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# THERMODYNAMIC PROPERTIES OF THE BINARY MIXTURE OF WATER AND *n*-BUTANOL

*Z. Nan*[1]* *and Z.-C. Tan*[2]

[1]Department of Chemistry, Qufu Normal University, Qufu Shandong 273165, P. R. China
[2]Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China

The molar heat capacities of the binary mixture composed of water and *n*-butanol were measured with an adiabatic calorimeter in the temperature range 78–320 K. The functions of the heat capacity with respect to thermodynamic temperature were established. A glass transition, solid–solid phase transition and solid–liquid phase transition were observed. The corresponding enthalpy and entropy of the solid–liquid phase transition were calculated, respectively. The thermodynamic functions relative to a temperature of 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:*** *adiabatic calorimetry, heat capacity, low temperature, n-butanol, water*

## Introduction

In previous reports, the heat capacities of azeotropic systems composed of water+ethanol and water+*n*-propanol have been investigated [1, 2]. Heat capacity is one of the more valuable thermophysical quantities to be considered when studying pure liquids and liquid mixtures. Accurate 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. Moreover, ascertainment of the heat capacity of liquids as a function of temperature is a source of important information concerning their molecular structure and is essential for checking the efficiency of estimation models used in industry [3]. The adiabatic calorimeter is the most important and accurate tool for heat capacity determination over a wide range of temperatures. An adiabatic calorimeter has been described and used to measure heat capacities of samples in our previous research [4–9]. Moving along these lines, the heat capacity of the binary mixture composed of water and *n*-butanol was studied.

In a series of alkane-mono-ols in increasing order of the number of carbon atoms, *n*-butanol (abbreviated as 1B hereinafter) is the first that exhibits a limited solubility in water [10]. At about $x_{1B}$=0.018 and 298.15 K phase separation occurs, where $x_{1B}$ is the mole fraction of 1B. The equilibrium composition of the 1B-rich phase is $x_{1B}$=0.49. Thermodynamic properties have been investigated for the systems composed of 1B and $H_2O$ at 298.15 K [11, 12].

In this study, the molar heat capacity of the binary mixture composed of 1B and $H_2O$ was measured by an adiabatic calorimeter in temperature range of 78–320 K. The thermodynamic functions of the binary mixture were derived based on the relationships of the thermodynamic functions and the function of the measured heat capacity with respect to temperature.

## Experimental

The *n*-butanol used for calorimetric study was purchased from Shenyang Chemical Agent Factory, and its purity was better than 99.8 mass%. The principal impurities were carbonyl compound and unsaturated compound, which contents were all smaller than 0.02%. The water used for preparing the binary mixture was deionized and distilled twice. The investigated system is composed of $x_{1B}$=0.0263, 0.311 and 0.686, respectively.

The mass of the binary mixture used for heat-capacity measurements was 29.6802, 29.8419 and 29.7322 g for the systems composed of $x_{1B}$=0.0263, 0.311 and 0.686, respectively.

Heat capacity measurements were carried out in a high-precision automatic adiabatic calorimeter described in detail elsewhere [2, 4]. The principle of the calorimeter is based on the Nernst stepwise heating method. All the data were automatically picked up through a Data Acquisition/Switch Unit (Model: 34970A, Aglient, USA) and processed by a computer.

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* Author for correspondence: zdnan65@163.com

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*Akadémiai Kiadó, Budapest, Hungary*
*Springer, Dordrecht, The Netherlands*

To verify the reliability of the adiabatic calorimeter, the molar heat capacities for the reference standard material $\alpha$-$Al_2O_3$ , water and 1B were measured. The deviations of our experimental results from the values were within ±0.2% in a temperature range of (80 to 400) K for $\alpha$-$Al_2O_3$ [13]. The molar heat capacities of water were given in reference [2]. Plots of molar heat capacities of 1B as a function of temperature are given in Fig. 1. In order to compare the results of the molar heat capacities of 1B measured in our laboratory with references [14, 15], the data of heat capacities gained from the references are given in Fig. 1 as well. The enthalpy $\Delta_{trs}H_m$ and entropy $\Delta_{trs}S_m$ of the phase transition were calculated according to the relationship given by,

$$\Delta_{trs}H_m = \frac{Q - n\int_{T_1}^{T_{trs}} C_{p,m(S)}\,dT - n\int_{T_{trs}}^{T_2} C_{p,m(L)}\,dT - \int_{T_1}^{T_2} C_0\,dT}{n} \qquad (1)$$

