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THERMODYNAMIC PROPERTIES OF THE AZEOTROPIC MIXTURE OF ACETONE AND METHANOL

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The molar heat capacities of the pure samples of acetone and methanol, and the azeotropic mixture composed of acetone and methanol were measured with an adiabatic calorimeter in the temperature range 78–320 K. The solid–solid and solid–liquid phase transitions of the pure samples and the mixture were determined based on the curve of the heat capacity with respect to temperature. The phase transitions took place at 126.16±0.68 and 178.96±1.47 K for the sample of acetone, 157.79±0.95 and 175.93±0.95 K for methanol, which were corresponding to the solid–solid and the solid–liquid phase transitions of the acetone and the methanol, respectively. And the phase transitions occurred at 126.58±0.24, 157.16±0.42, 175.50±0.46 and 179.74±0.89 K corresponding to the solid–solid and the solid–liquid phase transitions of the acetone and the methanol in the mixture, respectively. The thermodynamic functions and the excess thermodynamic functions of the mixture relative to standard temperature 298.15 K were derived based on the relationships of the thermodynamic functions and the function of the measured heat capacity with respect to temperature.

Keywords: *acetone, azeotropic mixture, heat capacity, methanol, thermodynamic property*

Introduction

The behavior of azeotropic mixtures is of great interest as they are treated as pure substances and have been extensively studied [1–7]. We recently investigated the thermodynamic properties of azeotropic systems composed of water and *n*-propanol [8], ethanol and toluene [9] and water and cyclohexane [10]. Acetone and methanol are all extensively applied as reagents or solvents in organic chemistry. However, the molar heat capacities of azeotropic mixture composed of acetone and methanol have not been investigated, as we know. Heat capacity is one of the more valuable thermophysical quantities to be considered when studying pure liquids and liquid mixtures. Accurate heat capacity values are needed in many areas of physics, chemistry, and chemical engineering for establishing energy balances, obtaining entropy and enthalpy values, or studying phase transitions. The heat capacity of the binary system composed of acetone and methanol was determined with an adiabatic calorimeter, and the thermodynamic properties of the azeotropic mixture were derived in this paper. The adiabatic calorimeter has been described and used to measure heat capacities of samples in our previous research [11–14].

The binary system acetone and methanol shows a minimum boiling point azeotrope at 328.85 K with molar composition of acetone and methanol 0.8003, and 0.1997 at 0.10325 MPa, respectively [15].

Experimental

The acetone and methanol used for calorimetric study were purchased from Shenyang Chemical Agent Factory, and their purities were all better than 0.998 mass fractions. The azeotropic system consists of 0.8003 molar fraction of acetone and 0.1997 molar fraction of methanol and prepared by weighing method.

The mean molecular mass of the sample is calculated to be 52.880 g mol^{-1} and 0.5312 mol (28.0926 g) of the sample was used in the experiment.

Heat capacity measurements were carried out in a high-precision automatic adiabatic calorimeter built by Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, described in detail elsewhere [11, 16]. 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.

To verify the reliability of the adiabatic calorimeter, the molar heat capacities for the reference standard material α-Al_2O_3, acetone, cyclohexane and methanol were measured. The deviations of our experimental results from the values recommended by the National Bureau of Standards [17] were within ±0.2% in the temperature range of 80~400 K for α-Al_2O_3.

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Results and discussion

Molar heat capacities of acetone and methanol

The molar heat capacities of the acetone and methanol were determined by using the adiabatic calorimeter in the temperature range from 78 to 320 K. The results of the molar heat capacities are shown in Figs 1 and 2. In order to compare the results of the heat capacities of acetone and methanol measured in our laboratory with [18–21], the data of heat capacities gained from [18–21] are given in Figs 1 and 2 as well. The phase transition temperatures are given in Table 1. The enthalpies of phase transition of the samples were calculated according the Ref. [11] and listed in Table 1 as well. Figures 1 and 2, and Table 1 show that the molar heat capacities, the transition temperature and the enthalpy of the phase transition determined in our laboratory are in excellent agreement with the data cited from [18–22]. The molar fraction purity of acetone and methanol used in the present calorimetric study was determined to be 99.993 and 99.991%, respectively, according to [11].

