

Thermodynamic Investigation of the Azeotropic Mixture Composed of Water and Benzene

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The molar heat capacity of the azeotropic mixture composed of water and benzene was measured by an adiabatic calorimeter in the temperature range from 80 to 320 K. The phase transitions took place in the temperature range from 265.409 to 275.165 K and 275.165 to 279.399 K. The phase transition temperatures were determined to be 272.945 and 278.339 K, which were corresponding to the solid-liquid phase transitions of water and benzene, respectively. The thermodynamic functions and the excess thermodynamic functions of the mixture relative to standard temperature 298.15 K were derived from the relationships of the thermodynamic functions and the function of the measured heat capacity with respect to temperature.

Keywords azeotropic mixture, water, benzene, heat capacity, adiabatic calorimetry

Introduction

The behavior of azeotropic mixtures is of great interest since they are treated as pure substances, and may be used to test the thermodynamic models.¹ The behavior of the azeotropic mixtures was extensively studied.²⁻⁸ However, the heat capacities of azeotropic mixtures were not studied until recently. Heat capacity is not only a fundamental thermodynamic property, but also a characteristic datum closely related to the structure of substances. The change of the structure of a system can be studied according to the change of the heat capacity of the system. The binary system of water and benzene shows a minimum boiling point azeotrope at 342.4 K with water molar fraction 0.296 at 0.10325 MPa.⁶

Adiabatic calorimeter is the most important and accurate tool for heat capacity determination over a wide range of temperatures. In previous reports,⁹⁻¹¹ the adiabatic calorimeter has been used to measure heat capacity of substance.

In this paper, the molar heat capacity of the azeotropic mixture was measured by an adiabatic calorimeter in temperature range of 80—320 K. The thermodynamic functions of the mixture were derived from the relationships of the thermodynamic functions and the function of the measured heat capacity with respect to temperature.

Experimental

Experimental materials

The benzene used for calorimetric study was purchased from Shenyang Chemical Agent Factory, and its purity was better than 0.998 mass fraction. The water used for preparing the azeotrope was deionized and distilled twice. The azeotropic system consists of 0.296 water molar fraction and 0.704 benzene molar fraction and was prepared by weighing method.

Adiabatic calorimeter

Heat-capacity measurements were carried out in a high-precision automatic adiabatic calorimeter described in detail elsewhere.^{9,12} The temperature increment in a heating period was 2—4 K, and temperature drift was maintained at about 10^{-3} K · min⁻¹ in equilibrium period. All the data were automatically acquired through a Data Acquisition/Switch Unit (Model: 34970A, Agilent, USA) and processed by a computer.

Results and discussion

Molar heat capacities of α -Al₂O₃, water and benzene

To verify the reliability of the adiabatic calorimeter, the molar heat capacities for the reference standard material α -Al₂O₃, water and benzene were measured. The deviations of our experimental results from the values recommended by the National Bureau of Standards¹³ were within $\pm 0.2\%$ in the temperature range of 80—400 K for α -Al₂O₃. The plots of molar heat capaci-

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ties of water and benzene as a function of temperature are given in Figures 1 and 2. In order to compare the results of the heat capacities of water and benzene measured in our laboratory with Refs. 14, 15, the data of heat capacities gained from Refs. 14, 15 are given in Figures 1 and 2 as well. The enthalpy $\Delta_{\text{trans}}H_m$ and entropy $\Delta_{\text{trans}}S_m$ of the phase transition were calculated according to the relationship as follows:¹⁶

$$\Delta_{\text{trans}}H_m = [Q - n \int_{T_1}^{T_{\text{trans}}} C_{p,m(S)} dT - n \int_{T_{\text{trans}}}^{T_2} C_{p,m(L)} dT - \int_{T_1}^{T_2} C_0 dT] / n \quad (1)$$

$$\Delta_{\text{trans}}S_m = \Delta_{\text{trans}}H_m / T_{\text{trans}}$$

where Q is the total amount of heat introduced into the sample cell; n the moles of substance of the sample; T_{trans} phase transition temperature, T_1 below T_{trans} ; T_2

