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THE THERMODYNAMICS OF A CYCLOALKANE + AN *n*-ALKANE

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ABSTRACT

The excess volumes of cyclopentane + *n*-hexane, + *n*-heptane, *n*-dodecane; cyclohexane + *n*-pentane; cycloheptane + *n*-pentane, *n*-octane and *n*-dodecane have been measured at two temperatures. The results together with literature values reported for other systems of the type cycloalkane + an *n*-alkane have been discussed and the trends highlighted.

V_m^E and H_m^E results from our work and from the literature, for the systems cyclopentane or cyclohexane + an *n*-alkane, have been analysed in the light of the statistical theory of Flory.

INTRODUCTION

We recently published V_m^E results for 12 cycloalkane + *n*-alkane mixtures [1,2]. In this work we present V_m^E results for seven more mixtures in the same series. These V_m^E results together with literature values [1–5] complete the series of a cycloalkane (cyclopentane, cyclohexane, cycloheptane and cyclooctane) + an *n*-alkane (*n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-dodecane and *n*-hexadecane) and allows us to complete the analysis using the Flory theory applied to V_m^E and H_m^E data for the cycloalkane + *n*-alkane systems. The other half of the analysis on cycloheptane and cyclooctane systems can be found in refs. 6 and 7.

EXPERIMENTAL

The purification procedures used [1,2] and the vibrating tube densitometer method for determining V_m^E [3] have been described.

RESULTS

The V_m^E results are given in Table 1 together with the deviations δV_m^E calculated from the smoothing equation

$$\delta V_m^E(\text{cm}^3\ \text{mole}^{-1}) = V_m^E(\text{cm}^3\ \text{mole}^{-1}) - x(1-x)\sum_{r=0}^{n} A_r(1-2x)^r \qquad (1)$$

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TABLE 1

Molar excess volumes, V_m^E, for $x\ C_yH_{2y} + (1-x)\ C_zH_{2z+2}$ and the deviations from eqn. (1) and the coefficients of Table 2

x	V_m^E (cm^3 mole^{-1})	$10^4\delta V_m^E$ (cm^3 mole^{-1})	x	V_m^E (cm^3 mole^{-1})	$10^4\delta V_m^E$ (cm^3 mole^{-1})	x	V_m^E (cm^3 mole^{-1})	$10^4\delta V_m^E$ (cm^3 mole^{-1})
$x\ C_5H_{10} + (1-x)\ C_6H_{14}$ at 288.15 K								
0.0814	−0.0164	−9	0.5371	−0.0520	10	0.7716	−0.0395	−16
0.1563	−0.0267	7	0.5805	−0.0517	3	0.8273	−0.0317	−10
0.2694	−0.0402	11	0.6449	−0.0502	−11	0.8807	−0.0232	−6
0.3805	−0.0481	18	0.6717	−0.0488	−15	0.9418	−0.0106	11
0.4888	−0.0514	18	0.7350	−0.0431	−12			
$x\ C_5H_{10} + (1-x)\ C_6H_{14}$ at 298.15 K								
0.0894	−0.0247	11	0.4387	−0.0671	−16	0.7530	−0.0602	25
0,1912	−0.0450	−4	0.5173	−0.0684	−2	0.8249	−0.0507	26
0.2527	−0.0536	−14	0.5510	−0.0691	−2	0.9271	−0.0304	16
0.3083	−0.0587	−13	0.6036	−0.0688	4			
0.3811	−0.0640	−15	0.06838	−0.0659	15			
$x\ C_5H_{10} + (1-x)\ C_7H_{16}$ at 288.15 K								
0.1105	0.0114	0	0.4089	0.0234	−5	0.7845	0.0174	1
0.1915	0.0168	−1	0.4354	0.0246	5	0.8450	0.0138	0
0.2900	0.0212	−1	0.5096	0.0248	6	0.9268	0.0075	0
0.3292	0.0226	2	0.6268	0.0221	−7			
$x\ C_5H_{10} + (1-x)\ C_7H_{16}$ at 298.15 K								
0.0836	0.0044	−3	0.4165	0.0132	−3	0.7950	0.0086	−2
0.1224	0.0068	3	0.4913	0.0136	−2	0.8555	0.0070	2
0.1832	0.0092	3	0.5276	0.0135	−2	0.9098	0.0045	−1
0.2688	0.0114	0	0.6039	0.0138	7			
0.3976	0.0135	1	0.7151	0.0108	−2			
$x\ C_5H_{10} + (1-x)\ C_{12}H_{26}$ at 288.15 K								
0.0851	0.0309	0	0.5150	0.0825	1	0.8655	0.0268	12
0.1834	0.0594	11	0.6115	0.0715	−7	0.9083	0.0171	2
0.2361	0.0688	−1	0.6929	0.0622	26	0.9398	0.0119	11

