mol^{-1}. These values are shown in Table IX. The currently accepted value for $^{\phi}V^{\infty}$ is 17.82 cm^3 mol^{-1} (*12*). Three sets of measurements, 4, 6, and 7, gave sufficient data to be analyzed by using eq 2; these analyses all agreed with the reported value. Our observed value of 17.80 cm^3 mol^{-1} lies well within the reported range of values and is in excellent agreement with the accepted value, considering the lowest molality at which we made measurements was 0.6520 mol kg^{-1}.

Hydrobromic Acid. For hydrobromic acid only one value for $^{\phi}V^{\infty}$ (25 °C), that of Zen (*14*) of 24.2 cm^3 mol^{-1}, is currently available. This value is calculated from density data in ICT (*13*) and differs slightly from our observed value of 25.07 cm^3 mol^{-1}. Our value does, however, show a better agreement with the accepted value for V^{∞}(ion) of 24.71 cm^3 mol^{-1} at 25 °C for the bromide ion reported by Dunn (*18*) and based on $V^{\infty}(H^+) = 0$ cm^3 mol^{-1}.

Hydriodic Acid. No value for the apparent molar volume at infinite dilution of hydriodic acid has been reported. However, measurements of the density of hydriodic acid solutions have been made by Nishikata et al. (*19*) and show a reasonable agreement with our data. These measurements, however, are quoted only to four decimal places in the density and to one decimal place in the concentration. Also no attempt was made to remove any free iodine present in the solutions. Thus, no accurate comparison or analysis by means of eq 2 was possible. Reasonable agreement is seen, however, between our observed values of 36.37 cm^3 mol^{-1} for $^{\phi}V^{\infty}$ and the value of $V^{\infty}(I^-)$ of 36.22 cm^3 mol^{-1} reported by Dunn (*18*) (again based on $V^{\infty}(H^+) = 0$ cm^3 mol^{-1}.

Perchloric Acid. Excellent agreement is seen between our observed value of 44.10 cm^3 mol^{-1} at 25 °C for $^{\phi}V^{\infty}$ and that of 44.12 cm^3 mol^{-1} reported by Wirth and Collier (*20*).

Acknowledgment

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Glossary

A_v	Debye-Hückel slope
M_2	molar mass of solute
m	molality of solute
$^{\phi}V$	apparent molar volume
$^{\phi}V^{\infty}$	apparent molar volume at infinite dilution
$^{\phi}V^{\text{rel}}$	$^{\phi}V$(smoothed) - $^{\phi}V^{\infty}$
ρ	density of solution
ρ_0	density of water

Registry No. HCl, 7647-01-0; HBr, 10035-10-6; HI, 10034-85-2; perchloric acid, 7601-90-3.

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Excess Heat Capacities for Mixtures of Benzene with Cyclopentane, Methylcyclohexane, and Cyclooctane at 298.15 K

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Excess heat capacities were measured by use of a flow calorimeter for binary mixtures of benzene with cyclopentane, methylcyclohexane, and cyclooctane at 298.15 K.

This paper reports excess heat capacities for binary mixtures of benzene with cyclopentane, methylcyclohexane, and cyclooctane at 298.15 K. The measurements were undertaken to provide information about thermodynamic properties of benzene–cycloalkane systems: determinations for the mixture of benzene (1)–cyclohexane (2) which were carried out as a part of the present series have been published previously (*1*).

Experimental Section

The purification of sample liquids were the same as in the previous work (*2*). The mixtures were prepared with specially devised vessels (*3*), and the error in composition x was less than 2×10^{-5}.

