HEATS OF MIXING OF NORMAL ALKANES WITH CYCLOHEXANE; COMPARISON OF THE RESULTS WITH THE LATTICE THEORY

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Heats of mixing at a constant volume and at 25°C were calculated from excess enthalpies measured at 25°C and 1 atm in systems cyclohexane- n-alkane (hexane, heptane, octane, decane, dodecane, hexadecane). The values thus obtained were compared with those calculated from the lattice model ("zero-th" approximation) for various coordination numbers and various lattice elements. A very good agreement was found for the first three systems over the entire concentration region. For the remaining systems, the lattice approximation gives semiquantitative results.

In the preceding paper[1] results were reported on the measurement of heats of mixing for systems of n-hexane, n-octane, and n-dodecane with cyclohexane (25°C, 1 atm) by means of a modified Scatchard calorimeter[2]. Values for n-heptane and n-hexadecane were used as published earlier[3]. Excess enthalpies for the system cyclohexane–n-decane were determined graphically using the dependence of the heat of mixing upon the number of carbon atoms in the n-hydrocarbon for various values of the cyclohexane mole fraction.

The aim of this paper was to investigate to which extent the experimental values agree with those calculated from the lattice theory for mixtures of different molecules[4].

THEORETICAL

The lattice theory ("zeroth" approximation) is based on the assumption that each molecule i is composed of r_i structural parts (elements, segments). Each element occupies one position in the lattice of coordination number z. The number of inter-actions (contacts) of the molecule i with segments of the other molecules is given by: $q_i z = r_i(z - 2) + 2$ (for chain molecules) and $q_i z = r_i(z - 2)$ (for cyclic molecules). In the case under consideration, the molecules contain only two types of segments, A and B. The fraction α_i is then defined so that $\alpha_i q_i z$ interactions are caused by segments A, and $(1 - \alpha_i) q_i z$ interactions by segments B.

In case of a binary mixture the following relations result from the configuration

partition function for the excess free energy F^E, the excess energy U^E, and the mixing volume V^E:

$$F^E/RT = x_1 \ln \left(\frac{r_1}{r_1 + (r_2 - r_1) x_2} \right) + \tfrac{1}{2} q_1 z x_1 \ln \left[\frac{q_1}{r_1} \left(\frac{r_1 + (r_2 - r_1) x_2}{q_1 + (q_2 - q_1) x_2} \right) \right] +$$

$$+ x_2 \ln \left(\frac{r_2}{r_1 + (r_2 - r_1) x_1} \right) + \tfrac{1}{2} q_2 z x_2 \ln \left[\frac{q_2}{r_2} \left(\frac{r_1 + (r_2 - r_1) x_2}{q_1 + (q_2 - q_1) x_2} \right) \right] +$$

$$q_1 q_2 (\alpha_1 - \alpha_2)^2 \left(\frac{x_1 x_2}{q_1 + (q_2 - q_1)} \right) w/kT , \qquad (1)$$

$$U^E/RT = q_1 q_2 (\alpha_1 - \alpha_2)^2 \left(\frac{x_1 x_2}{q_1 + (q_2 - q_1) x_2} \right) u/kT , \qquad (2)$$

$$V^E = 0 . \qquad (3)$$

In equations $(1)-(3)$, x_1 and x_2 are the mole fractions of both components, R is the gas constant, k is the Boltzmann constant, and T is the temperature (K). The parameter w represents the free energy of interchange of the process in which $2z$ of A—B contacts originate from z contacts B—B. The quantity $u = w - T(dw/dT)$ is the energy of interchange.

Gómez-Ibanez and coworkers[5,6] calculated the concentration dependence of the excess free enthalpy G^E from isothermal vapour–liquid measurements in the systems cyclohexane–dodecane and cyclohexane–hexadecane. They found an excellent agreement with values calculated from equation (1) for $z = 8$, and A = —CH$_3$, B = —CH$_2$—CH$_2$—, or A = —H, B = —CH$_2$—.

Therefore, the following questions were of interest to us: a) would this agreement hold also for heats of mixing; b) to what extent the length of the hydrocarbon chain and the cyclic structure of cyclohexane would influence the results; c) which type of lattice and which choice of elements A, B would give optimum results.

