*). The values of G^E are greater than H^E over most of the mole fraction range but become less than H^E at high x_1, indicating positive values of the entropy term

$$TS^E = H^E - G^E \tag{9}$$

as shown in Figure 6. This behavior has been attributed to the increasing orientational disorder associated with the breaking of hydrogen bonds between the alcohol molecules (*5*, *9*).

The excess volumes in Figure 5 also continue the pattern found previously (*5*, *9*). The series of systems formed by mixing cyclopentane, cyclohexane, cycloheptane, and cyclooctane with cyclopentanol has values of V^E which become increasingly more positive. This is in line with the increasing difficulty of accommodating the cycloalkanes interstitially within the hydrogen-bonded alcohol structure. In the case of cycloheptane–cycloheptanol, it appears from Figure 5 that interstitial accommodation of the cycloheptane is important below x_1 = 0.1, but above that mole fraction, the breakup of the alcohol structure predominates.

Nomenclature

A, B, C = Antoine constants in Equation 3
B_{ii} = second virial coefficient of pure component i, cm^3 mol^{-1}
B_{12} = cross virial coefficient, cm^3 mol^{-1}
$c_1 c_2, \ldots c_j$ = coefficients in representations of excess properties by Equation 1
d = density, g cm^{-3}
G^E = molar excess Gibbs free energy, J mol^{-1}
H^E = molar excess enthalpy, J mol^{-1}
m = number of experimental points in a set of results
n = number of coefficients in Equation 1
n_D = refractive index for sodium light
p = vapor pressure, kPa
p_i° = vapor pressure of pure component i, *kPa*
R = gas constant

S^E = molar excess entropy, J mol^{-1} K^{-1}
T = absolute temperature, K
V^E = molar excess volume, cm^3 mol^{-1}
V_i° = 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

γ_i = activity coefficient of component i in liquid phase
δ = difference of virial coefficients = $2B_{12} - B_{11} - B_{22}$
Φ_i = ratio of fugacity coefficients of pure component i and component i in the vapor-phase mixture, both evaluated at temperature and pressure of the mixture
σ = standard error

Subscripts

1 = cycloalkane component
2 = cycloalkanol component

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Apparent and Partial Molal Heat Capacities of Aqueous Rare Earth Perchlorate Solutions at 25°C

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Specific heats of aqueous solutions of the stoichiometric trivalent rare earth perchlorates (La, Pr, Nd, Sm, Gd, Eu, Tb, Dy, Ho, Er, Tm, Yb, and Lu) were measured over the concentration range of 0.1*m* to saturation at 25°C. Apparent molal heat capacities, ϕ_{cp}, were calculated for these solutions, and empirical polynomial equations were obtained which expressed ϕ_{cp} as a function of $m^{1/2}$ for each salt. From these equations the partial molal heat capacities of the solvent, $\bar{C}_{p1}$, and solute, $\bar{C}_{p2}$, were calculated. The $\bar{C}_{p1}$ data at given molalities exhibit a two-series effect across the rare earth series over the whole concentration range. For the lighter rare earths through Gd, ϕ_{cp} increases almost linearly with molality above 2.5*m*, whereas for the heavier rare earths, $\partial\phi/\partial m$ decreases with increasing concentration.

This investigation is part of an extensive research program to accurately determine thermodynamic and transport properties of aqueous solutions of the stoichiometric rare earth salts to aid in better understanding the behavior of solutions of higher valent salts. The regular decrease of the radii of the chemically similar trivalent rare earth ions, varying from 1.061 Å for La^{3+} to 0.848 Å for Lu^{3+} (*14*), provides a means of studying the effect of ionic radius upon solution properties.

Earlier work has shown that the properties of dilute aqueous rare earth salt solutions are not smooth monotonic functions of rare earth ionic radius. Rather, volume data (*8, 11–13*) and relative apparent molal heat content data (*1, 4, 7*) indicate that the rare earths, as they exist in dilute solution, are divided into two series. It has been proposed (*11*) that one series consisting of the larger light rare earths has a constant number of water molecules coordinated in the first sphere, and the other series consisting of the smaller heavy rare earths has a different and smaller number of water molecules coordinated in the first sphere. Furthermore, it was proposed that the intermediate rare earths exist in solution as an equilibrium of the two coordination types with the equilibrium shifting with decreasing ionic radius from the higher to the lower coordination type. However, the rare earth ion in dilute solution is hydrated beyond the first sphere and is the center of a large associated system.

When a water molecule is displaced because of steric hindrance from the first coordination sphere of the rare earth ion, the changes in size and symmetry of that sphere alter the environment beyond it. This results in the rearrangement of a large number of water molecules. Thus, a major portion of the observed effect on the macroscopic properties of solutions from the coordination change is probably due to the summation of a large number of small differences rather than simply the effect of a single water molecule, and an equation of the form $RE(H_2O)_x + H_2O \rightleftarrows RE(H_2O)_{x+1}$ would be an inadequate description of this equilibrium.

This study was undertaken to further investigate the two-series effect and to explore the effects of possible perchlorate ion–water and perchlorate ion–rare earth ion interactions on the heat capacities of these solutions. In

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