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INTERACTION OF CYCLOPENTANE WITH BENZENE, CARBON TETRACHLORIDE AND CYCLOHEXANE

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ABSTRACT

Heats of mixing cyclopentane + benzene, + carbon tetrachloride, + cyclohexane at 308.15 K and for cyclohexane + carbon tetrachloride at 298.15 K have been determined in an adiabatic calorimeter. The data have been examined for current theories (McGlashan, Flory and Barker) of solutions and show that McGlashan's theory predicts values for H^E and G^E that are in good agreement with their corresponding experimental values. Interaction energy between the components of these mixtures has also been determined.

INTRODUCTION

Cyclopentane forms interesting binary systems with benzene, carbon tetrachloride and cyclohexane as these involve only a minimum number of interaction pairs. There is thus adequate scope for a systematic theoretical interpretation of excess data in terms of the contemporary theories of solutions. The present work reports heats of mixing for these systems and examines the data in terms of these theories.

EXPERIMENTAL

Benzene, carbon tetrachloride and cyclohexane were purified and their purity was checked as reported earlier[1]. Cyclopentane (Fluka) was distilled a number of times and a constant boiling fraction (b.p. 48.9 °C at 750 Torr) was used for our present study. The purity of this sample was checked by measuring its density at 298.15 K which agreed to within 0.00005 g cm^{-1} with those in the literature[2]. Heats of mixing measurements were made in an adiabatic calorimeter described earlier[3].

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RESULTS

Heats of mixing values for various systems are recorded in Table 1. The results were fitted to the expression

$$H^E/x_1(1-x_1)\ \mathrm{J\ mol^{-1}} = h_0+h_1(2x_1-1)+h_2(2x_1-1)^2 \qquad (1)$$

where x_1 is the mole fraction of component 1. The constants h_0, h_1 and h_2 were evaluated by fitting $H^E/x_1(1-x_1)$ to eqn (1) by the method of least squares. They are recorded in Table 2 together with the standard deviations $\sigma(H^E)$.

TABLE 1

MEASURED HEATS OF MIXING, H^E AND COMPARISON OF VALUES CALCULATED ACCORDING TO VARIOUS THEORIES WITH VALUES INTERPOLATED FROM THE MEASURED VALUES AT MOLE FRACTIONS x_1 OF COMPONENT 1

		H^E (*J mol*$^{-1}$)			
x_1	*Exp.*	*McGlashan*	*Deshpande*	*Flory*	*Barker*
Cyclohexane(1) + carbon tetrachloride(2) (298.15 K)					
0.1920	96.94				
0.2736	125.68				
(0.3000)	(135.00)	118.29	138.60	131.50	—
0.3124	139.70				
(0.4000)	(158.00)	146.28	158.73	154.80	157.03
0.4443	161.04				
0.4916	165.96				
(0.5000)	(166.00)	$\xi = 0.8810$	$\xi = 0.9732$	—	160.50
0.5201	165.64				
0.5429	165.62				
0.5856	161.02				
(0.6000)	(160.00)	150.31	158.73	156.72	157.03
0.6129	158.01				
0.6621	150.82				
(0.7000)	(145.00)	120.31	138.60	156.07	—
0.7011	140.34				
0.7664	121.70				
0.8441	89.02				
0.8723	75.44				
Cyclopentane(1) + carbon tetrachloride (2)					
0.2011	50.65				
0.2827	62.14				
(0.3000)	(64.00)	63.69	65.54	46.52	—
0.3512	69.70				
(0.4000)	(72.00)	72.00	72.00	64.00	72.22
0.4121	73.28				
0.4621	74.02				

TABLE 1 (*continued*)