The heat capacities C_p were determined relative to that of the reference liquid by using a Picker flow calorimeter (Techneurop Inc., Montreal, Canada). Examinations and the improved operation for this apparatus have been described previously (*1*). The volumetric heat capacities (C_p/V), the heat capacity divided by the volume, were determined from the values of the effective power of heating P dissipated to the flowing liquids, the power change ΔP due to the change of C_p/V in the working cell tube, and the value of C_p/V of the reference liquid. In order to cancel the boundary effects (*1*) a pair of ΔP was taken by reversing the sequence of the liquids to be flowed, and C_p/V was calculated by the equation

$$(C_p/V)_s = (C_p/V)_r\{1 + \Delta P(r \rightarrow s)/P\}^{1/2}/\{1 + \Delta P(s \rightarrow r)/P\}^{1/2} \quad (1)$$

where the suffixes r and s indicate reference and sample liquid, respectively. Liquids were flowed at a rate of 0.013 cm^3·s^{-1} and heated with a temperature increment of 1 K. The liquid temperatures were centered on 298.15 ± 0.01 K. n-Heptane was used as the standard for the determinations: the adopted

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Table I. Heat Capacities Divided by Volume C_p/V, and Molar Heat Capacities C_p for the Component Liquids at 298.15 K, Determined Relative to n-Heptane by Single Reference Method

	$(C_p/V)_{\mathrm{measd}}$/J·K^{-1}·cm^{-3}	C_p/J·K^{-1}·mol^{-1}	
		measd	lit.
benzene	1.51792 ± 0.00004	135.718 ± 0.004	135.61[a]
cyclopentane	1.3374 ± 0.0015	126.74 ± 0.14	126.8[b]
methylcyclohexane	1.4410 ± 0.0007	184.96 ± 0.09	184.6[b]
cyclooctane	1.5980 ± 0.0007	215.53 ± 0.09	215.5[b]
n-heptane	1.52397[c]		224.731[c]

[a] Reference 6. [b] Reference 9. [c] Standard value used for the determinations.

Table II. Volumetric Heat Capacities C_p/V, and Molar Excess Heat Capacities C_p^E of Benzene (1)–Cyclohexane (2) at 298.15 K, Determined Relative to Benzene by Stepwise Reference Method

x_2	(C_p/V)/J·K^{-1}·cm^{-3}	C_p/J·K^{-1}·mol^{-1}	C_p^E/J·K^{-1}·mol^{-1}
	Benzene (1)–Cyclopentane (2)		
0.877 76	1.477 53	133.293	−1.331
0.727 47	1.437 14	130.987	−2.293
0.708 94	1.432 81	130.751	−2.363
0.590 05	1.407 33	129.393	−2.657
0.482 97	1.388 00	128.429	−2.664
0.389 35	1.373 64	127.770	−2.486
0.292 36	1.361 13	127.257	−2.131
0.198 30	1.351 27	126.928	−1.618
0.093 34	1.342 91	126.757	−0.851
0.0	1.337 74	126.773	0.0
	Benzene (1)–Methylcyclohexane (2)		
0.885 55	1.488 65	140.099	−1.258
0.771 35	1.468 15	144.951	−2.033
0.685 29	1.456 80	148.838	−2.387
0.592 92	1.447 71	153.194	−2.582
0.484 61	1.440 42	158.516	−2.596
0.390 83	1.436 62	163.300	−2.433
0.292 70	1.434 84	168.477	−2.091
0.199 51	1.435 07	173.558	−1.602
0.095 66	1.437 33	179.408	−0.869
0.0	1.441 24	184.990	0.0
	Benzene (1)–Cyclooctane (2)		
0.876 55	1.510 58	143.970	−1.602
0.764 71	1.511 03	151.959	−2.542
0.693 82	1.513 75	157.225	−2.936
0.590 76	1.520 12	165.104	−3.283
0.494 73	1.528 24	172.677	−3.376
0.393 61	1.538 96	180.914	−3.212
0.276 80	1.553 70	190.748	−2.703
0.197 74	1.565 15	197.623	−2.140
0.091 61	1.582 12	207.115	−1.120
0.0	1.598 11	215.548	0.0

Table III. Coefficients c_j and Standard Deviations $\sigma(C_p^E)$ of Eq 3 for C_p^E {Benzene (1)–Cycloalkane (2)}

component 2	c_1	c_2	c_3	c_4	$\sigma(C_p^E)$/J·K^{-1}·mol^{-1}
cyclopentane	−10.712	1.340	−0.952	0.339	0.002
methylcyclohexane	−10.422	1.196	−1.298	0.568	0.003
cyclooctane	−13.491	0.281	−1.137	1.069	0.003

