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### The Excess Enthalpies and Volumes of Mixing of 3-Methylhexane with Carbon Tetrachloride\*

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#### Abstract

The functions  $H^E$  and  $V^E$  have been measured between 293.15 and 303.15 K for the mixtures of ( $\pm$ ), (+) and (-) 3-methylhexane with carbon tetrachloride, using improved calorimetric and dilatometric systems. As expected, it is found that the excess functions are identical for the optical isomers, within experimental error.

The present work is a continuation of the calorimetric and volumetric study of liquid mixtures, initiated in this laboratory by *C. G. Boissonnas* over 30 years ago. The general purpose is to provide accurate data on a variety of systems, within the framework of thermodynamics of liquid mixtures [1, 2].

Experiments were carried out with a calorimeter similar to a model described earlier by *Boissonnas* and *Fernandez* [3], with the following modifications:

(a) In the present design, the calorimeter is U-shaped, with a filling capillary entering centrally at the lowest part of the U. This modification, along with the mixing technique, ensures complete mixing of the components.

(b) The calorimeter heater, now a fine Nichrome resistance of approximately 125 ohm, is wound around the outside of the body.

(c) The total volume of the calorimeter has been greatly reduced (less than 100 g when filled with mercury), which allows a more accurate weighing and also reduces the heat capacity of the system (glass, mercury and the liquid mixtures).

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The dilatometer, similar in design to the model described by *Boissonnas* et al [4], has also been modified in a similar way, so that the weighing of the components is more accurate.

The calorimeter was tested with the standard system n-hexane + cyclohexane at 298.15 K [5].

For the dilatometer, the system carbon tetrachloride + cyclohexane at 293.15 K [6] was used. The results are in good agreement with the sets of values found in the literature [5, 6], which fully justifies the modifications in the original designs. The experimental results for the enthalpies ( $H^E$ ) and the excess volumes ( $V^E$ ) are shown in fig. 1 and 2. All data were fitted to expressions of the type

$$H^E \text{ or } V^E = x(1-x) \sum_{n=0}^3 A_n(1-2x)^n \quad (1)$$

where  $x$  represents the mole fraction of the heavier component. The values of parameters  $A_0$  to  $A_3$  are given in tables 1-2, with the standard deviations  $\sigma$ .

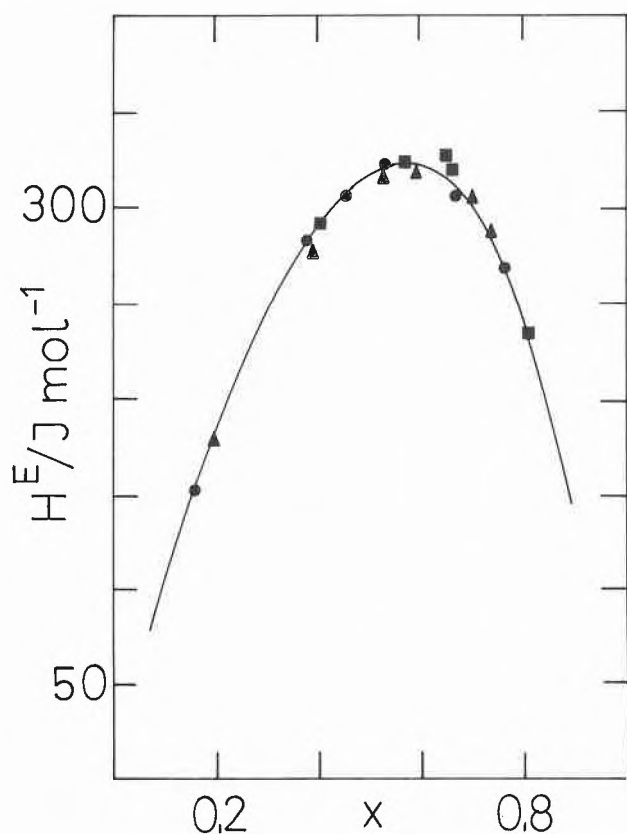
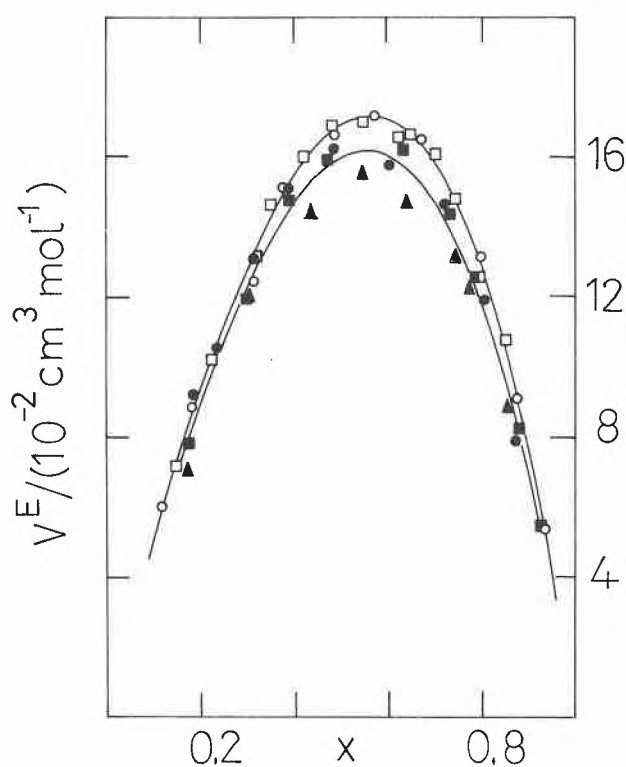
As expected, the experimental results for the enthalpies of mixing of ( $\pm$ ), (+) and (-) 3-methylhexane with  $\text{CCl}_4$  at 303.15 K are identical, within experimental error. In the case of  $V^E$  slightly smaller values were found with the (+) isomer, but the discrepancies are not large enough to be significant. Since the corresponding  $H^E$  values show no deviation, it may be assumed that the differences in the excess volumes are