0.3763	0.0835	−9	0.7880	0.0415	0	0.9512	0.0074	−11
0.4012	0.0832	−20	0.8499	0.0271	−16			
x $C_5H_{10} + (1-x)$ $C_{12}H_{26}$ at 298.15 K								
0.0904	0.0276	6	0.4058	0.0656	−1	0.8554	0.0197	5
0.1366	0.0369	−9	0.5549	0.0600	10	0.9107	0.0111	−1
0.2155	0.0517	−5	0.6237	0.0512	−7	0.9583	0.0048	−1
0.2927	0.0616	4	0.7272	0.0383	0			
0.3528	0.0650	2	0.7820	0.0298	−4			
x $C_6H_{12} + (1-x)$ C_5H_{12} at 288.15 K								
0.0715	−0.0405	0	0.5023	−0.1038	35	0.8521	−0.0090	13
0.1386	−0.0736	1	0.6251	−0.0725	−6	0.9456	−0.0005	0
0.2514	−0.1162	−23	0.7738	−0.0297	−25			
x $C_6H_{12} + (1-x)$ C_5H_{12} at 298.15 K								
0.0755	−0.0682	17	0.4307	−0.1572	25	0.8134	−0.0408	9
0.1300	−0.1108	−39	0.5281	−0.1407	−14	0.8566	−0.0302	−20
0.1917	−0.1381	−12	0.5476	−0.1378	−39	0.9055	−0.0143	7
0.3119	−0.1623	18	0.6301	−0.1082	−9			
0.3586	−0.1620	36	0.7155	−0.0744	21			
x $C_7H_{14} + (1-x)$ C_5H_{12} at 288.15 K								
0.0984	−0.2553	13	0.4223	−0.5703	19	0.7724	−0.3022	16
0.1167	−0.2970	−23	0.4862	−0.5605	−2	0.7824	−0.2886	20
0.2097	−0.4429	31	0.5124	−0.5500	−2	0.8742	−0.1657	−7
0.3026	−0.5377	−23	0.5753	−0.5123	−1	0.9166	−0.1067	−1
0.3220	−0.5470	−2	0.6768	−0.4207	−14			
0.3935	−0.5707	−2	0.7102	−0.3831	−16			
x $C_7H_{14} + (1-x)$ C_5H_{12} at 298.15 K								
0.0606	−0.1753	10	0.3869	−0.5889	49	0.8164	−0.2659	−11
0.1183	−0.3132	−26	0.5070	−0.5783	−1	0.8812	−0.1657	45
0.2149	−0.4723	−10	0.6002	−0.5209	−19	0.9032	−0.1404	−26
0.3080	−0.5607	3	0.7480	−0.3600	−14			
x $C_7H_{14} + (1-x)$ C_8H_{18} at 288.15 K								
0.1356	0.0584	6	0.4858	0.1902	20	0.8110	0.1933	−22

TABLE 1 (continued)

x	V_m^E (cm^3 mole^{-1})	$10^4\delta V_m^E$ (cm^3 mole^{-1})	x	V_m^E (cm^3 mole^{-1})	$10^4\delta V_m^E$ (cm^3 mole^{-1})	x	V_m^E (cm^3 mole^{-1})	$10^4\delta V_m^E$ (cm^3 mole^{-1})
0.2559	0.1080	−22	0.5524	0.2045	9	0.8454	0.1779	−5
0.3757	0.1548	−4	0.6618	0.2159	−20	0.8994	0.1387	8
0.3962	0.1627	7	0.7450	0.2164	24	0.9137	0.1237	0
x C_7H_{14} + $(1-x)$ C_8H_{18} at 298.15 K								
0.1817	0.0613	−6	0.4945	0.1578	−14	0.7632	0.1763	−5
0.1919	0.0647	−9	0.5067	0.1627	7	0.7680	0.1792	34
0.2900	0.0999	2	0.5773	0.1742	−13	0.8371	0.1578	54
0.3017	0.1068	31	0.5832	0.1733	−31	0.9188	0.0962	−18
0.4015	0.1373	25	0.6860	0.1834	−11			
0.4206	0.1399	−2	0.7013	0.1799	−42			
x C_7H_{14} + $(1-x)$ $C_{12}H_{26}$ at 288.15 K								
0.1152	0.1784	−17	0.5519	0.5207	16	0.8816	0.3289	33
0.1897	0.2782	34	0.5774	0.5229	−6	0.9246	0.2316	−6
0.3415	0.4175	5	0.6799	0.5160	−24	0.9517	0.1588	−9
0.4607	0.4869	−12	0.7281	0.4949	−45			
0.5031	0.5038	−14	0.8181	0.4274	43			
x C_7H_{14} + $(1-x)$ $C_{12}H_{26}$ at 298.15 K								
0.3771	0.3780	4	0.5680	0.4609	−2	0.8276	0.3662	−7
0.3909	0.3880	4	0.6640	0.4587	−13	0.8803	0.2970	5
0.4076	0.3963	−24	0.6704	0.4598	10	0.8816	0.2949	5
0.4732	0.4342	2	0.7450	0.4309	−12	0.9348	0.1909	11
0.4796	0.4392	24	0.7500	0.4300	5	0.9366	0.1842	−13
0.5672	0.4606	−4	0.8240	0.3714	5			

