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HEAT CAPACITIES OF BINARY CYCLOALKANE MIXTURES AT 298.15 K[*]

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ABSTRACT

Volumetric heat capacities of the six binary mixtures formed from cyclopentane, cyclohexane, cycloheptane and cyclooctane were determined at 298.15 K in a Picker flow microcalorimeter. Excess heat capacities obtained from the results are compared with the temperature variation of excess enthalpies from the literature.

INTRODUCTION

The cycloalkanes are of theoretical interest since they constitute a series of approximately globular molecules with homogeneous interaction surfaces and a range of molecular sizes. Excess Gibbs free energies, enthalpies, volumes and compressibilities of binary mixtures of cycloalkanes have been investigated in some detail[1–10].

The present paper describes calorimetric measurements of the volumetric heat capacities of binary cycloalkane mixtures. Although the temperature variation of the

TABLE 1

DENSITIES, ρ, REFRACTIVE INDICES, n_D, AND HEAT CAPACITIES, C_p, OF COMPONENT LIQUIDS AT 298.15 K

Component	*ρ(g cm^{-3})*		*n_D*		*C_p(J K^{-1} mole^{-1})*	
	Obs.	*Lit.*[11]	*Obs.*	*Lit.*[11]	*Obs.*	*Lit.*
Cyclopentane	0.74030	0.74045	1.40364	1.40363	126.87_3	130.6[a], 127.2_8[b]
Cyclohexane	0.77383	0.77389	1.42354	1.42354	156.14_9	157.7[a], 156.07[c]
Cycloheptane	0.80667	0.8066	1.44235	1.4424	180.61_4	180.8[a], 180.4_7[b]
Cyclooctane	0.83210	0.8320	1.45619	1.4563	215.46_1	215.5[a], 214.2_4[b]

[a] Ref. 11.
[b] Ref. 12, based on 156.2_0 J K^{-1} mole^{-1} for cyclohexane.
[c] Ref. 13.

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TABLE 2

MEASUREMENTS ON BINARY CYCLOALKANE MIXTURES AT 298.15 K

Experimental results for change of volumetric heat capacity, $\Delta(C_p/V)$, heat capacity, C_p, and excess heat capacity, C_p^E.

x_1	$\Delta(C_p/V)$ ($J\,K^{-1}\,cm^{-3}$)	C_p ($J\,K^{-1}\,mole^{-1}$)	C_p^E ($J\,K^{-1}\,mole^{-1}$)	x_1	$\Delta(C_p/V)$ ($J\,K^{-1}\,cm^{-3}$)	C_p ($J\,K^{-1}\,mole^{-1}$)	C_p^E ($J\,K^{-1}\,mole^{-1}$)
x_1 C_5H_{10} + $(1 - x_1)$ C_6H_{12}[a]				x_1 C_5H_{10} + $(1 - x_1)$ C_7H_{14}[b]			
1	0	126.873[c]	0	1	0	126.873[c]	0
0.90013	0.008132	129.543	−0.237	0.89862	0.016748	132.095	−0.233
0.80366	0.007983	132.155	−0.433	0.79838	0.015424	137.257	−0.465
0.69536	0.009395	135.155	−0.585	0.69938	0.014739	142.408	−0.641
0.59871	0.008551	137.871	−0.682	0.59729	0.014382	147.735	−0.807
0.49236	0.009748	140.918	−0.730	0.50061	0.013378	152.843	−0.902
0.39806	0.008863	143.663	−0.731	0.39620	0.014320	158.437	−0.926
0.29564	0.010102	146.714	−0.660	0.30222	0.012804	163.542	−0.878
0.19440	0.010470	149.803	−0.518	0.20263	0.013764	169.051	−0.728
0.09662	0.010634	152.862	−0.305	0.10081	0.014521	174.815	−0.442
0	0.011215	155.979	0	0	0.015059	180.682	0
x_1 C_5H_{10} + $(1 - x_1)$ C_8H_{16}[d]				x_1 C_6H_{12} + $(1 - x_1)$ C_7H_{14}[e]			
1	0	126.873[c]	0	1	0	156.149[c]	0
0.89761	0.034581	135.606	−0.302	0.89229	0.006695	158.867	0.082
0.79823	0.030870	144.129	−0.547	0.80281	0.005181	161.102	0.129
0.69847	0.028840	152.753	−0.725	0.70090	0.005606	163.635	0.169
0.59614	0.027539	161.658	−0.848	0.60728	0.004756	165.936	0.179
0.50186	0.023665	169.906	−0.920	0.49406	0.005393	168.697	0.170
0.39703	0.024806	179.144	−0.931	0.40201	0.004186	170.933	0.154
0.29885	0.022002	187.863	−0.875	0.29774	0.004472	173.450	0.120
0.20070	0.021164	196.668	−0.730	0.20856	0.003707	175.600	0.088
0.09875	0.021531	205.944	−0.449	0.09704	0.004477	178.282	0.042
0	0.020905	215.106	0	0	0.003793	180.614	0