Table 1: Parameters  $A_n$  for  $H^E$ , according to eq. (1), and standard deviations  $\sigma$ .

System	$t/^\circ\text{C}$	$A_0$	$A_1$	$A_2$	$A_3$	$\sigma/(\text{J mol}^{-1})$
1. n-C <sub>6</sub> H <sub>14</sub> + c-C <sub>6</sub> H <sub>12</sub>	25	874.4	266.6	-	-	3.1
2. ( $\pm$ ) 3-methylhexane + CCl <sub>4</sub>	30	1265.0	-206.3	208.3	-231.1	1.8
3. (-) 3-methylhexane + CCl <sub>4</sub>	30	1282.1	-421.1	-133.2	-	3.9
4. (+) 3-methylhexane + CCl <sub>4</sub>	30	1239.7	-383.0	331.8	-	1.4
5. 2, 3 and 4 combined	30	1265.5	-365.1	145.2	204.6	4.1

Table 2: Parameters  $A_n$  for  $V^E$ , according to eq. (1), and deviations  $\sigma$ .

System	$t/^\circ\text{C}$	$A_0$	$A_1$	$A_2$	$A_3$	$\sigma/(\text{cm}^3 \text{mol}^{-1})$
1. c-C <sub>6</sub> H <sub>12</sub> + CCl <sub>4</sub>	20	0.6474	0.0312	-0.0702	-0.1494	0.001
2. ( $\pm$ ) 3-methylhexane + CCl <sub>4</sub>	20	0.6690	-0.2125	0.0389	0.0881	0.002
3. (-) 3-methylhexane + CCl <sub>4</sub>	20	0.6753	-0.1610	0.0139	-	0.002
4. ( $\pm$ ) 3-methylhexane + CCl <sub>4</sub>	30	0.6511	-0.1215	0.0402	0.0398	0.003
5. (-) 3-methylhexane + CCl <sub>4</sub>	30	0.6513	-0.1997	-0.0005	0.0772	0.002
6. (+) 3-methylhexane + CCl <sub>4</sub>	30	0.6080	-0.1332	0.0054	-0.0808	0.001
7. 2 and 3 combined	20	0.6729	-0.1708	-0.0229	-	0.002
8. 4, 5 and 6 combined	30	0.6418	0.2013	-	-	0.005

Fig. 1: Enthalpies of mixing of (+), (-) and ( $\pm$ ) 3-methylhexane with CCl<sub>4</sub> at 303.15 K ( $\blacktriangle$ ,  $\blacksquare$  and  $\bullet$  respectively). Mole fraction  $x$  corresponds to CCl<sub>4</sub>.Fig. 2: Volumes of mixing of (-) and ( $\pm$ ) 3-methylhexane with CCl<sub>4</sub> at 293.15 K ( $\square$  and  $\circ$  respectively) and of (+), (-) and ( $\pm$ ) 3-methylhexane with CCl<sub>4</sub> at 303.15 K ( $\blacktriangle$ ,  $\blacksquare$  and  $\bullet$  respectively). Mole fraction  $x$  corresponds to CCl<sub>4</sub>.

due to the presence of a small and undetected impurity in the (+) isomer. As pointed out by *Sturtevant* [7] for example,  $V^E$  can be very sensitive to small amounts of impurities. The results for the mixtures of (-) 3-methylhexane with the racemate at 303.15 K indicate that both  $H^E$  and  $V^E$  are equal to zero at all concen-

trations, within experimental error. These experiments may be regarded as tests for the purity of the isomers and the accuracy of the equipment.

#### Materials:

Carbon tetrachloride and ( $\pm$ ) 3-methylhexane were supplied by Fluka AG, Switzerland, with stated purities of better than 99,5%. The (+) and (-) isomers of 3-methylhexane were

synthesized in our Institute, following the methods of *Easton* and *Hargreaves* [8] and of *Levene* and *Marker* [9], respectively. As shown by GLC, both isomers had a purity of better than 99,5%. All products were dried over Sikkon (Fluka AG, Switzerland) for 24 hours, redistilled and outgassed prior to use.

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