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 78 to 320 K, too. The results of the molar heat capacities are listed in Table 2 and shown in Fig. 3. No thermal anomaly was observed or no phase transition took place in the temperature range from 186 to 320 K.

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

For 186–320 K

$$C_{\mathrm{p,m}}/R = -2.033(T/100)^3 + 2.5432(T/100)^2 - 6.7536(T/100) + 18.09 \quad (1)$$

where R=8.314 J K^{-1} mol^{-1}, T/K is thermodynamic temperature and the standard error of this fit is 0.024.

Phase transition

$C_{\mathrm{p,m}}$ values reach the maxima in the temperature range of 126.34–126.82, 156.74–157.58, 175.04–175.96 and

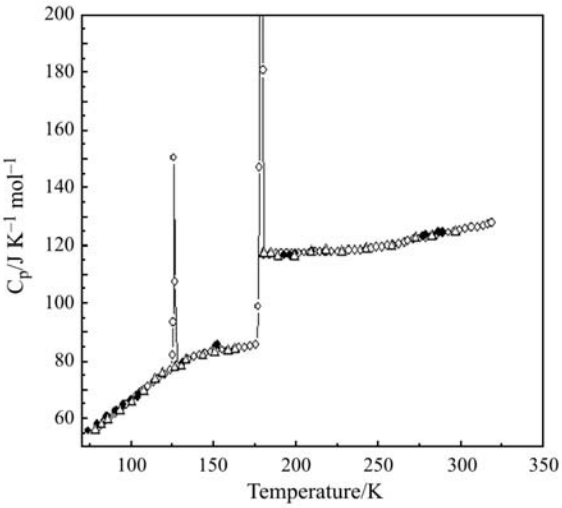

Fig. 1 Experimental molar heat capacities $C_{\mathrm{p,m}}$ of acetone: ○ – this work, ● – [18] and △ – [19]

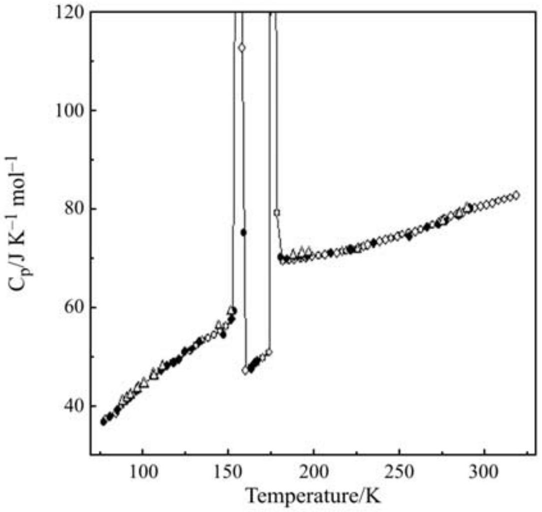

Fig. 2 Experimental molar heat capacities $C_{\mathrm{p,m}}$ of methanol: ○ – this work, ● – [20] and △ – [21]

Table 1 Temperatures of solid–solid phase transition ($T_{\mathrm{s-s}}$) and solid–liquid phase transition ($T_{\mathrm{s-l}}$) of acetone, methanol and the azeotropic mixture

	$T_{\mathrm{s-s}}$/K	$T_{\mathrm{s-l}}$/K	$\Delta H_{\mathrm{s-s}}$/kJ mol^{-1}	$\Delta H_{\mathrm{s-l}}$/kJ mol^{-1}
Acetone	126.16±0.68 126.0±2.0 [22]	178.96±1.47 178.5±0.2 [22]	0.042 0.042±0.010 [22]	5.765 5.77±0.12 [22]
Methanol	157.79±0.95 157.36±0.05 [22]	175.93±0.95 175.62±0.005 [22]	0.647 0.636±0.002 [22]	3.208 3.215±0.008 [22]
Azeotropic mixture	126.58±0.24 157.16±0.42	179.74±0.89 175.50±0.46	0.049* 0.628*	6.014* 3.041*

