

## Thermodynamics of Mixtures Excess Volumes and Energies of Mixing of Cycloalkane Mixtures (Cyclopentane to Cyclooctane)

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*Summary.* The volumes of mixing for the systems cyclopentane + cyclohexane, cyclopentane + cycloheptane, cyclohexane + cycloheptane (at 20°C), and cyclopentane + cyclooctane, cyclohexane + cyclooctane, cycloheptane + cyclooctane (at 30°C) have been measured with a dilatometer. All systems show volume contractions, except the first. The energies of mixing are also given. They vary from 7 to 55 J/mol for equimolar solutions.

**1. Introduction.** – In earlier investigations in this laboratory, the heats of mixing of several cycloalkane systems were determined [1–2]. In order to allow a further interpretation of the results, the excess volumes of mixing have now been determined. We wish to report here the results for binary systems containing the cycloalkanes from cyclopentane to cyclooctane.

**2. Experimental.** – The measurements were carried out in a dilatometer described earlier [3], and similar to the model of *Duncan et al.* [4].

The hydrocarbons were all supplied by *Fluka AG*, with a stated purity of better than 99%. Olefinic and aromatic hydrocarbons were eliminated by treatment with  $\text{H}_2\text{SO}_4$  conc., and after neutralisation (NaOH), washing ( $\text{H}_2\text{O}$  deionized), and drying over  $\text{CaSO}_4$  anh., the cycloalkanes were distilled. In the case of cycloheptane, it was not possible to prevent a slight reaction with mercury, in spite of repeated shaking with mercury.

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**3. Results and discussion.** – The excess volumes of mixing are shown in Fig. 1 and 2. The results were fitted to an analytical expression of the type

$$V^e = x(1-x) [A + B(1-2x)] \quad (1)$$

where  $x$  represents the mol fraction of the heavier compound.

The values of  $A$  and  $B$ , and the mean deviations  $\sigma$  for the systems are given in Table 1.

The results for the system cyclopentane + cyclooctane at 30°C are compatible with the results of *Ewing et al.* [5] at 15, 25 and 35°C. (It must be pointed out, that their results are more accurate, owing to the more advanced equipment used for the determination of  $V^e$ .)

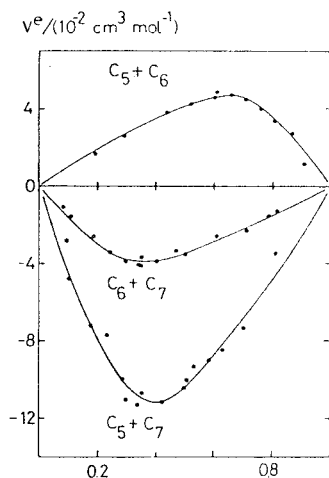


Fig. 1. The volumes of mixing  $V^e$  at 20°C, for the systems  $C_5 + C_6$ ,  $C_6 + C_7$  and  $C_5 + C_7$

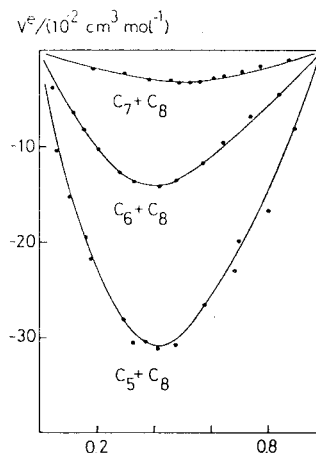


Fig. 2. The volumes of mixing  $V^e$  at 30°C, for the systems  $C_5 + C_8$ ,  $C_6 + C_8$  and  $C_7 + C_8$

Table 1. Parameters  $A$  ( $\text{cm}^3 \text{mol}^{-1}$ ) and  $B$  ( $\text{cm}^3 \text{mol}^{-1}$ ) for  $V^e$  of eq. (1) and  $\sigma$  ( $\text{cm}^3 \text{mol}^{-1}$ )

