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Heat Capacities of Binary Mixtures of Acetic Acid with Acetic Anhydride and Methenamine at Different Temperatures

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Heat capacities of binary mixtures of acetic acid with acetic anhydride and methenamine were measured by a cooling method with a simple calorimeter from (308.15 to 333.15) K at atmospheric pressure with different compositions. The excess molar heat capacities of the binary mixture of acetic acid with acetic anhydride were calculated from the experimental data and were fitted to the Redlich−Kister equation.

Introduction

Acetic acid, acetic anhydride, and methenamine are important materials required in chemical industry, pharmacy, and analytical chemistry. For example, phenol can be recovered from wastewater by phenol acylation with acetic acid or esterification with acetic anhydride.[1] Mixtures of them are also widely used in chemical processes, such as the synthesis of chloroacetic acid and dichloroacetic acid.[2−5] Furthermore, these compounds are fundamental materials for the production of some energy compounds and propellant. Therefore, the determination of their thermodynamic properties is important. Dai et al. have determined the densities and viscosities of these mixtures.[6] Heat capacities of these chemicals and mixtures of them are necessary for the calculation of thermochemical values, such as enthalpies and entropies. The values of heat capacities also provide important fundamental data for the design and optimization of heat exchangers, boiler operations, and many other chemical engineering processes.

However, few data for acetic anhydride and binary mixtures of acetic acid with acetic anhydride and methenamine were available. It is the purpose of this study to measure heat capacities of binary mixtures of acetic acid with acetic anhydride and methenamine from (308.15 to 333.15) K by the cooling method with a simple calorimeter. Excess molar heat capacities (C_p^{E}) over the entire molar fraction range for the binary mixture of acetic acid with acetic anhydride were calculated and fitted to the Redlich−Kister equation.

Experimental Section

Chemicals. All of the chemicals were of analytical reagent grade, and the mass purities were tested by gas chromatography. Acetic acid and acetic anhydride used in this work were obtained from Sinopharm Chemical Reagent Co., Ltd., and the mass fraction purities were higher than 0.995 and 0.985, respectively. Heptane was from Yixing no. 2 Chemical Reagent Co., Ltd., the mass fraction purity of which was higher than 0.985. Methenamine of mass fraction purity higher than 0.990 was from Zhejiang Sanying Chemical Reagent Co., Ltd. It was dried in vacuum at 40 °C for 24 h and stored in a desiccator.

Apparatus: Principle of Operation. By the cooling method, the heat capacity is determined by measuring the cooling rate ($\mathrm{d}T/\mathrm{d}t$) of the tested system.[7] According to the Newton cooling law, the cooling rate and difference in temperature between the tested system and surroundings have a relationship as follows:

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{K}{C_{\mathrm{S}}}(T - \theta) \tag{1}$$

where K is the cooling constant, T and θ are the temperatures of the tested system and surroundings, and C_{S} is heat capacity of the system, which contains the liquid, the vessel liquid, and the immersed section of thermometer used to measure the temperature. If the fluctuation of θ is small enough to take θ as constant, an integral equation can be obtained:

$$\ln(T - \theta) = \frac{K}{C_{\mathrm{S}}}t + b \tag{2}$$

A standard liquid with known heat capacities and the test liquid are measured in the same vessel, respectively. By constructing a plot of $\ln(T - \theta)$ against t, a slope coefficient can be obtained. Then the heat capacity can be calculated as follows:

$$C_{p\mathrm{x}} = \frac{1}{m_{\mathrm{x}}}\left[\frac{S_1}{S_2}(m_0C_{p0} + m_1C_1 + \delta) - m_1C_1 - \delta\right] \tag{3}$$

where m_0, C_{p0}, m_{x}, and $C_{p\mathrm{x}}$ are the masses and heat capacities of the standard liquid and the test liquid, m_1 and C_1 are the mass and heat capacity per unit mass of the vessel, δ is the heat capacity of the immersed section of thermometer, and S_1 and S_2 are the slope coefficients of plots of $\ln(T - \theta)$ against t for the standard liquid and the test liquid.