and

$$\Delta_{trs}S_m = \frac{\Delta_{trs}H_m}{T_{trs}} \qquad (2)$$

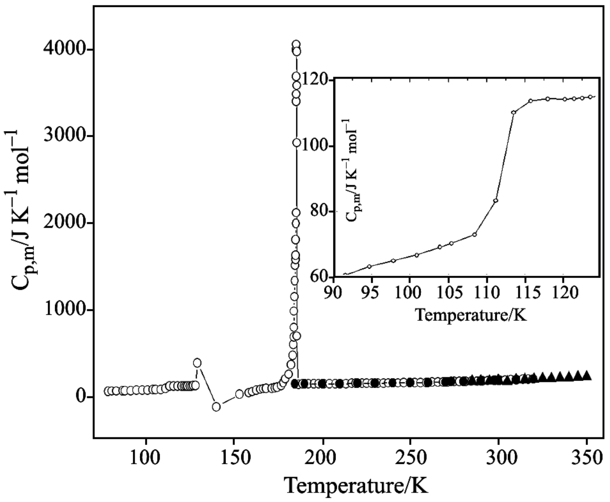

**Fig. 1** Molar heat capacities of *n*–butanol: ○ – this work, ▲ – [15], ● – [14]. Inset 1 shows the glass-transition of *n*–butanol

where $Q$ is the total mount of heat introduced into the sample cell; $n$ the amount of substance of the sample; $T_{trs}$ phase transition temperature, $T_1$ slightly below $T_{trs}$; $T_2$ slightly above $T_{trs}$; $C_{p,m(S)}$, $C_{p,m(L)}$, $C_0$ the heat capacity in solid and liquid state and heat capacity of empty cell, respectively. The phase transition temperatures, enthalpies and entropies for 1B are given in Table 1.

Figure 1 and Table 1 show that the molar heat capacities, the phase transition temperature and enthalpy determined in our laboratory are in excellent agreement with the data cited from the references.

## Result and discussion

### *Molar heat capacity of the binary mixture*

The molar heat capacities of the binary mixtures composed of $x_{1B}$=0.0263, 0.311 and 0.686, were determined by using the adiabatic calorimeter in the temperature range of 78–320 K. The results of the molar heat capacities are listed in Table 2 and shown in Fig. 2. No thermal anomaly was observed or no phase transition took place in the temperature range 185–260 K and 275–320 K, respectively.

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

$$C_{p,m}/R = \sum_{i=0} a_i\,(T/100)^i \qquad (3)$$

where $C_{p,m}$/J mol$^{-1}$ K$^{-1}$ is the molar heat capacity of the mixture, $T$/K thermodynamic temperature, $R$=8.314 J mol$^{-1}$ K$^{-1}$. The fitting results were given in Table 3.

### *Thermodynamic data of glass and phase transitions*

It can be seen from Figs 1 and 2a, and Table 2, that the heat capacity jump was found in the temperature range 105–115 K for the pure 1B and the binary mixtures composed of $x_{1B}$=0.311 and 0.686, respectively. The heat capacity changes clearly before and after glass transition temperature [16]. Then, the glass tran-

**Table 1** Data of the transition temperature, enthalpy and entropy for the glass transition, solid–solid and solid–liquid phase transition

| $x_{1B}$ | $T_g$/K | $T_{s–s}$/K | $T_{s–l}$/K | $\Delta H_{trs}$/kJ mol$^{-1}$ | $\Delta S_{trs}$/J mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|---|---|
| 1 | 111.21 | 129.26 | 184.45 | 9.278 | 50.30 |
| | | | 183.9 [14] | 9.282 [14] | |
| 0.686 | 111.65 | 130.07 | 181.44 | | |
| | | | 269.10 | 1.589 | 5.905 |
| 0.311 | 111.97 | 134.96 | 180.20 | | |
| | | | 269.37 | 3.847 | 14.28 |
| 0.0263 | | | 179.73 | 0.236 | 1.313 |
| | | | 270.33 | 5.482 | 20.28 |

sition took place in the temperature range. The temperatures of the glass transition for the systems, at which the value of d$C_{p,m}$/d$T$ reaches the maximum, were determined and listed in Table 1. It can be seen from Table 1 that the glass transition temperature $T_g$ for the systems is increasing with $x_{1B}$ decrease. $T_g$ increases when the molecular structure becomes more rigid [17]. The same phenomenon was found in the binary system of water and ethanol [1]. For $x_{1B}$=0.0263 system, the glass transition did not take place. The reason may be that, in the most water-rich region, the hydrogen-bond of bulk is high enough to retain the hydrogen-bond connectivity throughout the entire bulk called 'mixing scheme I' as pure water in this mixture [11]. A glass transition took place because of 1B added in the binary mixture. With $x_{1B}$ increasing, the structure of the bulk is changing into 'mixing scheme II' for the binary system.