TABLE 2 *(continued)*

x_1	$\Delta(C_p/V)$ ($J\ K^{-1}\ cm^{-3}$)	C_p ($J\ K^{-1}\ mole^{-1}$)	C_p^E ($J\ K^{-1}\ mole^{-1}$)	x_1	$\Delta(C_p/V)$ ($J\ K^{-1}\ cm^{-3}$)	C_p ($J\ K^{-1}\ mole^{-1}$)	C_p^E ($J\ K^{-1}\ mole^{-1}$)
x_1 C_6H_{12} + $(1 - x_1)$ C_8H_{10}[a]				x_1 C_7H_{14} + $(1 - x_1)$ C_8H_{10}[e]			
1	0	156.149[c]	0	1	0	180.614[c]	0
0.90010	0.023184	162.391	0.316	0.90260	0.012780	184.070	0.064
0.79833	0.021250	168.632	0.521	0.80049	0.012952	187.676	0.114
0.70170	0.018631	174.507	0.665	0.70024	0.012272	191.199	0.146
0.60119	0.017575	180.526	0.723	0.61599	0.009963	194.143	0.157
0.49936	0.015888	186.504	0.661	0.49934	0.013401	198.210	0.161
0.39330	0.015335	192.684	0.550	0.40335	0.010672	201.544	0.152
0.31059	0.011158	197.467	0.428	0.30263	0.010831	205.026	0.127
0.20317	0.013847	203.672	0.261	0.20639	0.010055	208.343	0.093
0.10078	0.012769	209.599	0.115	0.09962	0.010875	212.017	0.049
0	0.012322	215.461	0	0	0.009867	215.437	0

[a] V^E from ref. 6.
[b] V^E from ref. 8.
[c] Initial reference value from Table 1.
[d] V^E from ref. 3.
[e] V^E from ref. 9.

excess enthalpies of these mixtures has been studied several times[1–4, 8, 9], it appears that no direct determinations of their heat capacities have been reported previously.

EXPERIMENTAL

The component liquids were reagent grade solvents which were purified by GLC when necessary. Densities, ρ, refractive indices, n_D, and molar heat capacities, C_p, characterizing the samples used for the calorimetric studies are summarized in Table 1 along with values from the literature[11–13] for comparison.

A Picker flow microcalorimeter[14] was used to determine differences of volumetric heat capacity (C_p/V) between pairs of liquids flowing in the test and reference cells. Our equipment and operational procedures have been described previously[13, 15]. Through a series of comparisons, the value of the heat capacity of the test liquid is ultimately derived from the value adopted for an NBS standard sample of *n*-heptane[13]. A flow rate of 0.011 cm^3 s^{-1} and a temperature increment of about 1.4 K, centred on 298.15 K, was used for all of the present measurements.