Apparatus: Construction and Operation. The simple calorimeter used in this work was modified from a FD-LCD-A calorimeter which was manufactured by Shanghai Fudan Tianxin Scientific and Educational Instruments Co., Ltd. The calorimeter consisted of two vessels and exact thermometers. The outer vessel was a cylindrical container made of Plexiglas. It was about 20 cm tall, and its diameter was 29 cm. The outer vessel with isothermal water circulating in it could be taken as the surroundings of the experiment with constant temperature (with fluctuation of 0.05 K). The inner vessel of the original apparatus was made of copper which would be corroded by acid solutions. Therefore, a double-jacketed glass vessel with a piece of

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Table 1. Comparison of Experimental and Literature Values of Heat Capacities C_p for Pure Compounds

T/K	C_p/J·mol^{-1}·K^{-1} exp.	C_p/J·mol^{-1}·K^{-1} lit.	deviation
	n-Heptane		
313.15	230.37	230.68[19]	0.13 %
333.15	240.03	239.50[19]	0.22 %
	Acetic Acid		
313.15	135.50	135.2[19]	0.22 %
		128.33[20]	5.29 %
333.15	137.21	137.1[19]	0.08 %
		136.67[20]	0.39 %
	Acetic Anhydride		
313.15	200.73	200.0[19]	0.36 %
333.15	204.34	203.9[20]	0.22 %

adiabatic Teflon padding at the bottom was used to replace the copper vessel. The inner vessel was supported by an adiabatic pedestal fixed at the bottom of the outer vessel. The inner chamber of the inner vessel was 5 cm tall, and its diameter was 2.5 cm. To decrease heat loss into the atmosphere, both of the vessels were sealed with Teflon covers. Temperatures of tested liquid and water area were determined by exact thermometers with an uncertainty of ± 0.05 K. This apparatus was applicable to liquids, especially those that might corrupt general metals.

At the initial stage of the experiment, the temperature of the water area in the outer vessel should be set 10 K below determining temperature. The tested liquid was heated to a temperature that was higher than the determining temperature, and then about 10 mL of it was poured into the inner vessel as fast as possible. After the inner vessel was placed on the pedestal, the temperature of the tested liquid decreased steadily. Because the volume of water in the outer vessel was much bigger than the tested liquid, the temperature of the water area would be almost unchanged during the experiment. When the temperature of the tested liquid was 5 K higher than the determining temperature, the first group of temperatures of the tested liquid and water area were noted, and 20 groups of temperatures were needed with the interval of 1 min.

In this work, all mixtures for measurement were prepared by weighing on an analytical balance with an accuracy of ± 0.0001 g. Conversion to molar quantities was based on the IUPAC relative atomic mass table.[8] Heat capacities of distilled, deionized water, which was used as the standard liquid, were obtained from the Handbook of Chemistry.[9] Heat capacities of the glass used for the inner vessel were supplied by the Analyzing and Testing Center, Zhejiang University. The heat capacity of the immersed section of the thermometer was calculated as follows:[10]

$$\delta = 0.46V \tag{4}$$

where V was the volume of the immersed section of the thermometer.

To validate the apparatus, heat capacities of heptane were measured at (313.15 and 333.15) K. A comparison of experimental values and reported data is presented in Table 1.

Results and Discussion

1. Binary Mixture of Acetic Acid with Acetic Anhydride. Heat capacities of the binary mixture of acetic acid with acetic anhydride have been measured over the whole composition range. A comparison of measured and reported data for pure acetic acid and acetic anhydride is shown in Table 1.

Heat capacities obtained in this work for the binary mixture of acetic acid with acetic anhydride are represented in Table 2.