The molar heat capacity reaches maxima in temperature range of 130–150 K for $x_{1B}$=1, 0.686 and 0.311 systems, 178–185 K for $x_{1B}$=1, 0.686, 0.311 and 0.0263 systems, 266–271 K for $x_{1B}$=0.686, 0.311

**Table 2** Molar heat capacity of the binary mixture

| $T$/K | $C_{p,m}$/R | $T$/K | $C_{p,m}$/R | $T$/K | $C_{p,m}$/R | $T$/K | $C_{p,m}$/R | $T$/K | $C_{p,m}$/R |
|---|---|---|---|---|---|---|---|---|---|
| $x_{1B}$=0.686 | | | | | | | | | |
| 78.86 | 5.418 | 120.27 | 11.91 | 180.07 | 67.12 | 195.83 | 13.23 | 256.79 | 17.08 |
| 81.01 | 5.761 | 121.39 | 11.82 | 180.37 | 78.44 | 197.63 | 13.29 | 258.94 | 17.57 |
| 82.47 | 5.778 | 122.50 | 11.75 | 180.59 | 96.04 | 199.42 | 13.44 | 261.04 | 17.84 |
| 84.16 | 5.914 | 123.61 | 11.99 | 180.76 | 114.7 | 201.20 | 13.44 | 263.28 | 18.74 |
| 85.83 | 6.046 | 124.73 | 11.97 | 180.88 | 137.1 | 202.70 | 13.50 | 265.69 | 19.70 |
| 87.49 | 6.130 | 125.83 | 11.91 | 180.99 | 151.2 | 205.12 | 13.50 | 268.12 | 20.88 |
| 89.12 | 6.256 | 126.95 | 12.03 | 181.06 | 158.2 | 206.97 | 13.64 | 269.10 | 40.13 |
| 90.73 | 6.373 | 128.06 | 11.99 | 181.12 | 165.8 | 208.89 | 13.70 | 272.20 | 17.63 |
| 92.33 | 6.505 | 129.18 | 12.11 | 181.17 | 179.4 | 210.78 | 13.77 | 274.95 | 17.99 |
| 93.91 | 6.638 | 130.07 | 36.69 | 181.22 | 193.1 | 212.67 | 13.77 | 277.67 | 18.19 |
| 95.47 | 6.719 | 143.06 | –8.905 | 181.25 | 197.3 | 214.55 | 13.84 | 280.38 | 18.36 |
| 97.02 | 6.819 | 158.36 | 3.488 | 181.29 | 341.1 | 216.41 | 13.84 | 283.06 | 18.54 |
| 98.57 | 6.922 | 160.13 | 4.450 | 181.34 | 351.2 | 218.26 | 13.98 | 285.73 | 18.77 |
| 100.09 | 6.959 | 162.75 | 5.218 | 181.37 | 363.7 | 220.10 | 14.05 | 288.38 | 18.99 |
| 101.61 | 7.086 | 164.86 | 7.012 | 181.39 | 397.8 | 222.38 | 14.12 | 291.01 | 19.24 |
| 103.12 | 7.251 | 166.55 | 7.956 | 181.42 | 397.4 | 225.10 | 14.25 | 293.61 | 19.43 |
| 104.62 | 7.413 | 168.04 | 8.519 | 181.44 | 402.9 | 227.78 | 14.33 | 296.21 | 19.49 |
| 106.12 | 7.525 | 169.51 | 8.855 | 181.46 | 388.9 | 230.35 | 14.43 | 298.81 | 19.63 |
| 107.59 | 7.649 | 170.96 | 9.102 | 181.48 | 347.1 | 232.95 | 14.60 | 301.38 | 19.85 |
| 109.04 | 8.000 | 172.39 | 9.472 | 181.52 | 288.1 | 235.51 | 14.67 | 303.94 | 19.91 |
