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EXCESS ENTHALPIES OF BINARY MIXTURES FOR 1,3-CYCLOHEXADIENE AND 1,4-CYCLOHEXADIENE + CYCLOHEXANE, + n-HEXANE AND + BENZENE

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ABSTRACT

Molar excess enthalpies H_m^E were determined in an LKB flow calorimeter over the whole range of composition for all the binary mixtures of 1,3-cyclohexadiene and 1,4-cyclohexadiene + cyclohexane, + n-hexane and + benzene at 298.15 K. The position of the double bonds in cyclohexadiene has an effect on the H_m^E of mixing.

INTRODUCTION

The molar excess volumes V_m^E at 298.15 K for the binary mixtures of 1,3-cyclohexadiene and 1,4-cyclohexadiene + cyclohexane, + n-hexane and + benzene have been reported by the author [1,2]. In this work we present H_m^E measurements for these mixtures at 298.15 K. The results, together with H_m^E results for related systems, are discussed in terms of $\pi \cdots \pi$ interactions. The patterns thus generated are compared with the patterns in the V_m^E results [1,2].

EXPERIMENTAL

Cyclohexane, n-hexane and benzene were purified as previously described [2]. The cyclodienes were purified by repeated distillation. The samples of 1,3-cyclohexadiene and 1,4-cyclohexadiene were both used within 3 h of distillation and were used without stabilisers. They were kept in brown bottles to limit the exposure to sunlight. Densities of 0.8401 g cm^{-3} and 0.85103 g cm^{-3} were obtained for the 1,3-cyclohexadiene and 1,4-cyclohexadiene samples respectively. The density measurement for 1,3-cyclohexadiene as reported by Woycicki [3] was very different (0.8353 g cm^{-3}). Repeated spinning band distillation confirmed the density of 0.8402 g cm^{-3} on our samples. Analysis by GLC showed that impurities in the two cyclodienes were not greater than 0.5 mol per cent.

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The H^E measurements were determined using a commercial LKB 2107 flow calorimeter coupled with LKB Varioperpex peristaltic pumps. The technique has been described [4].

RESULTS

Results for H_m^E are given in Table 1 together with deviations δH_m^E

TABLE 1

Excess enthalpy H_m^E for 1,3-cyclohexadiene and 1,4-cyclohexadiene + cyclohexane, + n-hexane and + benzene at 298.15 K

x	H_m^E (J mol^{-1})	δH_m^E (J mol^{-1})	x	H_m^E (J mol^{-1})	δH_m^E (J mol^{-1})	x	H_m^E (J mol^{-1})	δH_m^E (J mol^{-1})
xc-C_6H_{12} + (1 − x)1,3-c-C_6H_8								
0.0925	121.1	−0.3	0.4261	327.7	0.2	0.7022	272.8	−0.5
0.1990	225.0	1.2	0.4715	330.9	−0.7	0.7876	217.8	−0.8
0.3186	295.8	−0.7	0.5536	327.8	2.0	0.8819	137.0	0.3
0.3722	315.1	−0.8	0.6032	314.2	0.0			
xc-C_6H_{12} + (1 − x)1,4-c-C_6H_8								
0.1102	126.9	−0.1	0.5089	375.0	2.6	0.7624	267.1	−2.9
0.2505	260.7	−0.4	0.5482	370.5	−0.2	0.8324	207.6	1.7
0.3114	305.1	0.0	0.6416	344.7	−0.8	0.8917	140.0	0.0
0.4542	366.1	−0.1						
xn-C_6H_{14} + (1 − x)1,3-c-C_6H_8								
0.1347	229.7	0.6	0.4496	435.6	−0.4	0.5678	421.7	0.1
0.2211	325.2	−1.4	0.4736	436.9	0.2	0.7188	340.1	−0.9
0.3334	405.1	0.1	0.5652	424.0	1.6	0.8024	266.9	0.2
xn-C_6H_{14} + (1 − x)1,4-c-C_6H_8								
0.1837	300.9	−0.4	0.4441	441.4	−0.9	0.6807	364.5	−1.2
0.2656	279.7	1.5	0.4955	443.3	−0.8	0.7921	270.1	−0.3
0.2915	395.8	−0.4	0.5712	427.7	2.9	0.9328	100.9	0.1
0.3612	429.8	−0.6						
xc-C_6H_6 + (1 − x)1,3-c-C_6H_8								
0.0927	42.4	−0.2	0.4434	127.2	−0.4	0.6735	116.3	0.2
0.1967	80.9	0.5	0.4863	129.0	−0.6	0.7969	86.0	−0.5
0.2914	105.6	−0.1	0.5577	128.8	0.1	0.8643	63.5	0.3
0.3715	120.5	0.5	0.6008	125.7	0.1			
xc-C_6H_6 + (1 − x)1,4-c-C_6H_8								
0.2030	33.3	−1.2	0.5598	85.0	−0.5	0.8063	55.3	−1.3
0.2983	57.0	2.2	0.6008	86.7	−0.2	0.8116	55.6	0.1
0.3811	69.9	0.0	0.6152	84.3	0.1	0.8661	42.4	0.9
0.4481	79.3	0.4	0.6829	78.2	−0.4			