Table 2. Heat Capacities C_p and Excess Molar Heat Capacities C_p^E for the Binary Mixture of Acetic Anhydride (1) with Acetic Acid (2) at T = (308.15 to 333.15) K over the Entire Molar Fraction of Acetic Anhydride

x_1	C_p/J·mol^{-1}·K^{-1}	C_p^E/J·mol^{-1}·K^{-1}	x_1	C_p/J·mol^{-1}·K^{-1}	C_p^E/J·mol^{-1}·K^{-1}
		T = 308.15 K			
0.0000	134.93	0.0000	0.4687	167.30	1.9246
0.0613	139.18	0.2724	0.5785	174.47	1.9659
0.1282	144.25	1.0012	0.7017	182.33	1.8208
0.2013	149.40	1.4000	0.8411	190.56	1.0028
0.2817	154.90	1.6738	1.0000	199.93	0.0000
0.3704	160.85	1.8652			
		T = 313.15 K			
0.0000	135.50	0.0000	0.4687	168.08	2.0059
0.0613	139.82	0.3237	0.5785	175.28	2.0451
0.1282	144.91	1.0496	0.7017	183.12	1.8530
0.2013	150.09	1.4589	0.8411	191.49	1.1249
0.2817	155.59	1.7155	1.0000	200.73	0.0000
0.3704	161.58	1.9181			
		T = 318.15 K			
0.0000	136.00	0.0000	0.4687	168.76	2.0219
0.0613	140.51	0.4991	0.5785	176.03	2.0958
0.1282	145.46	1.0562	0.7017	183.96	1.9426
0.2013	150.76	1.5617	0.8411	192.33	1.1726
0.2817	156.27	1.8018	1.0000	201.58	0.0000
0.3704	162.26	1.9710			
		T = 323.15 K			
0.0000	136.35	0.0000	0.4687	169.45	2.0826
0.0613	141.12	0.7096	0.5785	176.76	2.1313
0.1282	145.90	1.0706	0.7017	184.78	1.9946
0.2013	151.31	1.6357	0.8411	193.23	1.2242
0.2817	156.85	1.8550	1.0000	202.53	0.0000
0.3704	162.89	2.0239			
		T = 328.15 K			
0.0000	136.87	0.0000	0.4687	170.33	2.1463
0.0613	141.75	0.7816	0.5785	177.68	2.1607
0.1282	146.52	1.0836	0.7017	185.79	2.0483
0.2013	152.03	1.7076	0.8411	194.35	1.2861
0.2817	157.59	1.9052	1.0000	203.67	0.0000
0.3704	163.68	2.0654			
		T = 333.15 K			
0.0000	137.21	0.0000	0.4687	170.89	2.2182
0.0613	142.23	0.9069	0.5785	178.31	2.2620
0.1282	147.13	1.3127	0.7017	186.44	2.1200
0.2013	152.51	1.7899	0.8411	195.00	1.3244
0.2817	158.10	1.9844	1.0000	204.34	0.0000
0.3704	164.24	2.1638			

The values of C_p increased as temperature and the molar fraction of acetic anhydride increased.

The plots of C_p dependent on the molar fraction of acetic anhydride are shown in Figure 1. Because they show linear behavior, a polynomial function[11] as follows is used to correlate the experimental data:

$$C_p = A + Bx \tag{5}$$

where x is the molar fraction of acetic anhydride and A and B are temperature-dependent parameters which are correlated by eqs 6 and 7:

$$A = a_0 + a_1T \tag{6}$$

$$B = b_0 + b_1T \tag{7}$$

where the parameters a_i and b_i are obtained by correlating the values of A and B with temperatures by a least-squares method. The determined parameters a_i and b_i are presented in Table 3.

The root-mean-square deviation (rmsd) is defined as follows:[12]

$$\text{rmsd} = \left[\frac{1}{N}\sum_{i=1}^{N}\left(\frac{C_{p\text{exp}} - C_{p\text{cal}}}{C_{p\text{exp}}}\right)_i^2\right]^{(1/2)} \tag{8}$$

where N is the number of experimental data points. The rmsd of the mixtures of acetic acid with acetic anhydride is 0.46 %.