| 110.42 | 8.719 | 173.74 | 10.33 | 181.79 | 63.48 | 238.06 | 14.88 | 306.48 | 20.05 |
| 111.65 | 10.39 | 174.97 | 12.25 | 182.98 | 12.71 | 240.51 | 15.01 | 309.00 | 20.12 |
| 112.77 | 11.49 | 176.08 | 14.75 | 184.85 | 12.81 | 242.91 | 15.29 | 311.52 | 20.24 |
| 113.89 | 11.77 | 177.06 | 18.61 | 186.70 | 12.88 | 245.30 | 15.43 | 314.01 | 20.34 |
| 115.01 | 11.86 | 177.90 | 24.40 | 188.54 | 12.94 | 247.70 | 15.77 | 316.49 | 20.45 |
| 116.13 | 11.87 | 178.63 | 32.80 | 190.37 | 13.01 | 250.06 | 16.05 | 319.08 | 20.57 |
| 118.04 | 11.92 | 179.20 | 43.41 | 192.21 | 13.09 | 252.35 | 16.47 | | |
| 119.16 | 11.91 | 179.68 | 56.20 | 194.02 | 13.23 | 254.60 | 16.84 | | |
| $x_{1B}$=0.311 | | | | | | | | | |
| 79.51 | 2.862 | 129.14 | 6.013 | 186.45 | 6.770 | 246.12 | 9.230 | 280.84 | 13.33 |
| 83.27 | 3.011 | 131.28 | 6.032 | 190.13 | 6.837 | 248.94 | 9.504 | 283.30 | 13.46 |
| 86.84 | 3.111 | 133.38 | 6.331 | 193.78 | 6.902 | 251.69 | 9.851 | 285.74 | 13.59 |
| 90.30 | 3.232 | 134.96 | 15.18 | 197.38 | 6.989 | 254.32 | 10.28 | 288.15 | 13.68 |
| 93.64 | 3.350 | 154.78 | –2.875 | 200.96 | 7.080 | 256.87 | 10.72 | 290.53 | 13.80 |
| 96.88 | 3.475 | 170.21 | 4.373 | 204.49 | 7.173 | 259.33 | 11.17 | 292.88 | 13.84 |
| 100.05 | 3.595 | 174.53 | 6.949 | 207.98 | 7.293 | 261.67 | 11.84 | 295.42 | 13.93 |
| 103.15 | 3.712 | 176.92 | 13.76 | 211.44 | 7.390 | 263.87 | 12.44 | 298.15 | 14.01 |
| 106.21 | 3.879 | 178.36 | 34.11 | 214.84 | 7.516 | 265.90 | 13.38 | 300.82 | 14.11 |
| 109.20 | 4.133 | 178.88 | 65.77 | 218.21 | 7.659 | 267.78 | 14.91 | 303.44 | 14.19 |
| 111.97 | 4.889 | 179.13 | 95.81 | 221.52 | 7.817 | 268.98 | 49.57 | 306.52 | 14.29 |
| 114.26 | 5.831 | 179.44 | 147.8 | 224.78 | 7.977 | 269.37 | 410.3 | 309.87 | 14.38 |
| 116.50 | 5.945 | 179.98 | 212.2 | 227.99 | 8.142 | 269.52 | 108.4 | 312.48 | 14.46 |
| 118.70 | 5.952 | 180.20 | 256.6 | 231.16 | 8.279 | 269.77 | 53.06 | 315.62 | 14.56 |
| 120.50 | 5.962 | 180.30 | 209.2 | 234.29 | 8.450 | 270.85 | 13.06 | 318.74 | 14.66 |
| 122.68 | 5.967 | 180.61 | 129.2 | 237.34 | 8.588 | 273.36 | 13.06 | | |
| 124.84 | 5.986 | 181.04 | 26.82 | 240.32 | 8.853 | 275.87 | 13.15 | | |
| 127.00 | 5.998 | 182.73 | 6.699 | 243.25 | 9.022 | 278.36 | 13.28 | | |