System	Temp. (°C)	$-A$	$-B$	$\sigma$
c- $C_5$ + c- $C_6$	20	-0.170	0.104	0.001
c- $C_5$ + c- $C_7$	20	0.413	0.180	0.005
c- $C_6$ + c- $C_7$	20	0.141	0.086	0.002
c- $C_5$ + c- $C_8$	30	1.204	0.435	0.010
c- $C_6$ + c- $C_8$	30	0.518	0.242	0.005
c- $C_7$ + c- $C_8$	30	0.121	0.010	0.002

Using the combined results, which include earlier results for  $V^e$  at 298 K [1], it is found that the temperature gradient  $(\partial V^e / \partial T) = -0.0045 \text{ cm}^3 \text{mol}^{-1} \text{K}^{-1}$  for  $x = 0.4$ , near the maximum of all curves.

All the volumes of mixing are negative, except for the system cyclopentane + cyclohexane, which corresponds to the smallest cycloalkanes investigated.

This system shows a complete inversion with respect to the other systems, the maximum of the positive curve being near  $x = 0.6$ .

The result seems to be in contradiction with the behaviour of the other mixtures of cycloalkanes, and with the general pattern for the mixtures of *n*-alkanes, another class with negative volumes of mixing [6]. However, for this system, a relatively large and positive enthalpy of mixing was found [1-2], and consequently the internal energy of mixing  $U^e$  (at constant volume) is again consistent with the results obtained for the different systems, as shown below.

The quantity  $U^e$  is given by the relation (2) [6-8]

$$U^e = H^e - T(\alpha/\beta_T) V^e, \quad (2)$$

where  $\alpha = V^{-1}(\partial V/\partial T)_P$  and  $\beta_T = -V^{-1}(\partial V/\partial P)_T$ .

Experimental values of  $U^e$ , for different mol fractions, are given in Table 2. They were calculated by using the calorimetric values of  $H^e$  [1-2], and values of  $\alpha$  and  $\beta_T$  from the literature [9-11].

Table 2. *Excess volumes* ( $\text{cm}^3 \text{mol}^{-1}$ ), *enthalpies* ( $\text{J} \cdot \text{mol}^{-1}$ ) and *energies* ( $\text{J} \cdot \text{mol}^{-1}$ ) of mixing

x	$-V^e$	$H^e$	$U^e$
cyclopentane + cyclohexane (20°C)			
0.3	-0.027	17.4	9
0.4	-0.035	22.3	11
0.5	-0.042	26	13
0.6	-0.046	28	13
0.7	-0.045	27	12
cyclopentane + cycloheptane (20°C)			
0.3	0.105	- 1.7	30
0.4	0.112	- 1.8	32
0.5	0.102	- 1.5	29
0.6	0.087	- 0.8	25
cyclohexane + cycloheptane (20°C)			
0.3	0.038	2.7	10
0.4	0.038	4.8	15
0.5	0.034	7	18
0.6	0.029	9	20
cyclopentane + cyclooctane (30°C)			
0.3	0.288	- 43	47
0.4	0.309	- 45.6	53
0.5	0.300	- 42.2	55
0.7	0.216	- 22.5	50
cyclohexane + cyclooctane (30°C)			
0.3	0.127	- 2	40
0.4	0.134	+ 2	47
0.5	0.128	+ 7	50
0.7	0.087	+ 13	44
cycloheptane + cyclooctane (30°C)			
0.3	0.026	- 2	6
0.4	0.029	- 3	6
0.5	0.030	- 3	7
0.7	0.024	- 1	7

The energy of mixing is the *difference* of two experimental quantities, and in the present calculation, it was found that the error on  $U^e$  was about  $\pm 2$  J/mol, for all systems.

The results of Table 2 show a trend in the behaviour of the different systems, similar to earlier observations made for the mixtures of *n*-alkanes [12]:  $U^e$  is positive and it increases with the difference in size of the molecules.

The extension of an earlier theory [12] to the present case, was also attempted. It was assumed that the constants  $a_1$  and  $a_2$  in the *Van Laar-Lorentz* equation [8] could be written as  $a_1 \approx n_1^2$  and  $a_2 \approx n_2^2$ , in the case of cycloalkanes. The calculated values of  $U^e$  showed only a semi-quantitative agreement with the experimental values for the 6 systems considered.

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