

# Thermodynamic Study of the Deuterium Isotope Effect, the Molar Excess Enthalpies of $C_6D_6 + c-C_6H_{12}$ and of $C_6H_6 + c-C_6H_{12}$

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## Abstract

Molar excess enthalpies of  $C_6D_6 + c-C_6H_{12}$  and of  $C_6H_6 + c-C_6H_{12}$  have been measured at 298.15 K; the equimolar values are 818.7 and 797.0 J mol<sup>-1</sup> respectively.

There have been few thermodynamic studies of the deuterium isotope effect in liquid mixtures in which hydrogen bonding takes place between the like and/or unlike molecules. Benjamin and Benson<sup>1</sup> compared the molar excess enthalpies of  $CH_3OH + H_2O$  and  $CH_3OD + D_2O$ , the equimolar values at 298.15 K being -805.0 and -834.0 J mol<sup>-1</sup> respectively. The molar excess enthalpies of  $Me_2CO + CHCl_3$  and  $Me_2CO + CDCl_3$ , systems in which the only significant hydrogen bonding will be that between the unlike molecules, were compared by Morcom and Travers.<sup>2</sup> The equimolar values at 298 K are -1919 and -1972 J mol<sup>-1</sup> respectively. For liquid mixtures involving complex formation it is convenient to divide molar excess enthalpies into 'physical' (non-complexing) and 'chemical' contributions, with the latter due to the complex formation. In comparing corresponding hydrogen and deuterium systems such as those above, it is possible to relate the molar excess enthalpy differences to hydrogen bond changes arising from the deuterium isotope effect if it is assumed that the 'physical' contributions are the same for both systems. We have provided a test of this assumption by measuring the molar excess enthalpies of  $C_6D_6 + c-C_6H_{12}$  and of  $C_6H_6 + c-C_6H_{12}$ , liquid mixtures in which no complex formation is believed to take place.

## Experimental

The calorimeter and its testing have been discussed elsewhere.<sup>3</sup>

Benzene (Merck, for spectroscopy) and cyclohexane (BDH, special for spectroscopy) were dried over freshly activated molecular sieve (Union Carbide, type 13X) and used without further purification. Two samples of hexadeuterobenzene were used without further purification: Merck, for spectroscopy and Koch-Light Laboratories, puriss. For each, a high amplification n.m.r. spectral study gave a purity of 99 mole % with benzene and incompletely deuterated benzenes the only proton-containing impurities. The molar excess enthalpies obtained using the two  $C_6D_6$  samples were in excellent agreement with one another.

<sup>1</sup> Benjamin, L., and Benson, G. C., *J. Phys. Chem.*, 1963, **67**, 858.

<sup>2</sup> Morcom, K. W., and Travers, D. N., *Trans. Faraday Soc.*, 1965, **61**, 230.

<sup>3</sup> Mattingley, B. I., Handa, Y. P., and Fenby, D. V., *J. Chem. Thermodyn.*, in press.

## Results

The molar excess enthalpies  $H_m^E$  at 298.15 K of  $C_6D_6 + c-C_6H_{12}$  and  $C_6H_6 + c-C_6H_{12}$  are given in Table 1. The results were fitted by a least-squares computer program to the equation ( $x$  is mole fraction of  $c-C_6H_{12}$ )

$$H_m^E/J \text{ mol}^{-1} = x(1-x) \sum_{n=0}^m h_n(1-2x)^n$$

It was found that our results for each system could be fitted satisfactorily using two parameters  $h_n$ . These are given in Table 2 together with their standard deviations and the standard deviations  $\sigma$  of the molar excess enthalpies defined by

$$\sigma = [\sum \delta^2 / (N-m)]^{1/2}$$

where  $\delta$  is the deviation of the calculated from the experimental molar excess enthalpy,  $N$  the number of measurements and  $m$  the number of parameters.

Table 1. Molar excess enthalpies  $H_m^E$  at 298.15  
 $x$ , mole fraction of  $c-C_6H_{12}$

$x$	$H_m^E/J \text{ mol}^{-1}$	$x$	$H_m^E/J \text{ mol}^{-1}$	$x$	$H_m^E/J \text{ mol}^{-1}$
$C_6D_6 + c-C_6H_{12}$					
0.2015	546.9	0.4258	809.5	0.6468	737.7
0.2808	679.6	0.5106	813.2	0.7132	651.1
0.3980	789.5	0.5149	814.4	0.8549	394.4
0.4182	801.3	0.5569	809.2		
$C_6H_6 + c-C_6H_{12}$					
0.2218	573.0	0.4403	790.9	0.5339	788.8
0.3179	702.7	0.4631	795.1	0.6423	720.6
0.3214	713.4	0.4634	800.7	0.7336	603.9
0.3864	760.9	0.5282	794.2		

Table 2. Least-squares parameters  $h_n$  and the standard deviations of molar excess enthalpies  $\sigma$

System	$h_0$	$h_1$	$\sigma/J \text{ mol}^{-1}$
$C_6D_6 + c-C_6H_{12}$	$3274.9 \pm 5.2^A$	$178.1 \pm 18.3$	3.8
$C_6H_6 + c-C_6H_{12}$	$3188.0 \pm 4.6$	$197.4 \pm 17.6$	3.4

<sup>A</sup> Standard deviations.

## Discussion

There have been a large number of measurements of the molar excess enthalpy of  $C_6H_6 + c-C_6H_{12}$ . This work has been summarized by Watson *et al.*<sup>4</sup> At 298 K, equimolar  $H_m^E$  values range from 759 to 842 J mol<sup>-1</sup>. Our equimolar value at 298.15 K of 797 J mol<sup>-1</sup> is in good agreement with those of Watson *et al.*<sup>4</sup> (805 J mol<sup>-1</sup>) and Lundberg<sup>5</sup> (799 J mol<sup>-1</sup>).

<sup>4</sup> Watson, A. E. P., McLure, I. A., Bennett, J. E., and Benson, G. C., *J. Phys. Chem.*, 1965, **69**, 2753.

<sup>5</sup> Lundberg, G. W., *J. Chem. Eng. Data*, 1964, **9**, 193.

The difference between the molar excess enthalpies of  $\text{C}_6\text{D}_6$  and  $\text{C}_6\text{H}_6$  with  $\text{c-C}_6\text{H}_{12}$  is small (about  $20 \text{ J mol}^{-1}$  or  $2.5\%$  for the equimolar mixtures) but beyond experimental error (Table 2). Assuming that this difference does not arise from some undetected impurity effect, our results suggest that the 'physical' contributions to the molar excess enthalpies will not be quantitatively the same in corresponding hydrogen and deuterium systems. Consequently, in the calorimetric study of the deuterium isotope effect in liquid mixtures involving hydrogen bonding it will be reasonable to attribute molar excess enthalpy differences predominantly to hydrogen bond changes only if these differences are sufficiently large.

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