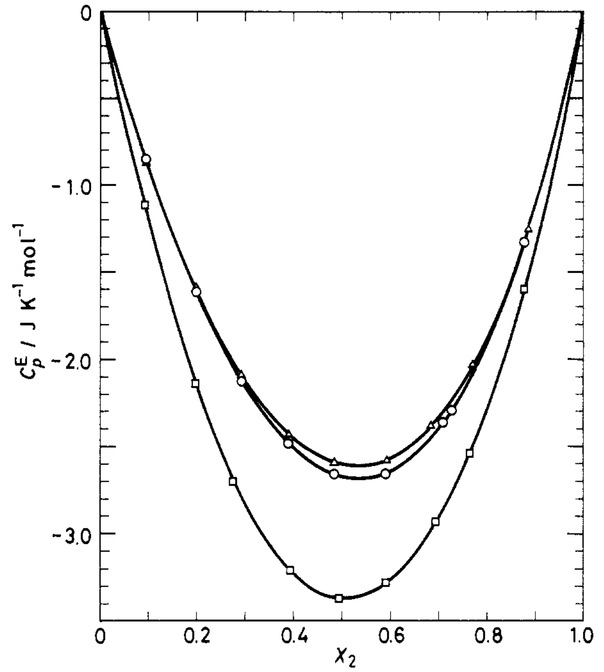

Figure 1. Molar excess heat capacities of benzene (1)–cycloalkane (2) at 298.15 K. Points are experimental results: (△) methylcyclohexane, (○) cyclopentane, (□) cyclooctane. Solid curves represent least-squares representation by eq 3.

values to which were 224.731 J·K^{-1}·mol^{-1} for the molar heat capacity (*4*), 0.679 51 g·cm^{-3} for the density (*5*), and 1.523 97 J·K^{-1}·cm^{-3} for the volumetric heat capacity at 298.15 K.

The heat capacities of the pure components were determined relative to that of n-heptane, and those results are listed in Table I with literature values for comparison. The measurements for the mixtures were carried out by a stepwise reference method starting with benzene as the initial one.

Results and Discussion

The experimental values of C_p/V were converted to molar heat capacity C_p by using the volumetric results obtained previously (*2*). The molar excess heat capacities C_p^E were calculated by the equation

$$C_p^E = C_p - x_1C^*_{p,1} - x_2C^*_{p,2} \tag{2}$$

where x_i is the mole fraction of benzene (1)–cycloalkane (2), and $C^*_{p,i}$ is the molar heat capacity of the pure component i. The values obtained from the stepwise reference method were used for $C^*_{p,2}$ in the above equation. The results for the mixtures are given in Table II.

The main source of systematic error was the uncertainty in evaluating the power loss, and most of the random error was propagated from the fluctuations appearing in the recording signal. Total uncertainties of the measurement except for that originating from the used standard value for n-heptane are indicated in Table I. The agreement between the values of $C^*_{p,2}$ which were obtained by the single reference method and the stepwise reference method is excellent. Those results certify the consistency for the overall process of the measurements. Since the precision is more important to calculate C_p^E, the experimental values are expressed with more digits in Table II.

The smoothing function

$$C_p^E/\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}} = x_1x_2\sum c_j(x_2 - x_1)^{j-1} \tag{3}$$

was fitted to each set of results by the least-squares method. Values of the coefficients c_j and the standard deviations $\sigma(C_p^E)$ are summarized in Table III. The observed values and the smoothed curves are represented graphically in Figure 1.

The values of C_p^E are negative and parabolic in all the mixtures studied. These observations of C_p^E are ordinary for the binary systems in which the component molecules interact only through the dispersion force, and positive excess enthalpies and excess volumes are accompanied. The negative C_p^E for the class of those systems would be attributed to the contribution due to a release from the restriction of molecular motions in the external degree of freedom when nonpolar components are mixed (*7*, *8*).