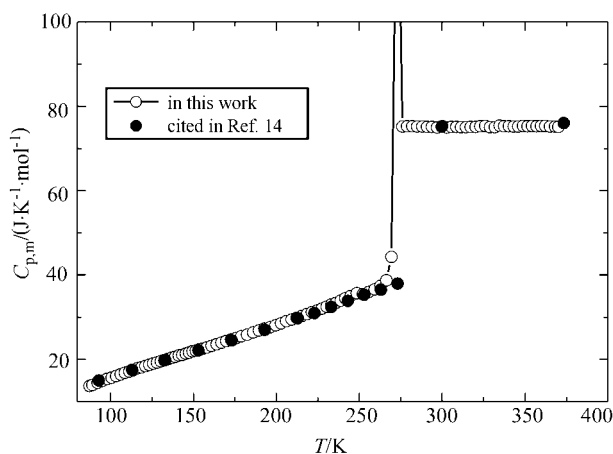


Figure 1 Molar heat capacities of water as a function of temperature.

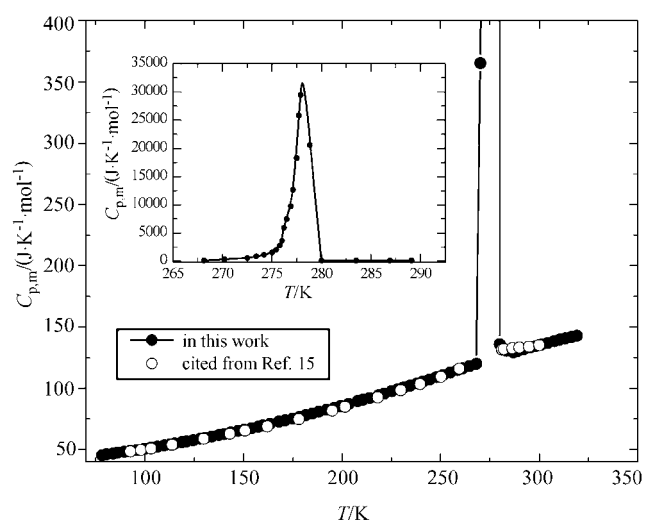


Figure 2 Molar heat capacities of benzene as a function of temperature. Inset shows solid-liquid phase transition of benzene.

above T_{trans} ; $C_{p,m(S)}$, $C_{p,m(L)}$, C_0 the heat capacity in solid and liquid state and heat capacity of empty cell, respectively. The phase transition temperatures and enthalpies of water and benzene are given in Table 1. Figures 1, 2 and Table 1 show that the molar heat capacities, the transition temperature and enthalpy determined in our laboratory are in excellent agreement with the data cited from Refs. 14, 15.

Table 1 Data of the phase transition temperature, enthalpy and entropy of phase transition

	$T_{\text{trans}}/\text{K}$	$\Delta H_{\text{trans}}/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta S_{\text{trans}}/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$
water	273.104	6.005	21.99
	273.15 ¹⁴	6.010 ¹⁴	
benzene	278.325	9.818	35.28
	278.6 ¹⁵	9.820 ¹⁵	
the mixture	272.945	1.661	6.085
	278.339	7.623	27.39

Molar heat capacity of the mixture

The molar heat capacities of the mixture were determined by using the adiabatic calorimeter in the temperature range from 80 to 320 K. The results of the molar heat capacities are listed in Table 2 and shown in Figure 3. No thermal anomaly was observed or no phase transition took place in the temperature range from 80 to 260 K and 290 to 320 K, respectively.

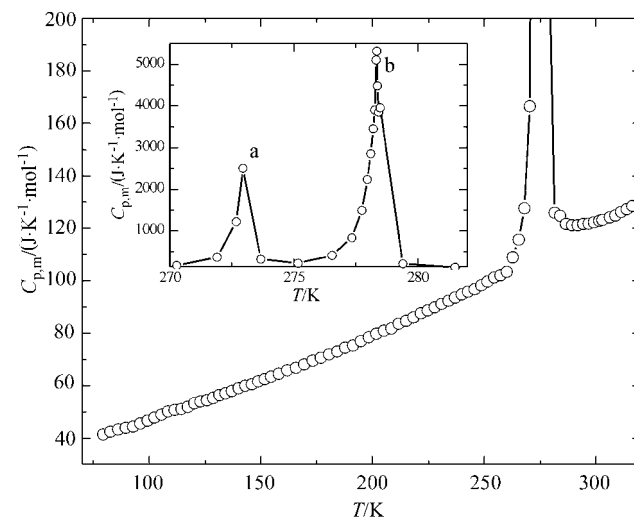


Figure 3 Molar heat capacity of the mixture. Inset shows these phase transitions of the mixture. "a" and "b" denote the solid-liquid phase transition of water and solid-liquid phase transition of benzene, respectively.