Table 2 Continued

| $T$/K | $C_{p,m}$/R | $T$/K | $C_{p,m}$/R | $T$/K | $C_{p,m}$/R | $T$/K | $C_{p,m}$/R | $T$/K | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $x_{1B}$=0.0263 | | | | | |
| 79.92 | 1.660 | 140.12 | 3.103 | 216.68 | 4.450 | 270.33 | 1143 | 283.85 | 10.34 |
| 81.16 | 1.695 | 142.93 | 3.116 | 219.73 | 4.520 | 270.34 | 659.1 | 285.52 | 10.35 |
| 82.95 | 1.775 | 145.54 | 3.124 | 222.74 | 4.586 | 270.34 | 534.0 | 287.19 | 10.35 |
| 85.25 | 1.861 | 148.14 | 3.157 | 225.70 | 4.636 | 270.34 | 488.2 | 288.86 | 10.36 |
| 87.83 | 1.933 | 150.76 | 3.165 | 228.60 | 4.691 | 270.35 | 383.4 | 290.54 | 10.36 |
| 90.38 | 2.040 | 153.98 | 3.202 | 231.47 | 4.750 | 270.35 | 317.9 | 292.21 | 10.36 |
| 92.86 | 2.117 | 157.78 | 3.254 | 234.33 | 4.802 | 270.36 | 280.7 | 293.89 | 10.37 |
| 95.28 | 2.176 | 161.53 | 3.315 | 237.16 | 4.865 | 270.36 | 259.1 | 295.56 | 10.37 |
| 97.65 | 2.225 | 165.27 | 3.414 | 239.93 | 4.931 | 270.37 | 263.8 | 297.24 | 10.37 |
| 99.98 | 2.286 | 168.90 | 3.535 | 242.63 | 4.980 | 270.38 | 231.5 | 298.93 | 10.37 |
| 102.28 | 2.344 | 172.47 | 3.642 | 245.36 | 5.022 | 270.40 | 197.1 | 300.61 | 10.38 |
| 104.54 | 2.391 | 175.95 | 3.813 | 248.13 | 5.092 | 270.45 | 162.9 | 302.29 | 10.38 |
| 106.76 | 2.447 | 178.14 | 5.055 | 250.85 | 5.180 | 270.51 | 120.0 | 303.97 | 10.38 |
| 109.36 | 2.526 | 179.73 | 7.852 | 253.56 | 5.272 | 270.59 | 59.86 | 305.66 | 10.39 |
| 112.32 | 2.665 | 184.53 | 3.898 | 256.23 | 5.368 | 270.68 | 21.45 | 307.35 | 10.39 |
| 115.19 | 2.757 | 187.89 | 3.929 | 258.87 | 5.492 | 270.77 | 10.98 | 309.04 | 10.39 |
| 118.00 | 2.809 | 191.21 | 4.003 | 261.46 | 5.624 | 270.87 | 10.29 | 310.73 | 10.40 |
| 120.79 | 2.866 | 194.51 | 4.061 | 264.00 | 5.838 | 272.07 | 10.30 | 312.42 | 10.40 |
| 123.54 | 2.917 | 197.77 | 4.111 | 266.46 | 6.200 | 273.77 | 10.32 | 314.02 | 10.40 |
| 126.25 | 2.960 | 200.99 | 4.161 | 268.76 | 7.161 | 275.46 | 10.32 | 315.11 | 10.40 |
| 128.93 | 3.018 | 204.18 | 4.215 | 270.07 | 47.91 | 277.13 | 10.33 | 316.01 | 10.41 |
| 131.57 | 3.053 | 207.35 | 4.268 | 270.30 | 464.7 | 278.81 | 10.33 | 316.45 | 10.41 |
| 134.21 | 3.034 | 210.49 | 4.339 | 270.32 | 620.9 | 280.50 | 10.34 | 318.17 | 10.41 |
| 136.85 | 3.103 | 213.60 | 4.378 | 270.32 | 942.9 | 282.17 | 10.34 | | |