*$\Delta H_{\mathrm{s-s}}$ and $\Delta H_{\mathrm{s-l}}$ were calculated as the following, $\Delta H_{\mathrm{s-s}}$ and $\Delta H_{\mathrm{s-l}}=\Delta H/(nx)$, where ΔH is corresponding to the solid–solid and solid–liquid phase change enthalpy of the azeotropic mixture and calculated according to [11], respectively, n is the moles of substance of the sample, x is the molar fraction of the composition, such as x values are equal to 0.8003 and 0.1997 for acetone and methanol, respectively

178.83–180.64 K, respectively, as observed in Fig. 3. The pure samples of acetone and methanol exist two kinds of phase transitions, as solid–solid and solid–liquid phase transition, respectively. And the corresponding temperatures and enthalpies of these phase transitions were obtained and listed in Table 1. The phase transition of the azeotropic mixture composed of acetone and methanol is more complicated. The solid–solid and solid–liquid phase transition of acetone and methanol were found in the binary system. And the corresponding temperatures ($T_{s\text{–}s}$ and $T_{s\text{–}l}$) and enthalpies were obtained and given in Table 1, respectively.

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

Excess thermodynamic properties can be used to investigate the interaction between the compositions in the mixture. The excess molar heat capacity for the binary system of x acetone $+y$ methanol was calculated by the following equation

$$C^{\mathrm{E}}_{\mathrm{p,m}} = C_{\mathrm{p,m}} - xC^{*}_{\mathrm{p,m,1}} - yC^{*}_{\mathrm{p,m,2}} \tag{2}$$

where $C^{*}_{\mathrm{p,m,1}}$ and $C^{*}_{\mathrm{p,m,2}}$ are the molar heat capacities for pure acetone and methanol, respectively, and $C_{\mathrm{p,m}}$ is the molar heat capacity of the mixture at the molar

Table 2 Experimental molar heat capacity of the mixture

T/K	$C_{\mathrm{p,m}}/R$	T/K	$C_{\mathrm{p,m}}/R$	T/K	$C_{\mathrm{p,m}}/R$
78.43	6.241	157.58	16.67	221.43	13.45
80.04	6.342	159.93	9.198	224.79	13.49
83.79	6.559	163.44	9.240	228.14	13.53
87.17	6.762	166.94	9.265	231.63	13.55
90.64	6.961	170.22	9.318	234.92	13.60
94.05	7.140	173.81	9.387	238.25	13.67
97.49	7.300	175.04	34.46	241.77	13.76
100.02	7.451	175.28	81.95	245.16	13.82
103.82	7.667	175.39	129.5	248.72	13.90
107.31	7.821	175.44	383.3	252.28	13.97
110.53	7.970	175.63	117.2	255.84	14.03
113.97	8.174	175.96	45.20	259.08	14.12
117.44	8.303	176.43	13.13	262.74	14.20
120.92	8.448	178.54	15.50	266.29	14.27
124.61	8.601	178.83	51.43	269.83	14.34
125.74	8.891	179.02	104.8	273.17	14.47
126.34	29.62	179.27	163.7	276.69	14.60
126.58	50.48	179.42	95.45	280.02	14.68
126.82	24.96	179.82	56.51	283.58	14.77
128.59	8.773	180.64	23.90	287.18	14.90
131.97	8.883	182.83	11.41	290.36	14.98
135.44	9.013	186.39	13.00	293.82	15.07
138.72	9.039	189.94	13.02	297.17	15.18
141.21	9.188	193.27	13.08	300.82	15.27
144.82	9.338	196.84	13.12	304.25	15.34
148.19	9.509	200.05	13.15	307.84	15.47
151.62	9.669	203.71	13.17	311.29	15.59
154.97	9.834	207.29	13.24	314.77	15.69
156.01	10.52	210.94	13.26	318.26	15.77
156.74	21.63	214.38	13.29		
157.06	26.33	217.96	13.35		

