Excess Heat Capacities for Mixture of Benzene with *n*-Heptane at 293.15, 298.15, and 303.15 K

Reiji Tanaka

Department of Chemistry, Faculty of Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka, Japan

Excess heat capacities for the binary mixture of benzene with *n*-heptane were determined at 293.15, 298.15, and 303.15 K by using a flow calorimeter.

This paper reports excess heat capacities for the binary mixture of benzene with *n*-heptane at 293.15, 298.15, and 303.15 K. The measurements were undertaken to provide the knowledge about the change of excess heat capacities with temperature for the mixtures consisted of nonpolar component liquids.

Experimental Section

The source and the purification of the sample liquids were the same as in the previous work (*1*). Densities of those liquids at 293.15, 298.15, and 303.15 K were 0.879 00, 0.873 65, and 0.868 32 g·cm^{-3} for the benzene, and 0.683 71, 0.679 52, and 0.675 27 g·cm^{-3} for the *n*-heptane, respectively. Those values agreed excellently with the previous ones within 4 × 10^{-5} g·cm^{-3}. The mixtures were prepared by mass in specially devised flasks (*2*), and the mole fractions x were determined within the error less than 2 × 10^{-5}.

The volumetric heat capacities $C_{p,m}/V_m$, where $C_{p,m}$ and V_m are the molar heat capacity and the molar volume, respectively, were determined relative to that of the *n*-heptane by using a Picker flow calorimeter (Techneurop Inc., Montreal, Canada). The details of the operational procedure and the test for this calorimeter have been described in the previous report (*3*). Liquids were flowed at a rate of 0.013 cm^3·s^{-1} and heated with a temperature increment of about 1 K. The liquid temperatures were centered on those of measurement within ±0.02 K. The values of $C_{p,m}/V_m$ for the used *n*-heptane were determined relative to the *n*-heptane (Phillips Petroleum Co., 99.98 mol %), to which the same standard values were adopted as the previous work (*3*). All the measurements for the mixtures were carried out by the stepwise reference method starting with the *n*-heptane as the initial one, and the run was made for both directions between the neighboring mixtures.

Results and Discussion

The experimental values of $C_{p,m}/V_m$ were converted to the molar heat capacities $C_{p,m}$ by using the volumetric results obtained previously (*1*). The molar excess heat capacities $C^E_{p,m}$ were calculated by the equation

$$C^E_{p,m} = C_{p,m} - x_1C^*_{p,m,1} - x_2C^*_{p,m,2} \qquad (1)$$

where x_i is the mole fraction of benzene (1)–*n*-heptane (2), and $C^*_{p,m,i}$ is the molar heat capacity of the pure liquid i. The values of $C^*_{p,m,i}$ determined by the present measurement were used for calculating $C^E_{p,m}$. The results of the heat capacities are given in Table I.

Table I. Heat Capacities of Benzene (1)–*n*-Heptane (2)

x_1	$(C_{p,m}/V_m)$/ J·K^{-1}·cm^{-3}	$C_{p,m}$/ J·K^{-1}·mol^{-1}	$C^E_{p,m}$/ J·K^{-1}·mol^{-1}
	293.15 K		
0.0	1.520 47	222.838	0.0
0.091 86	1.511 10	213.727	−1.008
0.196 78	1.501 17	203.487	−1.992
0.294 68	1.492 98	194.123	−2.721
0.385 45	1.486 56	185.618	−3.220
0.486 12	1.481 21	176.414	−3.543
0.583 98	1.478 03	167.693	−3.633
0.690 82	1.477 58	158.458	−3.443
0.777 34	1.480 43	151.249	−3.021
0.881 41	1.489 73	143.011	−2.078
1.0	1.514 95	134.629	0.0
	298.15 K		
0.0	1.523 88	224.721	0.0
0.088 83	1.515 06	215.872	−0.942
0.197 39	1.504 92	205.203	−1.948
0.297 48	1.496 80	195.579	−2.662
0.388 86	1.490 60	186.975	−3.132
0.489 16	1.485 34	177.730	−3.449
0.585 39	1.482 27	169.080	−3.532
0.692 40	1.481 79	159.743	−3.345
0.781 04	1.484 68	152.281	−2.916
0.884 96	1.493 91	143.969	−1.978
1.0	1.517 80	135.707	0.0
	303.15 K		
0.0	1.527 06	226.599	0.0
0.087 95	1.518 54	217.794	−0.901
0.197 23	1.508 70	207.012	−1.864
0.295 28	1.500 88	197.518	−2.547
0.385 68	1.494 74	188.929	−3.012
0.490 51	1.489 26	179.181	−3.340
0.584 45	1.486 19	170.652	−3.428
0.696 82	1.485 64	160.750	−3.232
0.778 39	1.488 15	153.806	−2.846
0.880 06	1.496 53	145.545	−1.971
1.0	1.520 01	136.738	0.0

Table II. Coefficients c_j and Standard Deviations $\sigma(C^E_{p,m})$ of Eq 2 for Benzene (1)–*n*-Hexane (2)

T/K	c_1	c_2	c_3	c_4	c_5	$\sigma(C^E_{p,m})$/ J·K^{-1}·mol^{-1}
293.15	−14.289	3.452	−2.216	2.686	−1.371	0.003
298.15	−13.872	3.405	−2.407	2.538	−0.899	0.007
303.15	−13.437	3.489	−2.089	2.221	−1.145	0.004