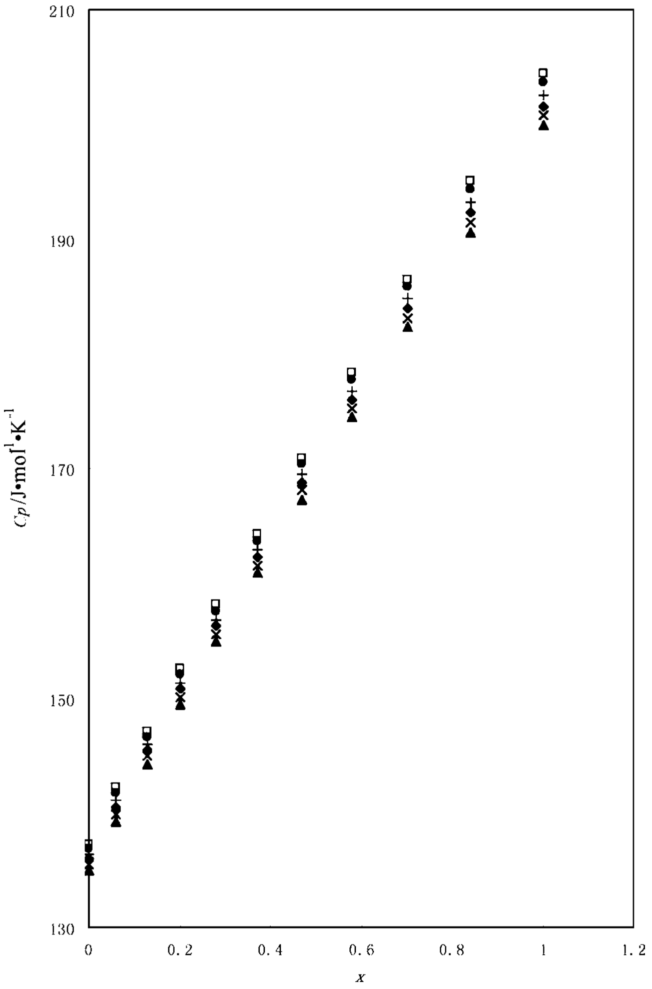

Figure 1. Heat capacities C_p vs the molar fraction of acetic anhydride x for the binary mixture of acetic acid with acetic anhydride. ▲, 308.15 K; ×, 313.15 K; ◆, 318.15 K; +, 323.15 K; ●, 328.15 K; ■, 333.15 K.

Table 3. Coefficients of Equations 6 and 7 for Heat Capacities of the Binary Mixture of Acetic Acid with Acetic Anhydride at T = (308.15 to 333.15) K over the Entire Composition Range

a_0	a_1	b_0	b_1
103.66	0.11	39.06	0.09

Excess molar heat capacity C_p^E which has shown to be a useful indicator of changes in liquid order during the mixing process is calculated using an equation as follows:[13−16]

$$C_p^E = C_P - (x_1 C_{p1} + x_2 C_{p2}) \tag{9}$$

where $C_{p,\,i}$ is the molar heat capacity of the pure component. The calculated C_p^E values from eq 9 for the binary mixture of acetic acid with acetic anhydride are also presented in Table 2. The values of C_p^E also increased as the temperature increased. As illustrated in Table 2, all of the excess molar heat capacities C_p^E of the mixture investigated here had positive values. In general, the values of C_p^E indicated the degree of nonideality of the mixture. The smaller the value of C_p^E is, the closer the mixture approached an ideal one.