TABLE 2

Smoothing coefficients A_r for $x\ C_yH_{2y}+(1-x)\ C_zH_{2z+2}$ at temperature T and the temperature coefficient $(\partial V_m^E/\partial T)_{x=0.5}$

y	z	T(K)	A_0	A_1	A_2	A_3	$(\partial V_m^E/\partial T)_{x=0.5}$
5	6	288.15	−0.2131	0.0048	0.0037		−0.0014
5	6	298.15	−0.2710	0.0597	−0.1419		
5	7	288.15	0.0971	0.0049	0.0242		−0.0011
5	7	298.15	0.0552	0.0037	0.0042		
5	12	288.15	0.3332	0.1194	−0.0498		−0.0021
5	12	298.15	0.2519	0.1162	−0.0285		
6	5	288.15	−0.4314	−0.4697	0.1583	0.1719	−0.0039
6	5	298.15	−0.5855	−0.4759	0.0101	−0.0330	
7	5	288.15	−2.2208	−0.8106	0.0900	−0.1514	−0.0026
7	5	298.15	−2.3234	−0.7928	0.0397	−0.1589	
7	8	288.15	0.7671	−0.4960	0.3553	−0.2620	−0.0032
7	8	298.15	0.6419	−0.4581	0.2624	−0.1548	
7	12	288.15	2.0164	−0.7145	0.7331	−0.2925	−0.0060
7	12	298.15	1.7779	−0.6995	0.2293	−0.8433	

where x denotes the mole fraction. The coefficients A_r are given in Table 2.

DISCUSSION

Three of the results presented here have been reported previously. The V_m^E results for cyclopentane + n-heptane at 298.15 K follow the extrapolated results of Siddiqi et al. [3] at high cyclopentane concentrations but differ by as much as 0.015 cm^3 mole^{-1} at lower cyclopentane compositions. The value of $(\delta V_m^E/\delta T)_{x=0.5}$ is also of opposite sign. Both sets of data were measured using the PAAR densitometer—a method which is perhaps not the best when using volatile liquids such as cyclopentane. Our results for cyclohexane + n-pentane at 288.15 K compare well with those of Mahl et al. [4] and are within 0.005 cm^3 mole^{-1} of the equation generated by their results. Our results for cycloheptane + n-octane at 298.15 K are generally lower than that by Martin and Symons [5] by 0.008 cm^3 mole^{-1}.

The V_m^E $(x = 0.5)$ values at 298.15 K for the cycloalkane + n-alkane systems reported here and in the literature [1–5] are summarised in Fig. 1. It is interesting to note that the curves generated by the cyclopentane systems do not conform to the pattern generated by the other cycloalkane systems. The same anomalous behaviour is seen for H_m^E $(x = 0.5)$ results [6–12] which are graphed in Fig. 2.

The Flory theory [6] has been reasonably successful in fitting the V_m^E and

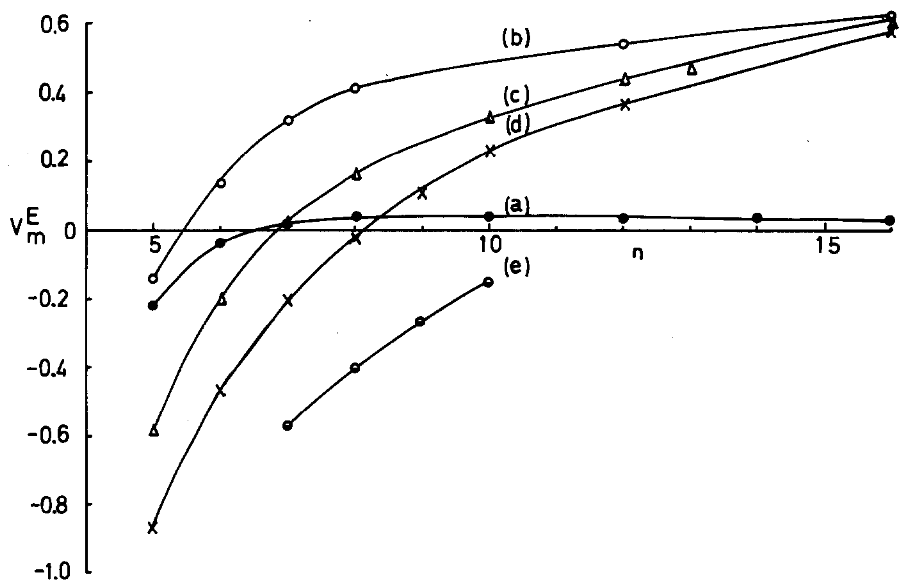

Fig. 1. Interpolated excess volume data, V_m^E $(x = 0.5)$, for cycloalkanes + *n*-alkanes. The *n*-alkane carbon number is referred to as *n*. Curve (a) cyclopentane, (b) cyclohexane, (c) cycloheptane, (d) cyclooctane, and (e) cyclodecane.