The single reference procedure[13] was used to obtain the heat capacities given in Table 1 from comparisons of the component liquids with *n*-heptane. Measurements of differences of volumetric heat capacity for a series of binary mixtures prepared by mass were carried out in the order of increasing concentration of one of the components, according to the stepwise procedure described previously[15]. Thus, starting from zero mole fraction, each mixture was used as a reference liquid for the next in the series. The precision of the final values of the excess heat capacities is believed to be about ±0.02 J K^{-1} mole^{-1}.

RESULTS AND DISCUSSION

The measurements are summarized in Table 2, where x_1 denotes the mole fraction of the component having the lower molecular mass in the mixture. Each

TABLE 3

REPRESENTATION OF EXCESS HEAT CAPACITIES OF BINARY CYCLOALKANE MIXTURES AT 298.15 K BY EQN (2)

Coefficients c_j and standard deviation, σ, determined by method of least squares.

Component					σ
1	*2*	c_1	c_2	c_3	*(J K^{-1} mole^{-1})*
C_5H_{10}	C_6H_{12}	−2.9259	−0.4963	−0.2395	0.003
C_5H_{10}	C_7H_{14}	−3.5958	−1.3846	−0.2153	0.006
C_5H_{10}	C_8H_{16}	−3.6765	−0.9727	−0.7927	0.007
C_6H_{12}	C_7H_{14}	0.6859	−0.2548		0.003
C_6H_{12}	C_8H_{16}	2.6649	−1.4536	−0.5561	0.012
C_7H_{14}	C_8H_{16}	0.6447	−0.1144		0.001

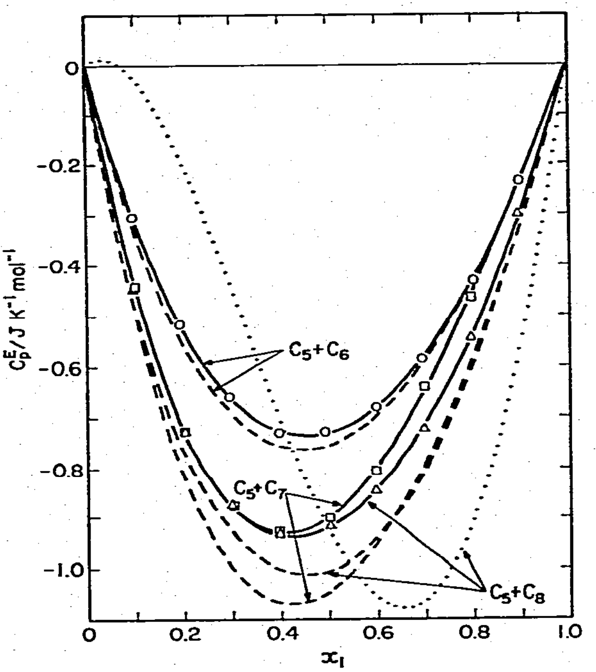

Fig. 1. Excess heat capacities of binary cycloalkane mixtures at 298.15 K. Experimental results: ○, $C_5H_{10}(1) + C_6H_{12}(2)$; □, $C_5H_{10}(1) + C_7H_{14}(2)$; △, $C_5H_{10}(1) + C_8H_{16}(2)$. Curves labelled with numbers of carbon atoms in the component molecules: ——, representations of present results by eqn. (2); ----, $(\partial H^E/\partial T)_p$ estimated from H^E results of Marsh and coworkers[1-3, 8]; ····, $(\partial H^E/\partial T)_p$ estimated from H^E results of Dias d'Almeida et al.[4].