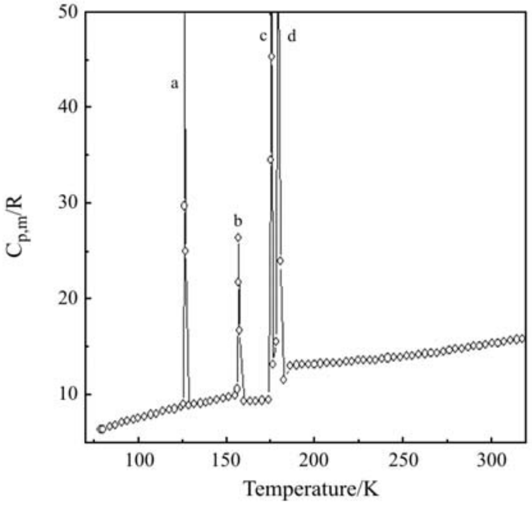

Fig. 3 Molar heat capacity of the mixture. ‘a’ and ‘b’ denote the solid–solid phase transitions of acetone and methanol; ‘c’ and ‘d’ denote the solid–liquid phase transitions of methanol and acetone, respectively

fraction of acetone *x*. The values of $C^{\mathrm{E}}_{\mathrm{p,m}}$ were calculated in the liquid phase and listed in Table 4. Table 4 shows that the $C^{\mathrm{E}}_{\mathrm{p}}$ values are increasing as the experimental temperature increases, and the values are all positive for the system in the temperature range of 190–320 K. Positive $C^{\mathrm{E}}_{\mathrm{p,m}}$ indicates more structure in the solution [23]. This means that the interaction between the molecules in the azeotropic mixture becomes stronger than that in pure samples.

Table 3 Thermodynamic functions of the azeotropic mixture composed of acetone and methanol in the liquid phase

T/K	$C_{\mathrm{p,m}}/R$	$H_{(\mathrm{T})}-H_{(298.15\mathrm{K})}$/ J mol^{-1}	$S_{(\mathrm{T})}-S_{(298.15\mathrm{K})}$/ J K^{-1} mol^{-1}
190	13.05	–125.0	–51.80
200	13.13	–114.2	–46.22
210	13.24	–103.2	–40.87
220	13.38	–92.14	–35.72
230	13.54	–80.95	–30.75
240	13.72	–69.62	–25.93
250	13.93	–58.12	–21.23
260	14.15	–46.45	–16.66
270	14.40	–34.58	–12.18
280	14.66	–22.51	–7.786
290	14.94	–10.20	–3.469
300	15.23	2.339	0.782
310	15.54	15.13	4.976
320	15.86	28.18	9.120
298.15	15.18	0	0

Table 4 Excess thermodynamic functions of the azeotropic mixture

T/K	$C^{\mathrm{E}}_{\mathrm{p,m}}/R$	$H^{\mathrm{E}}_{\mathrm{m,\,(T)}}-H^{\mathrm{E}}_{298.15\,\mathrm{K}}$/ J mol^{-1}	$S^{\mathrm{E}}_{\mathrm{m,\,(T)}}-S^{\mathrm{E}}_{298.15\,\mathrm{K}}$ J K^{-1} mol^{-1}
190	0.102	–5.481	–2.124
200	0.172	–5.368	–2.066
210	0.250	–5.193	–1.980
220	0.337	–4.948	–1.867
230	0.432	–4.628	–1.725
240	0.535	–4.226	–1.554
250	0.644	–3.737	–1.354
260	0.759	–3.155	–1.126
270	0.880	–2.475	–0.869
280	1.005	–1.693	–0.585
290	1.136	–0.805	–0.274
300	1.270	0.193	0.065
310	1.407	1.304	0.429
320	1.547	2.530	0.818
298.15	1.231	0	0

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

$$C^{\mathrm{E}}_{\mathrm{p,m}}/R=-0.0841(T/100)^3+0.9365(T/100)^2 -1.9888(T/100)+1.077 \tag{3}$$

where the standard error of this fit is 0.003.

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 capacities of the azeotrope composed of acetone and methanol and these two pure samples were determined from 78 to 320 K. The temperatures of the solid–solid ansd solid–liquid phase transitions of the azeotrope and the pure samples were obtained. The thermodynamic functions and excess thermodynamic functions of the mixture were calculated based on the curves of molar heat capacity with respect to temperature.

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