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APPLICATION OF THE FLORY THEORY OF LIQUID MIXTURES TO EXCESS VOLUMES AND ENTHALPIES OF BENZENE + CYCLOALKANE AND + *n*-ALKANE MIXTURES

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ABSTRACT

The molar excess volumes of benzene + *n*-pentane, + *n*-dodecane and + *n*-hexadecane and the molar excess enthalpies of benzene + cycloheptane, + cyclooctane and + cyclodecane have been measured over the whole composition range at 25°C. These results, together with literature values, have been analysed using the Flory theory of liquid mixtures.

INTRODUCTION

The Flory theory of liquid mixtures has previously been fitted by Benson and Singh [1] to the molar excess volumes and enthalpies of benzene + cycloalkane (cyclopentane, cyclohexane, cycloheptane and cyclooctane) mixtures. In this work, these calculations are repeated using improved experimental results together with literature values [2–4] and the work is extended to include calculations on benzene + cyclodecane using new data. The work is further extended to include calculations on benzene + *n*-alkane (*n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-dodecane and *n*-hexadecane) mixtures using new results reported here together with reliable literature values [5–8].

EXPERIMENTAL

The benzene (BDH, Analar grade) was fractionally crystallised four times, dried over sodium and stored. The purity, as judged by GLC was better than 99.9 mol%. The *n*-pentane (Riedel de Haën, A.G., spectranal grade) and cycloheptane (Aldrich Chemical Co., Gold label 99 + % grade) was fractionally distilled and dried over sodium. The *n*-dodecane, *n*-hexadecane and cyclooctane (all from Aldrich Chemical Co., Gold label 99 + % grade) were fractionally crystallised and also dried under sodium. The cyclodecane (Fluka, purum grade) was used without further purification. Analysis of

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TABLE 1

Molar excess volume, V_m^E, for x C_6H_6 + $(1-x)$ C_yH_{2y+2} and the deviations δV_m^E calculated from eqn. (1) and Table 3 at 25°C

x	V_m^E (cm^3 mol^{-1})	$10^4 \delta V_m^E$ (cm^3 mol^{-1})	x	V_m^E (cm^3 mol^{-1})	$10^4 \delta V_m^E$ (cm^3 mol^{-1})	x	V^E (cm^3 mol^{-1})	$10^4 \delta V_m^E$ (cm^3 mol^{-1})
n-C_5H_{12}								
0.0786	0.0297	0.7	0.4072	0.1128	9.4	0.6801	0.1018	23.3
0.1206	0.0452	6.7	0.4831	0.1153	−11.5	0.6934	0.0984	15.2
0.1983	0.0685	−9.3	0.5217	0.1149	−15.0	0.7715	0.0773	−11.0
0.2548	0.0848	−0.1	0.5952	0.1124	5.8	0.8987	0.0378	−3.2
0.3115	0.0964	−10.9						
n-$C_{12}H_{26}$								
0.0755	0.1917	−12.2	0.4911	0.9142	16.3	0.6586	0.9527	−5.5
0.1272	0.3156	−10.5	0.5374	0.9456	37.5	0.7419	0.8893	−7.5
0.2179	0.5150	−39.1	0.5503	0.9485	7.3	0.8275	0.7332	−51.9
0.3984	0.6707	−5.5	0.5947	0.9602	1.0	0.8992	0.5197	23.6
0.3920	0.8135	22.1						
n-$C_{16}H_{34}$								
0.1481	0.3812	−13.9	0.4981	1.0194	−23.7	0.6971	1.0802	−32.2
0.2205	0.5643	52.9	0.5507	1.0692	40.8	0.7849	0.9823	−35.1
0.2854	0.6974	−25.9	0.6176	1.0988	37.9	0.8783	0.7266	−2.4
0.3587	0.8352	−8.1	0.6496	1.1025	51.1	0.9248	0.5137	6.0
0.4224	0.9283	−47.5						

TABLE 2

Molar excess enthalpy H_{m}^{E} for x $C_6H_6 + (1-x)$ C_yH_{2y} and the deviations δH_{m}^{E} calculated from eqn. (2) and Table 4 at 25°C