RESULTS

Heats of Mixing at Constant Volume

It can be shown in a general way[7] that the difference $F^E - G^E$ is always negligible in comparison with experimental errors. Therefore, both above mentioned quantities can be directly compared. This is, however, by far not the case for the excess enthalpy H^E and the excess energy U^E.

McGlashan[7] and van der Waals[8] derived an expression for the relation between H^E and U^E in the form of a power function of V^E. If the terms of the second and higher orders are neglected, then

$$U^E = H^E - T\alpha V^E/\beta . \qquad (4)$$

The thermal expansion coefficient α and the isothermal compressibility β are obtained, for a given mixture, from the corresponding values for pure components and from the volume fraction φ_1

$$\alpha = \varphi_1\alpha_1 + (1 - \varphi_1)\alpha_2 ,$$

$$\beta = \varphi_1\beta_1 + (1 - \varphi_1)\beta_2 ,$$

$$\varphi_1 = x_1V_1/(x_1V_1 + x_2V_2) ,$$

where V_1 and V_2 are the molar volumes of the pure components.

The values of these quantities are summarized in Table I together with U^E and $T\alpha V^E/\beta$ for equimolar mixtures.

The volumes of mixing for cyclohexane–hexane and cyclohexane–dodecane were measured by Gómez - Ibanez[9]; for the other systems the values were obtained by Danusso[10].

As can be seen from Table I and Table III, the value of the second term of the right side of equation (4) represents 20—30% of the heat of mixing measured. Therefore, the inaccuracy in determining this term substantially influences the error in U^E.

The error of the ratio α/β is about 1%, the error in V^E is 2—5%. With 2% error in the determination of H^E this results in 4—6% error in the calculation of U^E. Such

TABLE I

Some Physical Properties of Cyclohexane and n-Alkanes and their Mixtures (25°C)

Compound	V ml/mol ref.	$10^3\alpha$ deg^{-1} ref.	$10^3\beta$ ml/J ref.	$V^E(x_1 = 0.5)$ ml/mol	$X(x_1 = 0.5)^a$ J/mol
Cyclohexane	108·73[1]	1·217[11]	1·111[12]		
Hexane	131·58[1]	1·386[13]	1·700[13]	0·150	41
Heptane	147·46[14]	1·251[13]	1·466[13]	0·234	66
Octane	163·51[1]	1·157[13]	1·303[13]	0·304	87
Decane	195·90[14]	1·049[13]	1·106[b]	0·416	125
Dodecane	228·55[1]	0·976[13]	0·980[8]	0·506	156
Hexadecane	294·08[8]	0·898[13]	0·869[8]	0·619	194

^{a} $X = T\alpha V^E/\beta$. ^{b} By interpolation of the dependence β on the number of carbons in the n-alkane.

a conclusion is valid around the maximum of U^E; the situation at the margins of the concentration region is worse (10% error).

Selection of Segments A, B. Lattice Coordination Number

Van der Waals and Hermans[15] were the first to assume that the equivalent segments were A: —CH_3, and B: —CH_2—CH_2—(denoted in the following as selection a)). Another possibility is to regard the hydrogen terminating a hydrocarbon chain and —CH_2— as equivalent[5,6]. McGlashan and coworkers[7] assessed for the mixture n-hexane–n-hexadecane A: —CH_3, B: —CH_2— (selection c)), and A: CH_3—CH_2—, B: —CH_2—CH_2— (selection d)). Other analogous possibilities used in this work are: A: CH_3—CH_2—, B: CH_3—CH_2—CH_2— f); A: CH_3—CH_2—CH_2—, B: —CH_2——CH_2—CH_2— g). The calculations were carried out for $z = 4, 8, 12$. Values of r_i, q_i, α_i needed in the calculations were obtained from the above mentioned simple relations (see, *e.g.*, Table II).