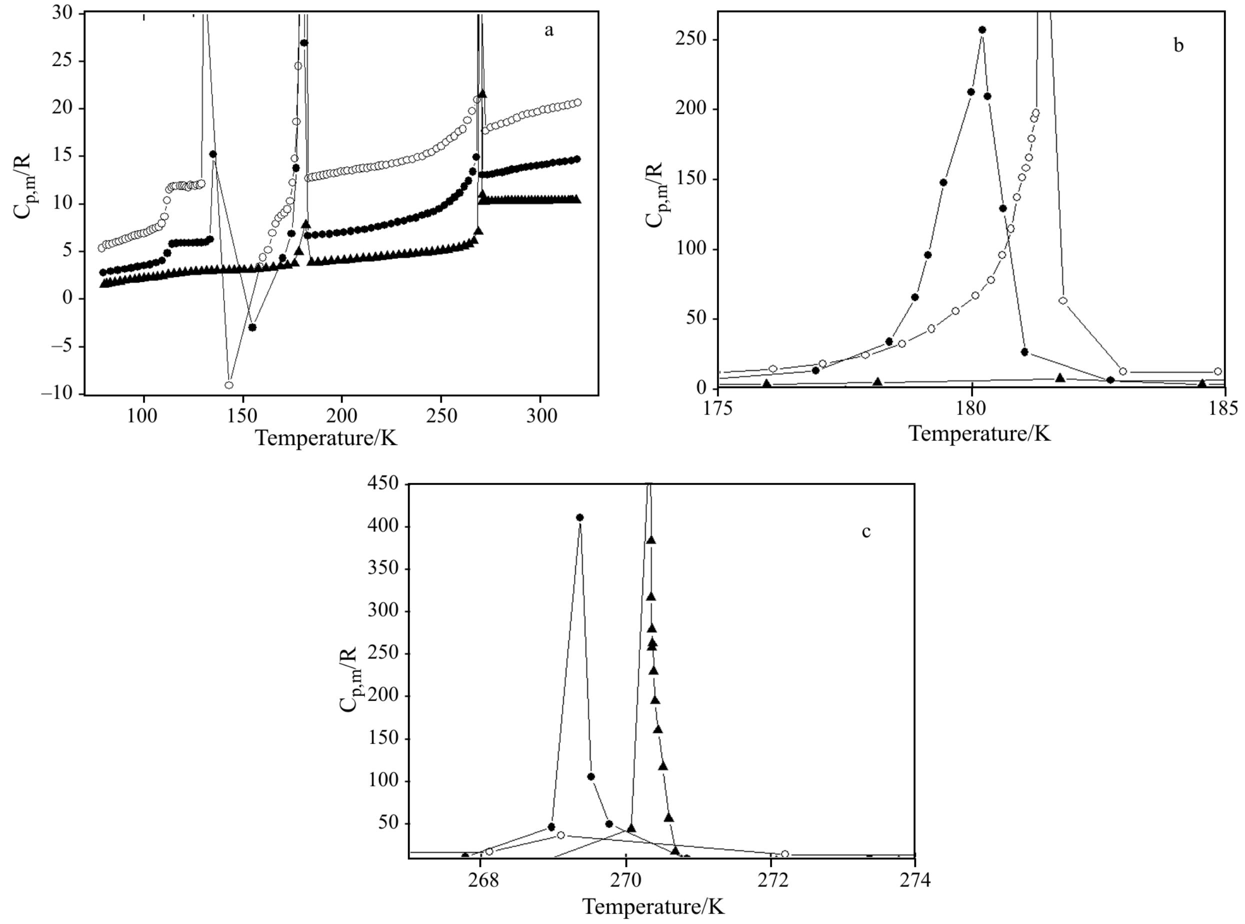

**Fig. 2** Molar heat capacities of the binary mixtures: a – ○ – $x_{1B}$=0.686; ● – $x_{1B}$=0.311; ▲ – $x_{1B}$=0.0263. b – and c – show the solid–liquid phase transitions for *n*-butanol and water in the system, respectively

**Table 3** Fitting coefficients $a_i$ and standard deviations $\delta$

| $x_{1B}$ | $T$/K | $a_3$ | $a_2$ | $a_1$ | $a_0$ | $\delta$ |
|---|---|---|---|---|---|---|
| 0.0263 | 185–260 | 2.1617 | –13.592 | 30.245 | –19.26 | 0.018 |
| | 275–320 | | –0.0526 | 0.5101 | 9.319 | 0.001 |
| 0.311 | 185–260 | 14.342 | –88.04 | 182.77 | –121 | 0.079 |
| | 275–320 | | –2.179 | 16.417 | –15.55 | 0.019 |
| 0.686 | 185–260 | 21.988 | –138.66 | 293.97 | –195.8 | 0.061 |
| | 275–320 | | –6.872 | 46.729 | –58.61 | 0.041 |