x	H_{m}^{E} (J mol^{-1})	δH_{m}^{E} (J mol^{-1})	x	H^{E} (J mol^{-1})	δH_{m}^{E} (J mol^{-1})	x	H_{m}^{E} (J mol^{-1})	δH_{m}^{E} (J mol^{-1})
Cyclo-C_7H_{14}								
0.1727	431.6	−1.7	0.4829	801.1	3.4	0.6956	721.7	−6.2
0.2385	552.6	−1.0	0.5458	807.0	0.0	0.8072	559.9	−1.6
0.3156	666.1	1.0	0.5828	800.6	0.6	0.9105	310.7	−1.7
0.4017	759.2	6.9	0.6015	793.2	−1.8			
Cyclo-C_8H_{16}								
0.1430	368.4	−5.1	0.4810	805.7	4.2	0.7137	718.4	−4.2
0.2156	517.6	1.5	0.5132	813.9	3.1	0.8262	536.1	−3.3
0.2748	616.7	5.4	0.5503	812.2	−1.8	0.9180	294.2	−4.3
0.3433	704.7	5.8	0.6346	785.2	−4.6	0.9455	212.1	4.2
0.4464	784.1	−1.0						
Cyclo-$C_{10}H_{20}$								
0.0924	252.1	−3.5	0.4556	801.5	3.3	0.7058	736.7	−6.3
0.1851	461.4	1.4	0.5436	827.4	3.1	0.7680	654.9	−4.0
0.3526	586.3	6.6	0.5893	814.7	−4.8	0.8602	453.4	−2.9
0.3687	733.8	3.1	0.6506	785.4	−6.1	0.9178	307.7	3.0
0.3805	746.4	4.2						

TABLE 3

Smoothing coefficients for $x\ C_6H_6 + (1-x)\ C_\nu H_{2\nu+2}$ at 25°C determined from the results of Table 1

n-Alkane	A_0 (cm^3 mol^{-1})	A_1 (cm^3 mol^{-1})	A_2 (cm^3 mol^{-1})	A_3 (cm^3 mol^{-1})
n-C_5H_{12}	0.4665	−0.0023	−0.0780	0.0
n-$C_{12}H_{26}$	3.6766	−1.4268	0.8984	−0.6273
n-$C_{16}H_{34}$	4.0944	−1.9251	1.3578	−1.0891

these compounds by GLC showed purity levels ranging between 99.6 (for *n*-hexadecane and cyclodecane) and 99.9 mol%.

The V_m^E measurements were done using a Paar (DMA 601) vibrating tube densitometer. The method has been described elsewhere [9]. The H_m^E measurements were done using an LKB 2107 microcalorimeter. The method has also been described elsewhere [10].

RESULTS

Excess molar volumes at 298.15 K are reported for systems for which such data is not available in the literature (e.g., benzene + *n*-pentane) and also where the results differ significantly from the literature (e.g., benzene + *n*-dodecane and + *n*-hexadecane). Excess molar enthalpies are also given on mixtures for which data is not available (e.g., benzene + cyclodecane) and on mixtures where the results differ significantly from the literature (e.g., benzene + cycloheptane and + cyclooctane). The V_m^E and H_m^E results are given in Tables 1 and 2, together with the deviations, δV_m^E and δH_m^E, calculated from the following smoothing equations

$$\delta V_m^E/(\mathrm{cm^3\ mol^{-1}}) = V_m^E/(\mathrm{cm^3\ mol^{-1}}) - x(1-x)\sum_{r=0}^{r} A_r(1-2x)^r \tag{1}$$

and

$$\delta H_m^E/(\mathrm{J\ mol^{-1}}) = H_m^E/(\mathrm{J\ mol^{-1}}) - x(1-x)\sum_{r=0}^{r} B_r(1-2x)^r \tag{2}$$

TABLE 4

Smoothing coefficients for $x\ C_6H_6 + (1-x)\ C_yH_{2y}$ at 25°C determined from the results of Table 2

Cycloalkane	B_0 (J mol^{-1})	B_1 (J mol^{-1})	B_2 (J mol^{-1})
Cyclo-C_7H_{14}	3210.1	−465.1	297.3
Cyclo-C_8H_{16}	3230.7	−543.3	401.8
Cyclo-$C_{10}H_{20}$	3267.8	−593.0	391.9

where x denotes the mole fraction. The coefficients A_r and B_r are given in Tables 3 and 4.

The H_m^E and V_m^E results together with literature data [2–8] have been fitted to the Flory theory of liquid mixtures as previously reported [10]. The properties of the pure liquids used in the calculations are given in Table 5 together with literature references to the properties. In a few cases the properties have been obtained by extrapolation. The results of Flory calculations, performed as previously [10], are given in Table 6. The quantities in this table have been defined previously [10].

DISCUSSION

No measurements for V_m^E at 25°C for benzene + n-pentane have been reported in the literature. The present results at 25°C are, however, within experimental error of the extrapolated results of Mahl et al. [18] who measured V_m^E for this system at 15 and 20°C.

Diaz Peña and Nuñez Delgado measured V_m^E for benzene + dodecane and + hexadecane at 25°C [19]; the results reported here are significantly different to these. No other workers have reported measurements at 25°C on these two systems. V_m^E was also measured for benzene + n-hexane, + n-heptane, + n-octane, + cyclopentane, + cyclohexane, + cycloheptane, + cyclooctane and + cyclodecane. The results in all cases are within the experimental errors of the data available in the literature [2,7] and have not, therefore, been reported here.