H_m^E results for cycloheptane [6] + an *n*-alkane and cyclooctane [7] + an *n*-alkane mixtures. Using the same treatment as before [6] we have fitted the V_m^E and H_m^E results [2,8–13] at 298.15 K for cyclopentane or cyclohexane + an *n*-alkane mixtures to the theory, and the results are given in Table 3. The properties used in the Table have been defined [6]. The values of the

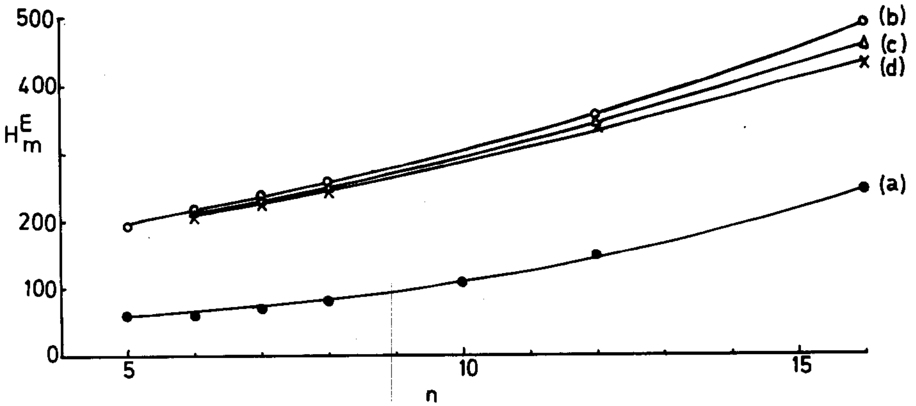

Fig. 2. Interpolated excess enthalpy data, H_m^E $(x = 0.5)$, for cycloalkanes + *n*-alkanes. The *n*-alkane carbon number is referred to as *n*. Curve (a) cyclopentane, (b) cyclohexane, (c) cycloheptane, and (d) cyclooctane.

TABLE 3

The results of fitting the Flory theory to the mixtures $x\ C_yH_{2y} + (1-x)\ C_xH_{2z+2}$

y	z	$10^7\chi_{12}(H_m^E)$ (J m^{-3})	$\sigma(H_m^E)$ (J m^{-3})	$\sigma^*(V_m^E)$ (cm^3 mole^{-1})	$10^7\chi_{12}(V_m^E)$ (J m^{-3})	$\sigma(V_m^E)$ (cm^3 mole^{-1})	$\sigma^*(H_m^E)$ (J mole^{-})
5	6	0.294	2.2	0.087	−0.223	0.005	81.5
5	7	0.330	2.3	0.093	−0.239	0.001	92.9
5	8	0.399	3.8	0.109	−0.283	0.004	114.9
5	12	0.727	10.1	0.123	−0.064	0.014	145.8
5	16	1.020	12.8	0.084	0.491	0.028	103.9
6	6	0.940	21.7	0.043	1.117	0.031	44.1
6	7	1.002	26.7	0.073	1.272	0.037	78.0
6	8	1.043	33.9	0.060	1.357	0.031	71.9
6	12	1.364	70.1	0.020	1.415	0.019	74.9
6	16	1.799	110.1	0.091	2.346	0.017	164.9

densities, coefficients of thermal expansion and isothermal compressibility of the *n*-alkanes have been reported [6]. For cyclopentane the values used were 0.7404 g cm^{-3}, 1.347×10^{-3} K^{-1} [15] and 1.331×10^{-9} Pa^{-1} [15], respectively, and for cyclohexane they were 0.77389 g cm^{-3} [14], 1.261×10^{-3} K^{-1} [16] and 1.136×10^{-9} Pa^{-1} [16], respectively.

The Flory one parameter equation again [6,7] provides a reasonable fit for both the H_m^E and V_m^E data, as judged by the values of $\sigma(H_m^E)$ and $\sigma(V_m^E)$ in Table 3. The ability of this simple Flory equation to predict H_m^E values from V_m^E data and V_m^E values from H_m^E data is summarised in the standard deviations $\sigma^*(H_m^E)$ and $\sigma^*(V_m^E)$. The results are similar to that obtained in our previous work [6,7].

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