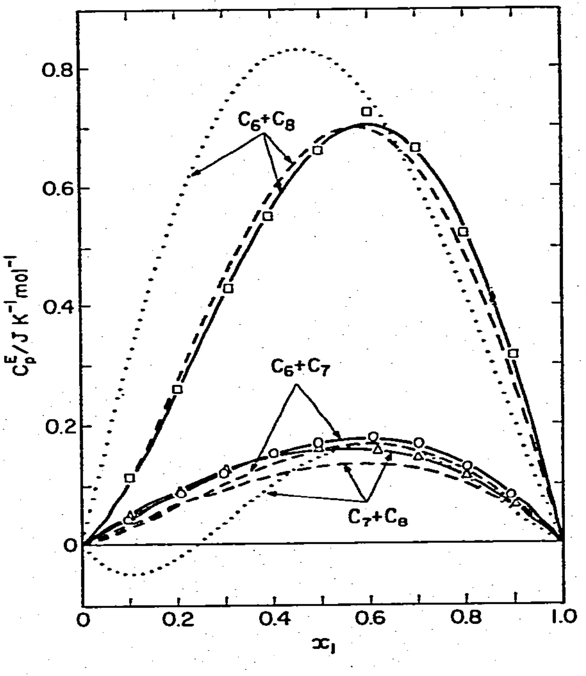

Fig. 2. Excess heat capacities of binary cycloalkane mixtures at 298.15 K. Experimental results: ○, $C_6H_{12}(1) + C_7H_{14}(2)$; □, $C_6H_{12}(1) + C_8H_{16}(2)$; △, $C_7H_{14}(1) + C_8H_{16}(2)$. Curves labelled with numbers of carbon atoms in component molecules: ——, representations of present results by eqn. (2); ----, $(\partial H^E/\partial T)_p$ estimated from H^E results of Marsh and coworkers[8, 9]; ····, $(\partial H^E/\partial T)_p$ estimated from H^E results of Dias d'Almeida et al.[4].

entry for $\Delta(C_p/V)$ represents the increase of the volumetric heat capacity of the particular mixture over the value for the preceding mixture. Molar heat capacities, C_p, were obtained from these results using the densities of the components given in Table 1 and excess volumes taken from the literature[3, 6, 8, 9]. The values of the heat capacities of component 2 resulting from the different stepwise comparisons are in reasonable agreement with one another and with those obtained from the direct comparisons of the component liquids with *n*-heptane. This confirms the self-consistency of the experimental technique. The last column of Table 2 contains molar excess heat capacities evaluated from the equation

$$C_p^E = C_p - x_1 C_{p1} - x_2 C_{p2} \tag{1}$$

where x_i and C_{pi} are the mole fraction and molar heat capacity of component i. The smoothing function

$$C_p^E = x_1 x_2 \sum_{j=1}^{n} c_j (1 - 2x_1)^{j-1} \tag{2}$$

was fitted to each set of results by the method of least squares with all points weighted equally. The values obtained for the coefficients c_j and standard deviations, σ, of these representations are listed in Table 3.

The results are presented graphically in Figs. 1 and 2. Also included in these figures are curves for $(\partial H^E/\partial T)_p$ estimated from published excess enthalpies[1-4, 8, 9]. The present results for C_p^E are in good agreement with the values of $(\partial H^E/\partial T)_p$ derived from the H^E values reported by Marsh and coworkers[1-3, 8, 9]. The asymmetry of the $(\partial H^E/\partial T)_p$ curves estimated from the H^E values reported by Dias d'Almeida et al.[4] is very different from that of our C_p^E curves.

It is interesting to note that C_p^E is negative for the three mixtures containing cyclopentane but positive for the other three mixtures. This latter behavior differs from that usually observed for binary mixtures of non-polar liquids[16]. Ewing and Marsh[5, 10] found that the Flory theory[17] provides good predictions of the excess volumes of binary cycloalkane mixtures from the properties of the pure components when the value of the interaction parameter X_{12} is selected to fit excess enthalpy data. Assuming that X_{12} and the characteristic values of pressure, volume, and temperature (p^*, V^*, and T^* in Flory's formulation) for the pure components are independent of temperature, the Flory theory leads to small negative values of C_p^E at 298.15 K for all of the present systems.

It has been suggested[10] that the different behavior of C_p^E for mixtures formed from cycloalkanes larger than cyclopentane is due to the ability of the higher cycloalkanes to undergo conformational changes. In cases where the differing molecular environments in the pure components and in the mixtures favor different conformations, small temperature changes could alter the equilibrium between conformations and lead to positive contributions to C_p^E.

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