The values of molar heat capacities of the mixture were fitted in the following polynomial expressions with least square method

Table 2 Experimental molar heat capacity of the mixture

<i>T</i> /K	$C_{p,m}/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$	<i>T</i> /K	$C_{p,m}/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$	<i>T</i> /K	$C_{p,m}/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$
79.267	41.403	180.460	71.933	272.947	2507.537
82.624	42.418	184.093	73.121	273.669	323.676
86.040	43.358	187.678	74.500	275.165	225.617
89.425	43.973	191.211	75.312	276.535	409.128
92.730	44.401	194.718	77.050	277.334	832.435
95.978	45.582	198.182	78.499	277.740	1491.395
99.161	46.690	201.601	79.798	277.966	2230.929
102.291	47.864	204.993	80.966	278.106	2850.262
105.371	49.004	208.361	81.807	278.199	3453.810
108.407	50.150	211.685	83.596	278.264	3903.054
111.396	50.801	214.979	84.679	278.311	5109.961
114.346	51.140	218.227	85.994	278.339	5320.840
117.251	51.963	221.457	87.540	278.373	4488.655
120.125	53.260	224.630	88.704	278.423	3853.516
122.973	53.988	227.738	89.898	278.485	3960.310
125.778	54.518	230.816	91.126	279.399	206.750
128.565	55.366	233.887	92.358	281.500	125.938
131.325	56.360	236.911	93.601	283.929	124.798
134.046	57.111	239.825	94.772	286.518	121.649
136.914	57.944	242.692	95.904	289.183	121.192
139.928	59.036	245.613	96.803	291.825	121.212
142.901	60.034	248.560	98.255	294.260	121.601
145.863	60.567	251.470	99.689	296.765	121.808
148.762	61.689	254.348	101.310	299.184	122.202
151.659	62.514	257.184	102.051	301.471	122.798
154.515	63.491	259.990	103.412	302.900	123.192
157.886	64.539	262.728	108.967	306.236	124.201
161.759	65.901	265.409	115.661	308.654	124.994
165.585	66.885	267.977	127.644	311.238	126.163
169.366	68.174	270.275	166.519	313.780	127.300
173.101	69.634	271.907	365.318	316.285	128.448
176.809	70.613	272.683	1220.751	319.752	130.407

For 80—260 K

$$C_{p,m} = 4.0459X^2 + 30.768X + 68.372 \quad (3)$$

where, $C_{p,m}/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$ is the molar heat capacity of the azeotropic mixture, T/K thermodynamic temperature, reduced temperature $X = (T/\text{K} - 169.5)/90.5$, and the standard error of this fit is $0.28 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.

For 290—320 K

$$C_{p,m} = 2.0853X^2 + 4.6958X + 123.77 \quad (4)$$

where, reduced temperature $X = (T/\text{K} - 305)/15$, and the standard error of this fit is $0.07 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.

In order to fit well, the temperature T was replaced

by the reduced temperature X ,

$$X = \frac{T - \frac{T_{\max} + T_{\min}}{2}}{\frac{T_{\max} - T_{\min}}{2}} \quad (5)$$

where T_{\max} and T_{\min} denote the maximum and the minimum temperatures in the experiment. Then, $-1 \leq X \leq 1$.

Thermodynamic data of phase transitions

It can be seen from Figure 3 that the molar heat capacity reaches maxima in temperature ranges from

capacity reaches maxima in temperature ranges from 265.409 to 275.165 K and 275.165 to 279.399 K corresponding to "a" and "b", respectively. In order to see clearly the change of the heat capacities, the inset figure was used in Figure 3.

The phase transitions took place in these temperature ranges. The phase transition temperatures were determined to be 272.945 and 278.339 K, which were corresponding to the solid-liquid phase transition of water and solid-liquid phase transition of benzene. Compared with the data in Table 1, the phase transition temperatures of water and benzene in the mixture were almost equal to those of pure water and benzene.

The enthalpies and entropies of the phase transition were calculated according to Eqs. (1) and (2). The data are given in Table 1.