		H^E ($J\ mol^{-1}$)			
x_1	*Exp.*	*McGlashan*	*Deshpande*	*Flory*	*Barker*
Cyclopentane(1)+carbon tetrachloride(2) (continued)					
(0.5000)	(77.00)	$\xi = 0.9720$	$\xi = 0.9842$	—	76.30
0.5111	73.44				
0.5429	72.70				
(0.6000)	(68.00)	72.00	75.00	68.20	72.22
0.6019	69.20				
0.6528	66.16				
(0.7000)	(60.00)	63.69	65.54	54.39	—
0.7418	53.70				
0.8126	42.30				
0.8513	34.50				
Cyclopentane(1)+benzene(2)					
0.1918	376.98				
0.2639	466.52				
(0.3000)	(495.50)	493.37	480.60	385.35	
0.3142	512.32				
(0.4000)	(562.00)	560.34	574.25	490.68	578.67
0.4028	568.88				
0.4551	590.21				
0.4929	594.94				
(0.5000)	(597.50)	$\xi = 0.9297$	$\xi = 0.8928$	—	592.58
0.5221	597.02				
0.5598	595.70				
(0.6000)	(580.00)	590.30	574.25	660.24	578.94
0.6129	577.60				
(0.7000)	(530.00)	563.35	480.60	676.55	
0.7019	526.70				
0.7928	424.98				
0.8211	387.68				
Cyclopentane(1)+cyclohexane(2)					
0.1746	12.32				
0.2289	17.64				
0.2991	23.90				
(0.3000)	(22.00)	27.30	30.28	22.68	—
0.3184	24.70				
(0.4000)	(29.00)	32.80	34.67	29.60	34.61
0.4292	31.02				
0.4956	33.12				
(0.5000)	(33.50)	$\xi = 1.047$	$\xi = 0.8994$	—	37.82
0.5598	33.31				
0.5963	32.04				
(0.6000)	(32.00)	33.80	34.67	34.48	34.61
0.6727	29.30				
(0.7000)	(28.00)	30.25	30.28	32.00	—
0.7429	24.50				
0.8369	15.64				
0.8876	11.35				

TABLE 2

PARAMETERS OF EQN (1) TOGETHER WITH THE STANDARD DEVIATIONS $\sigma(H^E)$ AND INTERACTION ENERGY u

System	h_0	h_1	h_2	$\sigma H^E (J\ mol^{-1})$	$u (J\ mol^{-1})$
Cyclopentane(1) + benzene(2)	2390.38	151.62	349.82	5.30	104.70
Cyclopentane(1) + carbon tetrachloride(2)	296.40	−29.81	−2.45	1.00	12.55
Cyclopentane(1) + cyclohexane(2)	131.98	22.30	−66.125	1.24	6.28
Cyclohexane(1) + carbon tetrachloride(2)	660.02	45.21	−35.40	3.30	28.03

DISCUSSION

Comparison with earlier results

H^E values for carbon tetrachloride + cyclohexane at 298.15 K and + cyclopentane at 308.15 K are in excellent agreement (within 1 J mol^{-1}) with those of Ewing and Marsh[4]. However, our H^E values at 308.15 K for cyclopentane + cyclohexane are consistently more positive than those of Ewing and Marsh[4], the deviation being 14 J mol^{-1} for an equimolar composition. We are unaware of any H^E data at 308.15 K with which to compare our results for cyclopentane + benzene; however, they are comparable to the H^E values[5] at 298.15 K.

Comparison with theory

We now examine our results for the corresponding state theory of McGlashan[6]. Following Marsh et al.[7] we calculated H^E using the one fluid approximation and van der Waals combining rules together with the van der Waals equation of state, from the relations

$$H^E = -\langle a\rangle/\langle v\rangle + x_1 a_1/v_1 + x_2 a_2 v_2^{-1} \tag{2}$$

$$V_i = (a_i/2RT)[1-\{1-4b_i RT/a_i\}^{1/2}] \tag{3}$$

where a_i and b_i are the usual van der Waals constants and x_1 is the mole fraction of component 1. The averaged quantities were evaluated from the following expression:

