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Note

Excess heat capacities of mixtures of benzene with cyclohexane at 298.15 K*

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This note reports determinations of the excess heat capacities of benzene + cyclohexane mixtures. The work was undertaken to provide supplemental data needed to obtain excess isothermal compressibilities from measurements of ultrasonic velocities currently in progress in our laboratory.

MATERIALS AND METHODS

Phillips Petroleum Co. Pure Grade Reagent benzene was used as received, for all of the measurements. Cyclohexane sample A (Fisher Scientific Co. spectranalyzed reagent, also without further purification) was used in the initial work (runs 1 and 2). Confirmatory measurements (run 3) were done with cyclohexane sample B which was derived from A by g.l.c. using a column packed with Chromosorb P (60/80 mesh) containing 18% Apiezon L. Densities of the component liquids at 298.15 K were determined in an Anton Paar densimeter[1]. The value for the benzene was 0.87360 g cm^{-3} (lit.[2] 0.87368 g cm^{-3}). The density of cyclohexane sample A, 0.77253 g cm^{-3}, was significantly lower than the literature value[2], 0.77387 g cm^{-3}; that of sample B, 0.77380 g cm^{-3}, was in closer agreement.

Binary mixtures were prepared by mass and differences of their volumetric heat capacities were determined in a Picker flow calorimeter, following a stepwise procedure as described in an earlier work[3]. A temperature increment of about 1.2 K, centred on 298.15 K, was used for all measurements. The initial reference liquid was benzene and a value of 135.76 J K^{-1} mol^{-1} (taken from ref. 4) was adopted for its heat capacity at 298.15 K. The precision of the final values of the excess heat capacities is believed to be about ± 0.02 J K^{-1} mol^{-1}.

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RESULTS AND DISCUSSION

Three independent runs were carried out at about 5 month time intervals. The measurements are summarized in Table 1, where x_1 denotes the mole fraction of benzene, and each entry for $\Delta(C_p/V)$ represents the increase in the volumetric heat capacity of the particular mixture over the value for the preceding mixture. Molar heat capacities, C_p, were obtained from these results using the densities of the components (stated above) and excess volumes reported previously[5]. The last

TABLE 1

MEASUREMENTS ON BENZENE(1) + CYCLOHEXANE(2) MIXTURES AT 298.15 K.

Experimental results for change of volumetric heat capacity $\Delta(C_p/V)$, heat capacity C_p, and excess heat capacity C_p^E.

x_1	$\Delta(C_p/V)$ $(J\ K^{-1}\ cm^{-3})$	C_p $(J\ K^{-1}\ mol^{-1})$	C_p^E $(J\ K^{-1}\ mol^{-1})$
Run 1			
1	0	135.76[a]	0
0.90203	−0.025974	136.632	−1.152
0.80168	−0.020811	137.878	−1.979
0.70522	−0.015589	139.345	−2.504
0.59538	−0.013405	141.284	−2.835
0.51828	−0.006706	142.826	−2.885
0.39563	−0.006941	145.527	−2.717
0.28730	−0.002384	148.181	−2.301
0.19745	0.000529	150.569	−1.770
0.10759	0.002781	153.134	−1.061
0	0.005977	156.417	0
Run 2			
1	0	135.76[a]	0
0.89112	−0.028784	136.725	−1.283
0.79945	−0.018840	137.869	−2.032
0.69597	−0.016548	139.450	−2.588
0.59594	−0.011827	141.246	−2.857
0.50086	−0.008059	143.160	−2.906
0.39657	−0.005698	145.468	−2.751
0.28833	−0.002412	148.116	−2.337
0.19986	0.000576	150.474	−1.807
0.09808	0.003292	153.392	−0.990
0	0.005686	156.407	0
Run 3			
1	0	135.76[a]	0
0.79530	−0.048607	137.851	−2.052
0.50407	−0.035614	142.926	−2.872
0.19646	−0.007907	150.300	−1.724
0	0.008136	156.001	0

[a] Taken from ref. 4.