The melting temperatures of the azeotropic mixture are almost equal to those of the corresponding pure samples as listed in Table 1. The enthalpies of the azeotropic mixture is lower than that of corresponding pure water and higher than that of corresponding pure benzene at 272.945 and 278.339 K, respectively. The enthalpies of melting 0.296 mol of pure water and 0.704 mol of pure benzene are calculated to be 1.777 and 6.912 kJ, respectively. Then, the interaction between molecules in the azeotropic mixture is lower than that of pure water and higher than that of pure benzene, respectively. Low-temperature jet beam experiments have shown the existence of benzene-water van der Waals complexes and Suzuki¹⁷ suggested that hydrogen bonding is responsible for the strong interaction. Calculated values¹⁸ of the minimum energy of the benzene-water complex obtained from the thermodynamic measurements are consistent with it. However, Parker¹⁹ suggested that quadrupole-quadrupole coupling is likely to be important. Therefore, the interaction between molecules of benzene and water is complex.

Thermodynamic functions of the mixture

The thermodynamic functions of the mixture in liquid phase were calculated based on the function of the molar heat capacity with respect to thermodynamic temperature and the relationships of the thermodynamic functions. The results are given in Table 3.

Excess thermodynamic functions of the azeotrope

The excess molar heat capacity for the binary system of x water + $(1-x)$ benzene was calculated by the following equation

$$C_{p,m}^E = C_{p,m} - xC_{p,m,1}^* - (1-x)C_{p,m,2}^* \quad (6)$$

where $C_{p,m,1}^*$ and $C_{p,m,2}^*$ are the molar heat capacities for water and benzene, respectively, and $C_{p,m}$ is the molar heat capacity of a mixture at the molar fraction of water x . The values of $C_{p,m}^E$ were calculated in the liquid phase and listed in Table 4.

Table 3 Data of the thermodynamic functions of the mixture in liquid phase

T/K	$C_{p,m}/$ ($J \cdot K^{-1} \cdot mol^{-1}$)	$[H_{(T)} - H_{(298.15 K)}]/$ ($kJ \cdot mol^{-1}$)	$[S_{(T)} - S_{(298.15 K)}]/$ ($J \cdot K^{-1} \cdot mol^{-1}$)
290	121.160	-1.013	-3.445
295	121.566	-0.393	-1.324
300	122.436	0.231	0.774
305	123.770	0.862	2.857
310	125.567	1.500	4.933
315	127.827	2.149	7.009
320	130.551	2.811	9.094
298.15	122.060	0	0

Table 4 Excess thermodynamic functions of the mixture

T/K	$C_{p,m}^E /$ ($J \cdot K^{-1} \cdot mol^{-1}$)	$[H_m^E(T) - H_{298.15 K}^E] /$ ($J \cdot mol^{-1}$)	$[S_m^E(T) - S_{298.15 K}^E] /$ ($J \cdot K^{-1} \cdot mol^{-1}$)
290	6.800	-51.56	-0.1755
295	5.612	-18.39	-0.0620
300	4.944	10.22	0.0342
305	4.796	36.87	0.1223
310	5.167	64.17	0.2111
315	6.058	94.71	0.3088
320	7.469	131.1	0.4233
298.15	5.131	0	0

The function of the excess molar heat capacity of the mixture with respect to the temperature was established as follows,

$$C_{p,m}^E = 2.3387X^2 - 0.3345X + 4.796 \quad (7)$$

where the fitting coefficient $R^2 = 1$, $X = (T/K - 305)/15$.

From Eq. (7), it can be derived that the value of $C_{p,m}^E$ reaches the minimum $4.784 J \cdot K^{-1} \cdot mol^{-1}$ at $T = 303.927 K$. The larger the $C_{p,m}^E$, the more different the interaction between the molecules in the system. The deviation of the solution from the ideal one is the largest at this temperature.

The other excess thermodynamic functions of the mixture such as excess enthalpy and excess entropy were derived from the relationships of the thermodynamic functions and the function of the excess molar heat capacity with respect to thermodynamic temperature. The results were listed in Table 4.

Conclusions

The heat capacity of the azeotrope composed of water and benzene was determined from 80 to 320 K. The temperatures of the phase transitions of the azeotrope were affected little as compared with the pure water and benzene. The value of $C_{p,m}^E$ of the azeotrope reaches

the minimum $4.784 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ at $T=303.927 \text{ K}$.

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