$$\langle a\rangle = a_1 x_1^2 + 2a_{12} x_1 x_2 + a_2 x_2^2 \tag{4}$$

$$\langle b\rangle = b_1 x_1^2 + 2b_{12} x_1 x_2 + b_2 x_2^2 \tag{5}$$

where $a_{12} = \xi(a_1 a_2)^{1/2}(b_{12}^2/b_1 b_2)^{1/2}$ (6)

$$b_{12} = (b_1^{1/3} + b_2^{1/3})/8 \tag{7}$$

and ξ is a number close to unity. In principle ξ can be obtained from second virial coefficient data but the practice in all the theories has been to devise an experimental excess function like H^E or G^E which agrees with the calculated value at one specified composition and then to calculate the other function. As G^E data are available for benzene + cyclopentane and carbon tetrachloride + cyclohexane mixtures only, we evaluated ξ from a forced fit of H^E_{exp} for an equimolar composition and then calculated[7] the corresponding G^E values. The calculated G^E values are recorded in Table 3 and considering the simplified nature of this theory, they are in satisfactory agreement with their corresponding experimental values[8,9]. H^E values were then recalculated at $x_1 = 0.3, 0.4, 0.6$ and 0.7 for all the mixtures and these values (Table 1) are in good agreement with their corresponding experimental values. The van der Waal's constants were evaluated from critical data[10].

TABLE 3

COMPARISON OF CALCULATED AND EXPERIMENTAL G^E VALUES

System		G^E (*J mol*$^{-1}$) *McGlashan*	*Deshpande*	*Exp.*	*Flory*
Cyclohexane(1) + carbon tetrachloride	298.15 K	89.04	−31.46	69.87[8]	36.02
Cyclopentane(1) + benzene(2)	308.15 K	140.67	41.55	271.96[9]	150.00

At the time this paper was drafted, the authors' attention was drawn to a recent publication[11] which incorporates the contributions of the difference in intermolecular energy θ, in size ϕ, and deviations from Berthelot's rule to this theory and expresses H^E by the expression[11]

$$\begin{aligned} H^E/x_1(1-x_1) &= [2(1-\xi)(1+\theta/2)+\theta^2/4-\theta\phi/2]\,[-u+TC_p] \\ &\approx [2(1-\xi)-\theta\phi/2]\,[-u+TC_p] \end{aligned} \tag{8}$$

where u and C_p are the configurational energy and heat capacity of component 1 taken as reference. For a liquid following the van der Waals equation of state

$$-u+TC_p = (a/V)(2-V/b)^{-1} \approx a/V \tag{9}$$

and the energy and size difference parameters θ and ϕ are given by

$$1+\theta = T_{c,2}/T_{c,1} \tag{10}$$

$$1+\phi = V_{c,2}/V_{c,1} \tag{11}$$

In examining our data in terms of expression (8) we calculated ξ from H^E_{exp} and calculated the corresponding G^E values for benzene + cyclopentane and carbon tetrachloride + cyclohexane mixtures. The data indicate that G^E values thus calculated do not improve those evaluated from McGlashan's original theory, although the predicted H^E values at $x_1 = 0.3$, 0.4, 0.6 and 0.7 are comparable to values calculated from expression (2).

It would now be instructive to consider our results for Flory's theory[12]. Flory supposes that a molecule in a liquid is made up of segments each having a "hard-core" volume v^* but occupying an effective volume v in the liquid so that the reduced volume $\tilde{v}_i = v_i/v_i^*$ for a pure substance i can be calculated from its expansivity α_i according to the relation[12]

$$\tilde{v}_i = [1+\alpha_i T/3(1+\alpha_i T)]^3 \qquad (i = 1, 2) \tag{12}$$

Heats of mixing, H^E were then calculated from Flory's formula[11]