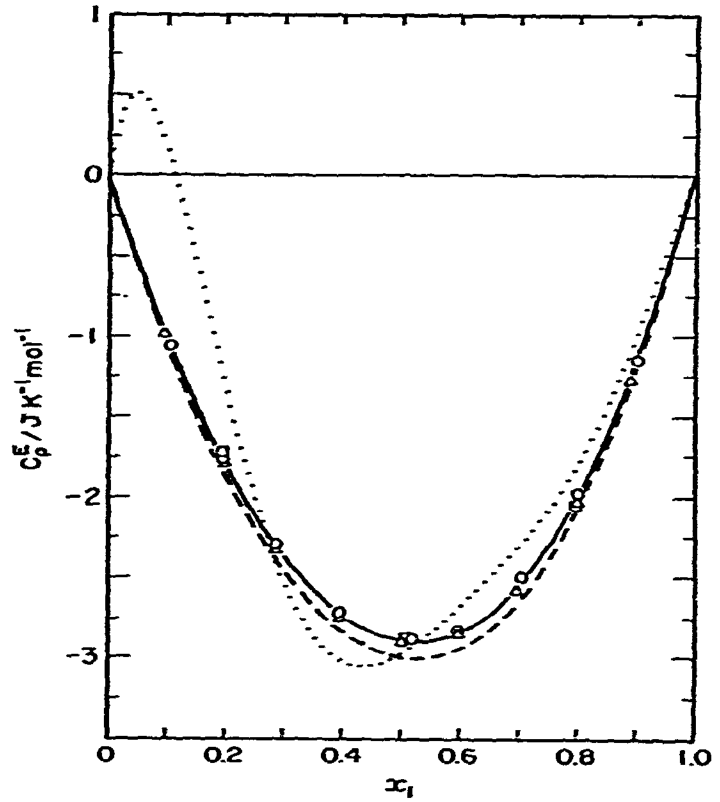

Fig. 1. Excess heat capacities of benzene(1) + cyclohexane(2) mixtures at 298.15 K. Experimental results: ○, run 1; △, run 2; □, run 3. Curves: —— representation of present results by eqn (2); ..... Atwood[6]; – – – $\delta H^E/\delta T$ from Elliott and Wormald[7].

column of Table 1 contains molar excess heat capacities evaluated from the equation

$$C_p^E = C_p - x_1 C_{p1} - x_2 C_{p2} \tag{1}$$

where x_i and C_{pi} are respectively the mole fraction and molar heat capacity of component i. The values of C_p^E are plotted against x_1 in Fig. 1.

It can be seen from Table 1 that Runs 1 and 2 give an average value of 156.412 ± 0.005 J K^{-1} mol^{-1} for the molar heat capacity of cyclohexane sample A. This falls within the range of values reported by other authors (see summary in ref. 4) but is somewhat larger than the result 156.07 J K^{-1} mol^{-1} measured previously in our laboratory[4]. Taken in conjunction with the low density value, we believe this discrepancy must be attributed to the presence of some impurity in sample A. The measurements with sample B support this view. However, it is important to note that, although the C_p values for mixtures formed with sample A are probably slightly high, there is no significant difference between the values of C_p^E obtained from the three runs when the experimental values of C_{p2} are used in calculating the excess.

The combined results of Runs 1 to 3 can be represented by the expression

$$C_p^E/JK^{-1}mol^{-1} = x_1x_2[-11.5735 + 1.1524(x_2 - x_1) - 0.8489(x_2 - x_1)^2] \tag{2}$$

with a standard error of the estimate equal to 0.021 $\mathrm{J\,K^{-1}\,mol^{-1}}$. The solid curve in Fig. 1 was calculated from this equation.

There have been very few previous investigations of the excess heat capacities of benzene + cyclohexane. Atwood[6] measured heat capacities of 17 benzene + cyclohexane mixtures as a function of temperature, in a conventional (static) calorimeter, and obtained C_p^E from the results by using heat capacities of the component liquids taken from the literature. Between 283.15 and 303.15 K he found a region of positive C_p^E at low mole fractions of benzene. The dotted curve in Fig. 1 represents our interpolation of his data to 298.15 K. This curve is subject to a relatively large uncertainty since the uncertainty of the C_p values was estimated[6] to be ± 1%. It is therefore quite possible that the positive values found for C_p^E are spurious.

Most recently, Elliott and Wormald[7] reported a very careful investigation of the excess enthalpies of benzene + cyclohexane between 280.15 K and 393.15 K. Values of $\partial H^E/\partial T$ calculated for 298.15 K from the equation representing their results as a function of temperature and mole fraction are shown as a broken curve in Fig. 1. This is in good agreement with our results.

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REFERENCES

1 O. Kiyohara and G. C. Benson, *Can. J. Chem.*, 51 (1973) 2489.
2 *Selected Values of Properties of Hydrocarbons and Related Compounds*, American Petroleum Institute Research Project 44, Thermodynamics Research Center, Texas A & M University, College Station, TX (loose-leaf data sheets dated October 31, 1950 and October 31, 1952).
3 J.-L. Fortier and G. C. Benson, *J. Chem. Thermodyn.*, 8 (1976) 411.
4 J.-L. Fortier, G. C. Benson and P. Picker, *J. Chem. Thermodyn.*, 8 (1976) 289.
5 R. Tanaka, O. Kiyohara, P. J. D'Arcy and G. C. Benson, *Can. J. Chem.*, 53 (1975) 2262.
6 G. R. Atwood, *Ph. D. Thesis*, University of Pittsburgh, 1958.
7 K. Elliott and C. J. Wormald, *J. Chem. Thermodyn.*, 8 (1976) 881.