Glossary

$c_1, c_2, \ldots, c_j$	coefficients in representation of molar excess heat capacity by eq 3
C_p	molar heat capacity
C_p^E	molar excess heat capacity
$C_{p,i}$	molar heat capacity of component i
P	heating power
r	reference liquid
s	sample liquid
V	molar volume
x_i	mole fraction of component i

Greek Letters

σ	calculated standard deviation in eq 1

Subscripts

1	benzene
2	cycloalkanes

Registry No. Benzene, 71-43-2; cyclopentane, 287-92-3; methylcyclohexane, 108-87-2; cyclooctane, 292-64-8.

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Solubility of Hydrogen in 10 Organic Solvents at 298.15, 323.15, and 373.15 K

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The solubility of hydrogen in *n*-hexane, *n*-octane, *n*-decane, toluene, acetonitrile, acetone *N*,*N*-dimethylformamide, tetrahydrofuran, 1,4-dioxane, and 1-methylpyrrolidone-2 was determined with two different measuring methods at 298.15, 323.15, and 373.15 K and, in general, at up to 10 MPa. The error of measurements is estimated to be less than $0.02x_2$, where x_2 is the mole fraction of dissolved hydrogen.

Introduction

A knowledge of the solubility of gases in liquids is important in a wide range of scientific and technological disciplines. Although the repeatability of the methods adopted today for its measurement is frequently 1% or even less, great differences sometimes exist between sets of results obtained by different working groups on the same system at the same temperature and pressure, despite the fact that the methods and apparatus adopted are reliable and the data are consistent. It is evident that, even if the layout and instruments are checked with the utmost care, systematic errors occur that are very difficult to trace and eliminate. Hence, in the light of the current state of the art in instrumentation, it is indeed desirable to improve the precision of measurements, but it would appear more important to obtain consistent sets of results by different methods on a few representative systems than to improve the repeatability or even the reproducibility.

The solubility of hydrogen at near-atmospheric and high pressures in a few organic compounds is known with sufficient accuracy. In the course of our studies, we measured its solubility in 10 organic solvents at 298.15, 323.15, and 373.15 K, and partially at pressures of up to 14 MPa.

Literature data on the solubility of hydrogen in liquids has been critically evaluated by Young (*1*). Table I lists all references that have reported experimental results obtained on the solvents investigated in this paper.

Experimental Section

Apparatus and Procedure. Method I. The apparatus is essentially the same as that described for earlier measurements (*27–29*). Vapor-liquid phase equilibrium is established in a static cell fitted with a stirrer; afterwards, a liquid sample is withdrawn and analyzed by stripping. The solvent is saturated with hydrogen in a 1000-cm^3 high-pressure autoclave with vigorous stirring, and a sample of the saturated liquid is taken through high-pressure capillaries and decompressed to atmospheric pressure at constant temperature. The mass of the sample depends on the solubility of the gas and varies between 30 and 200 g. The hydrogen mole fraction x_2 in the solution is calculated by eq 1,

$$x_2 = (n_2^v + n_2^l)/(n_1^v + n_1^l + n_2^v + n_2^l) \qquad (1)$$

where n_1^v and n_1^l are the moles of solvent and vapor, and n_2^v and n_2^l are the moles of hydrogen in the vapor and liquid phases of the decompressed sample, n_1^v and n_2^l being merely correction terms.

The liquid should be degassed at as low a temperature as possible in order to restrict the correction term n_1^v to a minimum, particularly since the actual vapor density of the solvent is not always known with sufficient accuracy. The decompression apparatus (*27*, *29*) consists of the variable-volume gas buret and the liquid sampler, and care must be taken to ensure that the pressure at which the vapor is flashed is kept as constant as possible during the entire sampling operation. If the pressure changes during sampling, solvent vapor may condense in the gas buret, or the gas sample may not be completely saturated with solvent vapor. As a result, the errors incurred in determining the moles of gas and liquid in the entire