As an illustration, in Table III deviations Δ between the calculated and experimental values of U^E are compared for two systems ($z = 8$). Subscripts indicate the selection of elements. As numerical values of the parameter u are not known, the following procedure was used: the ratio u/k was calculated from the experimental U^E for $x = 0.5$ with the use of equation (2); this ratio was then used to calculate the excess energies for the other equidistant mol fractions of cyclohexane. Though for the mixtures cyclohexane–dodecane and cyclohexane–hexadecane parameters w/k and their temperature dependences are available[5,6], they cannot be used to calculate u^7. Equation (4) was derived assuming a constant volume of the system. As, however, the volume changes with temperature, neither the relation $U^E = F^E - T(dF^E/dT)$

TABLE II
Values of Geometrical Parameters in Eq. (2) for $z = 8$

Selection	Cyclohexane			Hexane		
	r_i	q_i	α_i	r_i	q_i	α_i
(a)	3	9/4	0	4	14/4	1/2
(b)	6	18/4	0	8	25/4	7/25
(c)	6	18/4	0	6	19/4	7/19
(e)	3	9/4	0	3	10/4	7/10
(f)[a]	2	6/4	0	8/3	9/4	7/9
(g)	2	6/4	0	2	7/4	1

[a] Has no exact physical meaning[16].

TABLE III

Comparison of Calculated and Measured Values of U^E (J/mol) for Various Segments A, B

System: cyclohexane(1)-n-hydrocarbons(2); z = 8.

x_1	Hexane							Heptane							Dodecane						
	U^E_{exp}	Δ_a	Δ_b	Δ_c	Δ_d	Δ_f	Δ_g	U^E_{exp}	Δ_a	Δ_b	Δ_c	Δ_d	Δ_f	Δ_g	U^E_{exp}	Δ_a	Δ_b	Δ_c	Δ_d	Δ_f	Δ_g
0·1	52	2	0	−5	−5	1	−4	64	10	10	5	6	9	7	108	40	39	37	37	40	37
0·2	94	2	−1	−9	−8	1	−7	111	11	11	4	5	12	6	178	48	48	43	45	49	45
0·3	127	2	−2	−8	−8	0	−7	146	10	9	3	4	10	5	221	39	45	34	35	39	35
0·4	148	−1	−4	−8	−8	−2	−8	169	6	6	2	3	7	3	248	24	24	21	21	24	21
0·5	163	0	0	0	0	0	0	177	0	0	0	0	0	0	253	0	0	0	0	0	0
0·6	163	0	1	6	4	0	3	178	−1	0	5	4	−1	3	243	−22	−17	−18	−19	−23	−20
0·7	147	−2	0	9	6	−2	4	160	−5	−3	5	4	−6	2	226	−29	−28	−21	−22	−31	−24
0·8	118	−1	2	12	10	−1	8	122	−10	−8	1	0	−12	2	182	−34	−33	−22	−24	−36	−26
0·9	69	−2	1	9	7	−1	6	78	−1	−1	9	8	−2	6	127	−10	−9	0	−1	−12	−2
u/k, K	114	191	125	68	72	49		132	249	170	91	93	65		376	724	577	294	261	205	
δ	1·5	1·0	7·1	6·1	0·9	5·1		5·5	5·0	3·7	3·7	5·9	3·8		15·5	15·3	12·4	12·8	16·0	13·2	

$\Delta = E^E_{exp} - U^E_{calc}$; δ is mean absolute deviation in %.

nor $u = w - T(\mathrm{d}u/\mathrm{d}T)$ is valid any more. For instance, in case of dodecane (selection a) calculation would give $u/k = 1232°\mathrm{K}$, while $u/k = 370$ K follows from U^E.

Table IV summarizes the excess energies U^E calculated for the system coclohexane–octane and using $z = 4, 8, 12$ (selection (c)). The other systems yield analogous results.

DISCUSSION

The agreement between the calculated and measured values of U^E is very good for the first three systems over the entire concentration region. For the system cyclohexane–hexane the selections (a), (b) (f) are more suitable. This is understandable, as these selections better satisfy the requirement that segments in the lattice should be of a similar size (in case of selections (a), (b), (f) the volumes of the segments A, B differ by 9%, while in case of the selections (c), (d), (g) by 21%). Because of this reason, the selections (c), (d), (g) are more suitable for selections starting from heptane (Table III and IV).