$$H^E = x_1 P_1^* V_1 \tilde{v}_1^{-1}(\tilde{v}_1^{-1} - \tilde{v}_{\text{calc.}}^{-1}) + x_2 P_2^* V_2 \tilde{v}_2^{-1}(\tilde{v}_2^{-1} - \tilde{v}_{\text{calc.}}^{-1}) + \\ + x_1 V_1 \tilde{v}_1^{-1} \theta_2 \chi_{12} \tilde{v}_{\text{calc.}}^{-1} \tag{13}$$

where

$$\tilde{v}_{\text{calc}} = (\phi_1\tilde{v}_1 + \phi_2\tilde{v}_2) + (\phi_1\tilde{v}_1 + \phi_2\tilde{v}_2)^{7/3}[\tfrac{4}{3} - (\phi_1\tilde{v}_1 + \phi_2\tilde{v}_2)]^{-1} \times \\ \times [(\phi_1 P_1^* \tilde{T}_1^0 + \phi_2 P_2^* \tilde{T}_2^0)(\phi_1 P_1^* + \phi_2 P_2^*)^{-1}\{1 - \phi_1 \theta_2 \chi_{12}(\phi_1 P_1^* + \phi_2 P_2^*)^{-1}\} - \\ - \{(\phi_1\tilde{v}_1 + \phi_2\tilde{v}_2)^{1/3} - 1\}(\phi_1\tilde{v}_1 + \phi_2\tilde{v}_2)^{-4/3}] \tag{14}$$

The various terms have their usual significance[12] and were calculated as described earlier[1]. Evaluation of H^E by this theory requires a knowledge of $\theta_2\chi_{12}$ which was obtained by fitting H^E_{exp} to expression 13 for an equimolar mixture. This value of $\theta_2\chi_{12}$ was next used to calculate the corresponding G^E value for benzene + cyclopentane and carbon tetrachloride + cyclohexane mixtures. These calculated G^E values do agree equally well with their corresponding experimental values as the ones calculated from McGlashan's original theory. The theory nevertheless gives a good reproduction of H^E values for all the mixtures at $x_1 = 0.3$, 0.4, 0.6 and 0.7. However, any satisfactory theory of solutions of non-electrolytes should be in a position to predict reasonably well the values of H^E, G^E and V^E and the present study on simple mixtures gives credit to McGlashan's theory.

In an alternate attempt to understand the nature of interaction between the components of these mixtures, we examined our results for Barker's theory[13]. This generalized lattice model theory allows a molecule to have contact points of several types; each type having a definite interaction energy. The total number of contacts, which a molecule occupying r_A sites on a Z-coordinated lattice, is capable of making, is given by

$$q_A Z = r_A Z - 2r_A + 2 \tag{15}$$

As the components of these binary mixtures are all non-polar, the theory prescribed that they have only one type of contact point. The heats of mixing values were then calculated from the relation

$$H^E = -4RTX_S X_A \eta_1 \ln \eta_1 \tag{16}$$

where X_A and X_S can be solved from:

$$X_A[X_A\eta_{A-A}+X_S\eta_{A-S}] = q_A Z x_A/2 \tag{17}$$

$$\eta_1 = \eta_{A-S} = e^{-u_1/kT}$$

$$X_S[X_A\eta_{A-S}+X_S\eta_{S-S}] = q_S Z x_S/2 \tag{18}$$

A value of $Z = 4$, $r_A = 2$ for cyclopentane, and $r_S = 2$ for carbon tetrachloride, benzene and cyclohexane used throughout. It is further supposed that interaction between molecules of the same type have zero interaction energy so that $\eta_{A-A} = \eta_{S-S} = e^{-u=0/kT} = 1$. H^E values calculated in this manner for the various systems are recorded in Table 1 and they reproduce well the experimental curves of H^E for all the systems. The interaction energy of cyclopentane with benzene, carbon tetrachloride and cyclohexane are recorded in Table 2, these are also repulsive in character and vary in the order benzene > carbon tetrachloride > cyclohexane.

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