The smoothing function

$$C^E_{p,m}/\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}} = x_1x_2\sum c_j(x_2 - x_1)^{j-1} \qquad (2)$$

was fitted to each set of results by the least-squares method. The values of coefficients c_j and standard deviations $\sigma(C^E_{p,m})$ are summarized in Table II. The observed values and the smoothed curves of $C^E_{p,m}$ are represented graphically in Figure 1. The variations of $C^E_{p,m}$ with temperature expressed by

$$\Delta C^E_{p,m}(T) = \{C^E_{p,m}(T) - C^E_{p,m}(\text{calcd, 298.15 K})\} \qquad (3)$$

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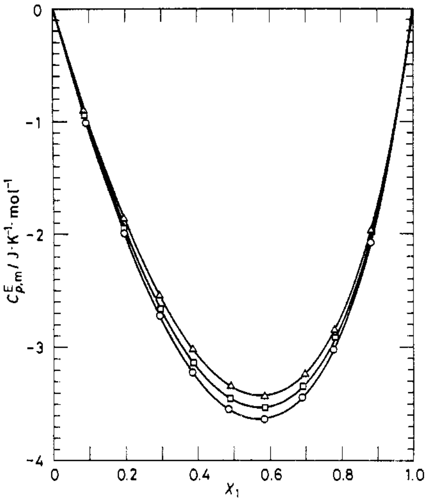

Figure 1. Molar excess heat capacities of benzene (1)–*n*-heptane (2) at (○) 293.15 K, (□) 298.15, (△) 303.15 K. Solid curves are least-squares representations calculated by eq 2.

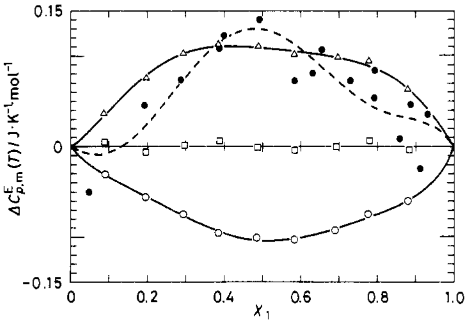

Figure 2. Variations of molar excess heat capacities $\Delta C^E_{p,m}(T)$ expressed by eq 3 for benzene (1)–*n*-heptane (2) at (○) 293.15 K, (□) 298.15 K, and (△) 303.15 K; (●), Karbalai Ghassemi and Grolier at 298.15 K (*4*).

are shown in Figure 2.

Karbalai Ghassemi and Grolier have measured $C^E_{p,m}$ for the preset system at 298.15 K by using the same calorimeter (*4*). Their results are plotted in Figure 2. Their values scatter with the standard deviation larger by about 7 times than the present work. Their smoothed values are less negative at the mole fraction $x_1 > 0.1$ and are closer to the present results at 303.15 K.

The molar excess heat capacities are negative at all the mole fractions with the minimum values of about -3.4 to -3.6 J·K^{-1}·mol^{-1}. The value of $C^E_{p,m}$ at a fixed composition varies linearly with temperature in the whole range of x, and $\partial C^E_{p,m}/\partial T$ is parabolic for x, with a value of 0.02 J·K^{-2}·mol^{-1} at the equimolar composition.

The heat capacities for the nonpolar mixtures containing *n*-alkanes as one component have been investigated from the view point of the structural change in *n*-alkanes (*5*, *6*). The negative $C^E_{p,m}$ and the positive $\partial C^E_{p,m}/\partial T$ for the present system are possibly attributed to an indication of the destruction of orientational order in the *n*-heptane by the benzene, according to the classification by Bhattacharyya and Patterson (*5*).

Glossary

$C_{p,m}$	molar heat capacity, J·K^{-1}·mol^{-1}
$C^E_{p,m}$	molar excess heat capacity, J·K^{-1}·mol^{-1}
c_1, c_2, ..., c_j	coefficients in representations of excess heat capacities by eq 2
T	thermodynamic temperature, K
x_i	mole fraction of component *i*
V_m	molar volume, cm^3·mol^{-1}

Greek Letters

σ	standard deviation calculated from eq 2

Superscripts

•	pure liquid

Subscripts

1	benzene
2	*n*-heptane

Registry No. Benzene, 71-43-2; heptane, 142-82-5.

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Densities of Some Alkali Halides in Water–Acetamide Mixtures at 298.15 K

Marian Woldan

Research and Development Centre for Standard Reference Materials, WZORMAT—Branch in Lodz, 90-132 Lodz, Poland

Densities of solutions of NaCl, NaI, KCl, KBr, and CsI in water–acetamide mixed solvents in the miscibility range at 298.15 K have been measured with the magnetic float densimeter. The apparent molal volumes, Φ_v, of the investigated electrolytes calculated from the experimental data were extrapolated to infinite dilution by means of the Masson equation. The dependence of the partial molal volumes of alkali halides and partial molal volumes of transfer from water to water–acetamide mixtures on the solvent composition is discussed.

Introduction

The study of partial molal volumes of electrolytes in mixed solvents has contributed to our knowledge about the interactions that occur in solution and helped gain a better understanding of electrolyte–nonelectrolyte–water interactions. The results of measurements of the enthalpy of solution of some electrolytes in water–acetamide mixtures (*1*) show that the structure of water–acetamide mixtures changes gradually.

It must be interesting to examine whether comparable information can be obtained from a determination of molal vol-

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