Systems with decane, dodecane, and hexadecane give less satisfactory results, though the selections (c), (d), (g) give comparatively better agreement. Deviations Δ are too large for $x_1 < 0.5$, maxima on the calculated U^E-curves are distinctly shifted towards higher values of x_1 (Figs 1, 2), even though the difference in volume of the elements A and B is (for the system cyclohexane–hexadecane) only 1·4% (selection (c), (d), (g)).

The deviations Δ do not increase with increasing length of the hydrocarbon chain. Therefore, it may be concluded that the reason lies presumably in the fact that in mixtures containing higher hydrocarbons the six-membered ring of cyclohexane cannot be neglected or included solely in the calculation of $q_i z$. In another words: the sole

TABLE IV

Comparison of Values of Δ for Various z
    System: cyclohexane(1)–n-octane(2); A: —CH$_3$, B: —CH$_2$—.

z	x_1									u/k, K	δ, %
	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9		
4	13	16	14	9	0	—6	—12	—11	—5	232	7·7
8	12	14	12	8	0	—4	—9	—8	—2	226	6·2
12	11	13	11	7	0	—4	—9	—7	—1	223	5·6
U^E_{exp} J/mol	73	126	164	187	193	187	164	129	78		

δ Is mean absolute deviation, $\Delta = U^E_{exp} - U^E_{calc}$.

change of the parameter u/k from one system to another cannot compensate the difference between —CH_2 — groups of cyclohexane and those of an alkane in higher alkanes (though — according to the lattice model — u/k should be the same for all systems).

Having in mind this situation, Brzostowski[17] derived general relations for F^E. However, relations for U^E that follow from the equations are identical with equation (2).

Another possibility of a semiempirical correlation (e.g., expressing u/k as a function of the number of interactions $q_i z$ of both molecules) has not been checked so far.

On the other hand, the choice of a lattice type is not substantial. The results for $z = 8$, $z = 12$, and $z = \infty$ (not included in Table III and IV) are practically identical, calculated values of U^E for $z = 4$ are only slightly different.

Fig. 1 and Fig. 2 show a comparison between the values of U^E calculated with the use of equation (2) for $z = 8$ and A: —CH_3, B: —CH_2— (curves), and the values calculated from the heats of mixing (points).
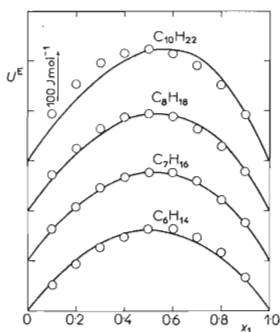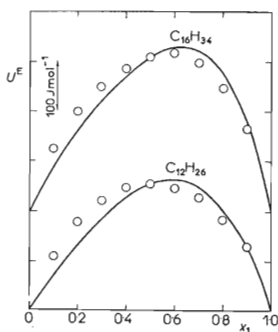

FIG. 1

Dependence of Excess Energy U^E (J/mol) on Molar Fraction of Cyclohexane x_1 in the Mixture with n-Alkane at 25°C

Curves calculated from the lattice model ($z = 8$); points show heats of mixing recalculated from a constant pressure to a constant volume.

FIG. 2

Dependence of Excess Energy U^E (J/mol) on Molar Fraction of Cyclohexane x_1 in the Mixture with n-Alkane at 25°C

Curves calculated from the lattice model ($z = 8$); points show heats of mixing recalculated from a constant pressure to a constant volume.

CONCLUSIONS

In order to correlate the dependence of the excess energies upon the mole fraction of cyclohexane in systems cyclohexane– n-alkane it is convenient to select the segments A: —CH_3, B: —CH_2—, and the lattice coordination number $z = 8$ (or 12). For the system cyclohexane–hexane the selection A: —H, B: —CH_2— leads to better results.

While very satisfactory results were obtained for the first three systems studied, the lattice model fits only semiquantitatively the dependence $U^E - x_1$ for systems cyclohexane–higher hydrocarbons.

However, the main and substantial drawback of the "zeroth" approximation in correlating U^E is that the ratio u/k is not the same in all the mixtures[5,6].

No improvement of the results was obtained, if three elements[18] were considered instead of two; e.g. A: —CH_3, B: —CH_2— (n-alkane), C: —CH_2— (cyclohexane). The results were similar to those listed in Table III and Table IV.

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