**Table 4** The data of the thermodynamic functions of the binary mixture

| $T$/K | $C_{p,m}$/ J mol$^{-1}$ K$^{-1}$ | $\Delta H$*/ kJ mol$^{-1}$ | $\Delta S$**/ J mol$^{-1}$ K$^{-1}$ | $C_{p,m}$/ J mol$^{-1}$ K$^{-1}$ | $\Delta H$*/ kJ mol$^{-1}$ | $\Delta S$**/ J mol$^{-1}$ K$^{-1}$ | $C_{p,m}$/ J mol$^{-1}$ K$^{-1}$ | $\Delta H$*/ kJ mol$^{-1}$ | $\Delta S$**/ J mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| | | $x_B$=0.686 | | | $x_B$=0.311 | | | $x_B$=0.0263 | |
| 190 | 108.0 | –12.91 | –53.45 | 56.62 | –10.72 | –42.69 | 32.97 | –9.748 | –37.70 |
| 200 | 111.4 | –11.81 | –47.81 | 59.16 | –10.14 | –39.72 | 34.55 | –9.410 | –35.97 |
| 210 | 113.7 | –10.69 | –42.32 | 61.37 | –9.534 | –36.78 | 36.03 | –9.057 | –34.25 |
| 220 | 116.0 | –9.539 | –36.98 | 63.97 | –8.907 | –33.87 | 37.51 | –8.689 | –32.54 |
| 230 | 119.3 | –8.364 | –31.76 | 67.66 | –8.251 | –30.95 | 39.10 | –8.306 | –30.84 |
| 240 | 124.8 | –7.146 | –26.57 | 73.17 | –7.548 | –27.96 | 40.92 | –7.907 | –29.14 |
| 250 | 133.5 | –5.858 | –21.31 | 81.22 | –6.779 | –24.82 | 43.06 | –7.487 | –27.42 |
| 260 | 146.7 | –4.461 | –15.84 | 92.51 | –5.913 | –21.43 | 45.64 | –7.044 | –25.69 |
| 270 | Phase transition | | | Phase transition | | | Phase transition | | |
| 280 | 152.6 | –2.871 | –9.932 | 110.9 | –2.066 | –7.148 | 85.92 | –1.562 | –5.406 |
| 290 | 158.9 | –1.313 | –4.464 | 114.2 | –0.941 | –3.199 | 86.10 | –0.702 | –2.388 |
| 300 | 164.0 | 0.303 | 1.012 | 117.1 | 0.216 | 0.723 | 86.27 | 0.160 | 0.534 |
| 310 | 168.0 | 1.964 | 6.459 | 119.7 | 1.401 | 4.608 | 86.42 | 1.023 | 3.365 |
| 320 | 170.9 | 3.659 | 11.84 | 122.0 | 2.610 | 8.445 | 86.57 | 1.888 | 6.111 |
| 298.15 | 163.2 | 0 | 0 | 116.6 | 0 | 0 | 86.24 | 0 | 0 |

*$\Delta H=H_T-H_{298.15\,K}$; **$\Delta S=S_T-S_{298.15\,K}$

and 0.0263 systems, respectively, as shown in Figs 1 and 2. The phase transition temperatures were determined and listed in Table 1, which were corresponding to the solid–solid and solid–liquid phase transitions for the 1B, and solid–liquid phase transition for the water, respectively. Comparing the data in Table 1, the solid–solid phase transition temperatures are increasing with $x_{1B}$ decrease. The solid–liquid phase transition temperatures of 1B and water in the mixture are lower than those of pure 1B and water. For $x_{1B}$=0.0263 system, the solid–solid phase transition for the 1B did not take place. This is in agreement with the discussion for the glass transition.

The unusual phenomenon is that the mixtures absorbed energy first and then released energy in temperature range 140–150 K for $x_{1B}$=1, 0.686 and 0.311 systems, as shown in Figs 1 and 2a. A kind of phase transition of a metastable crystal to a stable crystal exists has been found in the azeotropic mixture composed of water and ethanol [1]. The similar phenomenon may occur in these systems.

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

### *Thermodynamic functions of the binary systems*

The thermodynamic functions of the binary systems 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 4.

## Conclusions

The molar heat capacity of the binary systems were measured 78–320 K. The glass transition temperature and the solid–solid phase transition temperature are increasing with $x_{1B}$ decrease for the systems. The solid–liquid phase transition temperatures for 1B and water in the binary systems are lower than those of pure 1B and water.

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