Excess molar heat capacities C_p^E of the binary mixture of acetic acid with acetic anhydride are fitted to the Redlich−Kister equation as follows:

$$C_p^E = x_1 x_2 \sum_{i=1}^{n} A_i (x_1 - x_2)^{i-1} \tag{10}$$

The temperature-dependent parameter A_i is correlated by eq 11:

$$A_i = \sum_{j=1}^{n} a_{i,j} T^j \tag{11}$$

where the parameters $a_{i,j}$ are determined from the C_p^E calculated with eq 9 by the experimental values of C_p. The calculated values of C_p^E are then obtained from eqs 10 and 11. Since the binary mixture of acetic acid with acetic anhydride is not strongly nonideal, in this study, a three-term Redlich−Kister equation is used in the calculation.

The determined parameters $a_{i,j}$ and the average absolute percentage deviations (AADs) for C_p^E are presented in Table 4. A comparison of the calculated values and experimental data is shown in Figure 2.

2. Binary Mixture of Acetic Acid with Methenamine. Heat capacities of the binary mixture of acetic acid with methenamine have been measured at T = (308.15 to 333.15) K with the molar fraction range of x_1 = (0.0220 to 0.2221). The values of C_p increased as the temperature and molar fraction of methenamine increased. The experimental data listed in Table 5 are correlated by a polynomial function as follows:[17,18]

$$C_p = A + BT \tag{12}$$

where A and B are composition-dependent parameters correlated by eqs 13 and 14:

$$A = a_0 + a_1 x + a_2 x^2 \tag{13}$$

$$B = b_0 + b_1 x + b_2 x^2 \tag{14}$$

where the parameters a_i and b_i are obtained by correlating the values of A with molar fractions of methenamine by a least-squares method. The determined parameters a_i and b_i are presented in Table 6.

A comparison of calculated values and experimental data is shown in Figure 3. The rmsd is 1.47 %.

Table 4. Coefficients of the Redlich−Kister Equation and AAD for C_p^E of the Binary Mixture of Acetic Acid with Acetic Anhydride

i	$a_{i,0}$	$a_{i,1}$	$a_{i,2}$	data points	100 AAD[a]
1	14.5317	−0.0719	0.0002	66	5.68
2	−163.7180	1.0367	−0.0016		
3	−14.6243	−0.0739	0.0004		

[a] AAD = $(1/N)\sum_{i=1}^{N} |(C_{p,i}^{E,\mathrm{exp}} - C_{p,i}^{E,\mathrm{calc}})/C_{p,i}^{E,\mathrm{exp}}|$; N = number of data points.

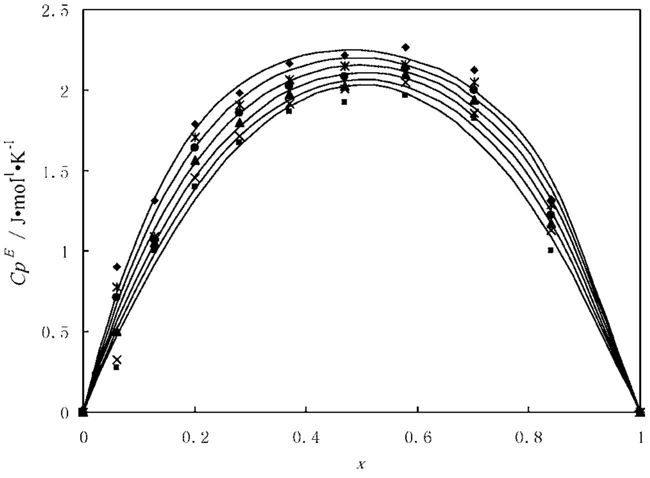

Figure 2. Excess molar heat capacities C_p^E vs the molar fraction of acetic anhydride x for the binary mixture of acetic acid with acetic anhydride. ■, 308.15 K; ×, 313.15 K; ▲, 318.15 K; ●, 323.15 K; ∗, 328.15 K; ◆, 333.15 K; lines, values of C_p^E calculated by eq 10.