The only reported measurements of H_m^E on benzene + cycloheptane are

TABLE 5

Properties of the pure liquids at 25°C used in the Flory theory (the estimated values were extrapolated from the data of the relevant homologue series)

Hydrocarbon	ρ (g cm^{-3})	Ref.	$10^3\alpha$ (K^{-1})	Ref.	$10^{12}k$ (Pa^{-1})	Ref.
C_6H_6	0.8736	11	1.260	12	966	13
C_5H_{10}	0.7404	11	1.347	14	1331	14
C_6H_{12}	0.7739	11	1.217	15	1136	16
C_7H_{14}	0.8073	11	1.00	17	967	17
C_8H_{16}	0.8315	11	0.979	14	803	14
$C_{10}H_{20}$	0.8550	This work	0.740	This work	530	(Estimate)
C_5H_{12}	0.6212	11	1.643	(Estimate)	2120	(Estimate)
C_6H_{14}	0.6548	11	1.375	12	1669	12
C_7H_{16}	0.6795	11	1.245	12	1438	12
C_8H_{18}	0.6985	11	1.150	12	1282	12
$C_{12}H_{26}$	0.7452	11	0.970	12	988	12
$C_{16}H_{34}$	0.7699	11	0.898	12	857	12

TABLE 6

The results of fitting the Flory theory to mixtures of $x\ C_6H_6 + (1-x)$ cyclo-C_yH_{2y} and $+(1-x)$ n-C_yH_{2y+2}

Hydrocarbon	Ref. to the V_m^E data	Ref. to the H_m^E data	$10^7\chi_{12}(H_m^E)$ (J m^{-3})	$\sigma(H_m^E)$ (J mol^{-1})	$\sigma^*(V_m^E)$ (cm^3 mol^{-1})	$10^7\chi_{12}(V_m^E)$ (J m^{-3})	$\sigma(V_m^E)$ (cm^3 mol^{-1})	$\sigma^*(H_m^E)$ (J mol^{-1})
C_5H_{10}	2	3	3.294	13.5	0.065	2.727	0.008	95.1
C_6H_{12}	2	4	4.155	6.4	0.006	4.118	0.004	7.5
C_7H_{14}	2	This work	4.109	8.1	0.167	2.600	0.005	151.1
C_8H_{16}	2	This work	4.036	9.6	0.034	3.828	0.027	13.9
$C_{10}H_{20}$	2	This work	4.099	14.0	0.167	5.796	0.062	293.8
C_5H_{12}	This work	5	4.471	44.4	0.100	3.862	0.036	223.6
C_6H_{14}	7	6	4.427	24.9	0.192	3.117	0.027	241.3
C_7H_{16}	7	8	4.495	45.4	0.215	3.000	0.034	230.3
C_8H_{18}	7	5	4.496	24.1	0.226	2.887	0.031	214.5
$C_{12}H_{26}$	This work	5	4.811	38.1	0.272	2.833	0.035	227.4
$C_{16}H_{34}$	This work	5	5.339	46.2	0.265	3.379	0.028	223.8

within experimental error of the extrapolated results of Mahl et al. [18]. They used a batch calorimeter which had a small vapour space. The present results for the cycloheptane system in the equimolar regions are of the order of 50 J mol^{-1} lower than those of Watson et al. [20]. For the cyclooctane system, the H_m^E results are consistently lower than those of Watson et al., and in the equimolar region the discrepancy is greater than 20 J mol^{-1}. The present H_m^E results for the benzene + cyclopentane and cyclohexane are within the combined experimental errors of this work and that recorded in the literature [3,4], and have therefore, not been reported here. No measurements on benzene + cyclodecane have been previously reported.

The H_m^E measurements on benzene + *n*-pentane, + *n*-hexane, + *n*-heptane, + *n*-octane, + *n*-dodecane and + *n*-hexadecane are within the experimental errors of the literature values [5,6,8] and have, therefore, not been reported here. In comparing the results, it is evident that there are errors in sign for the coefficients in table 3 of ref. 5. These have been corrected in a recent compilation of H_m^E data [21].

The present results of Flory calculations for the benzene + cycloalkane mixtures are very similar to those obtained by Benson and Singh [1] and support the remarkable success of this simple theory in fitting V_m^E and H_m^E data for binary systems of differing molecular size and nature. The poor fit for the benzene + cyclodecane system may be due to errors in the prediction of the properties of cyclodecane.

The application of this theory to benzene + *n*-alkane mixtures is also remarkably good although inferior to that obtained for the benzene + cycloalkane mixtures. This is remarkable considering the differences in size, shape and nature of the benzene and *n*-alkane molecules.

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