TABLE 2

Values at 298.15 K of coefficients A_r for eqn. (1)

Mixture	A_0 (J mol^{-1})	A_1 (J mol^{-1})	A_2 (J mol^{-1})
xc-C_6H_{12}			
$+(1-x)$1,3-c-C_6H_8	1325.9	80.5	81.8
$+(1-x)$1,4-c-C_6H_8	1488.2	−102.6	−187.1
xc-C_6H_{14}			
$+(1-x)$1,3-c-C_6H_8	1741.1	191.8	156.9
$+(1-x)$1,4-c-C_6H_8	1773.7	295.9	120.9
xc-C_6H_6			
$+(1-x)$1,3-c-C_6H_8	519.2	−21.7	7.4
$+(1-x)$1,4-c-C_6H_8	333.6	−126.5	−127.6

calculated from the smoothing equation

$$\delta H_m^E(\text{J mol}^{-1}) = H_m^E(\text{J mol}^{-1}) - x(1-x)\sum_{r=0}^{r=2} A_r(1-2x)^r \qquad (1)$$

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

DISCUSSION

Results for H_m^E 1,3-cyclohexadiene and 1,4-cyclohexadiene + cyclohexane have been reported by Woycicki [3] and are higher than the results obtained in this study. $H_m^E(x = 0.5)$ for the 1,3-cyclohexadiene mixture is 359 J mol^{-1} (as opposed to 331 J mol^{-1} reported here) and 423 J mol^{-1} for the 1,4-cyclohexadiene mixture, compared with 372 J mol^{-1} in this work).

Results for $H_m^E(x = 0.5)$ for mixtures of cyclohexane + cyclohexene (92 J mol^{-1}) [3], +1,3-cyclohexadiene (331 J mol^{-1}), +1,4-cyclohexadiene (372 J mol^{-1}) and +benzene (800 J mol^{-1}) [5] show a pattern which can be explained by the breakdown of $\pi \cdots \pi$ interactions on mixing the double-bonded compounds with cyclohexane.

Results for $V_m^E(x = 0.5)$ [1,2] for cyclohexane + cyclohexene (0.097 cm^3 mol^{-1}), +1,3-cyclohexadiene (0.311 cm^3 mol^{-1}), +1,4-cyclohexadiene (0.360 cm^3 mol^{-1}) and +benzene (0.652 cm^3 mol^{-1}) reflect the same explanation if volume expansion is considered to be related to the strength of dissociation.

Results for $H_m^E(x = 0.5)$ for n-hexane + cyclohexane (215 J mol^{-1}) [6], +cyclohexene (245 J mol^{-1}) [7], +1,3-cyclohexadiene (436 J mol^{-1}), +1,4-cyclohexadiene (443 J mol^{-1}) and +benzene (897 J mol^{-1}) [8] show a similar trend to that seen in the above cyclohexane mixtures. V_m^E results [1,2] for those mixtures, however, do not form a simple pattern.

Results for $H_m^E(x = 0.5)$ for benzene + cyclohexane (800 J mol^{-1}) [5], + cyclohexene (389 J mol^{-1}) [7], + 1,3-cyclohexadiene (130 J mol^{-1}) and + 1,4-cyclohexadiene (83 J mol^{-1}) show a trend which reflects an increasing association of the second compound with benzene. This is related to the increasing number of double bonds.

Again results for $V_m^E(x = 0.5)$ [1,2] for benzene + cyclohexane (0.652 cm^3 mol^{-1}), + cyclohexene (0.245 cm^3 mol^{-1}), + 1,3-cyclohexadiene (0.072 cm^3 mol^{-1}) and 1,4-cyclohexadiene (0.042 cm^3 mol^{-1}) support the same hypothesis.

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