Table 5. Heat Capacities C_p for the Binary Mixture of Methenamine (1) with Acetic Acid (2) at $T = (308.15 \text{ to } 333.15)$ K with the Molar Fraction $x_1 = (0.0220 \text{ to } 0.2221)$

T/K	C_p/J·mol^{-1}·K^{-1}	T/K	C_p/J·mol^{-1}·K^{-1}
	$x_1 = 0.0220$		
308.15	137.35	323.15	152.45
313.15	142.53	328.15	157.24
318.15	147.51	333.15	161.64
	$x_1 = 0.0454$		
308.15	144.80	323.15	160.18
313.15	150.32	328.15	165.08
318.15	155.25	333.15	169.05
	$x_1 = 0.0703$		
308.15	151.94	323.15	166.78
313.15	157.16	328.15	172.00
318.15	162.14	333.15	176.96
	$x_1 = 0.0967$		
308.15	159.76	323.15	175.70
313.15	165.58	328.15	180.88
318.15	170.38	333.15	185.28
	$x_1 = 0.1249$		
308.15	170.64	323.15	186.63
313.15	176.29	328.15	191.96
318.15	181.92	333.15	197.37
	$x_1 = 0.1551$		
308.15	180.97	323.15	198.28
313.15	187.61	328.15	204.18
318.15	193.63	333.15	209.36
	$x_1 = 0.1873$		
308.15	191.09	323.15	209.59
313.15	198.06	328.15	214.96
318.15	203.66	333.15	220.93
	$x_1 = 0.2221$		
308.15	203.69	323.15	222.76
313.15	210.89	328.15	222.35
318.15	216.63	333.15	235.17

Table 6. Coefficients of Equation 13 for Heat Capacities of the Binary Mixture of Methenamine with Acetic Acid at $T = (308.15 \text{ to } 333.15)$ K of Molar Fraction $w_1 = (0.0220 \text{ to } 0.2221)$

a_0	a_1	a_2	b_0	b_1	b_2
0.95	0.60	3.30	−167.03	237.13	−1364.03

Conclusion

Heat capacities C_p of the binary mixture of acetic acid with acetic anhydride have been measured at different temperatures and atmospheric pressure over the whole composition range. The excess molar heat capacities C_p^E were calculated from the experimental data and were fitted to the Redlich−Kister equation. The values of C_p increased as the temperature increased and decreased as the molar fraction of acetic anhydride increased, and the rmsd of these mixtures was 0.46 %. Heat capacities of the binary mixture of acetic acid with methenamine have been measured with the molar fraction range of $x_1 = (0.0220 \text{ to } 0.2221)$. The values of C_p increased as the temperature and molar fraction of methenamine increased, and the rmsd is 1.47 %.

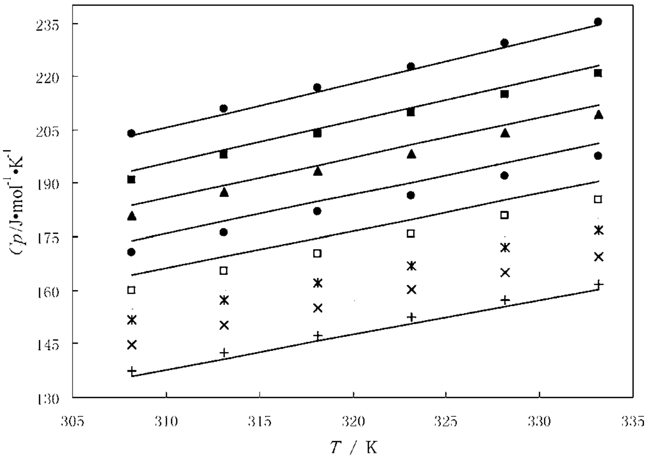

Figure 3. Heat capacities C_p vs temperature T for the binary mixture of acetic acid with methenamine. +, $x = 0.0220$; ×, $x = 0.0454$; ∗, $x = 0.0703$; □, $x = 0.0967$; ●, $x = 0.1249$; ▲, $x = 0.1551$; ■, $x = 0.1873$; ◆, $x = 0.2221$; lines, values of C_p calculated by eq 12.

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