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Thermodynamic investigation of the binary system of ethanol + benzene

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Abstract

The molar heat capacity of the binary system ethanol + benzene was measured by an adiabatic calorimeter in the temperature range from 80 to 320 K. The glass transition and phase transitions of the mixture were determined based on the curve of the heat capacity with respect to temperature. The glass transition occurred at 97.536 K, the enthalpy and entropy of the glass transition were calculated to be 1.796 kJ mol^{-1}, 18.414 J mol^{-1} K^{-1}, respectively. The phase transitions took place in temperature ranges 115.875–128.400, 146.778–159.015 and 256.645–274.981 K corresponding to the solid–solid phase transition of ethanol, solid–liquid phase transition of ethanol and solid–liquid phase transition of benzene, respectively. The corresponding enthalpies and entropies of the phase transition were calculated to be −1.266 kJ mol^{-1}, −10.745 J K^{-1} mol^{-1}; 2.166 kJ mol^{-1}, 13.818 J K^{-1} mol^{-1}; 5.390 kJ mol^{-1}, 19.856 J K^{-1} mol^{-1}, 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: Heat capacity; Ethanol; Benzene; Low temperature; Adiabatic calorimetry

1. Introduction

The behavior of azeotropic mixtures is of great interest as they are treated as pure substances, and they 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 data 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 ethanol + benzene shows a minimum boiling point azeotrope at 341.4 K with ethanol mole fraction 0.4483 at 1 atm (1 atm = 101,325 Pa) [6].

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

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2. Experimental

2.1. Experimental materials

Commercial analytical purity grade ethanol (0.998 mass fraction) and benzene (0.998 mass fraction) were used to prepare the sample. The concentration of ethanol and benzene were 0.4483 and 0.5517 molar fraction. The mean molecular weight of the sample is 43.09 and 0.2266 mol (9.7648 g) of the sample was used in the experiment. The sample was sealed into the container. So that the weight of the sample did not change before and after measurements with an adiabatic calorimeter.

2.2. Adiabatic calorimeter

Heat-capacity measurements were carried out in a high-precision automatic adiabatic calorimeter described in detail elsewhere [9,10]. The principle of the calorimeter is based on the Nernst stepwise heating method. The calorimeter mainly consists of a sample cell, an adiabatic (or inner) shield, a guard (outer) shield, a platinum resistance thermometer, an electric heater, two sets of chromel–copel thermocouples and a high vacuum can. The sample cell was made of gold-plated copper and had an inner volume of 48 cm^3. Eight gold-plated copper vanes of 0.2 mm thickness were put into the cell to promote heat distribution between the sample and the cell. The platinum resistance thermometer was inserted into the copper sheath which was soldered in the middle of the sample cell. The heater wire was wound on the surface of the thermometer. The evacuated can was kept within ca. 1×10^{-3} Pa during the heat-capacity measurements so as to eliminate the heat loss due to gas convection. Liquid nitrogen was used as the cooling medium. One set of chromel–copel thermocouples was used to detect the temperature difference between the sample cell and the inner shield. Likewise, the other set of thermocouples was installed between the inner and outer shields. The temperature difference between them was kept to within 0.5 mK during the whole experimental process. The sample cell was heated by the standard discrete heating method. The temperature of the cell was alternatively measured by a platinum resistance thermometer which was made by the Instrument Manufactory of Yunnan, China, and calibrated at the National Institute of Metrology in terms of the IPTS-90. The temperature increment in a heating period was 2–4 K, and temperature drift was maintained at about $10^{-3}\ \mathrm{K\,min^{-1}}$ in equilibrium period. All the data were automatically acquired through a Data Acquisition/Switch Unit (model 34970A, Aglient, USA) and processed by a computer.

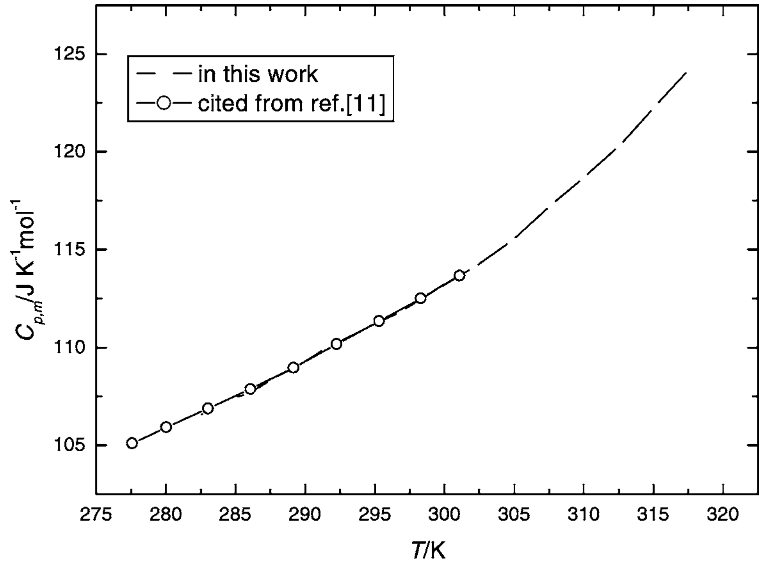

Fig. 1. Molar heat capacities of ethanol as a function of temperature.

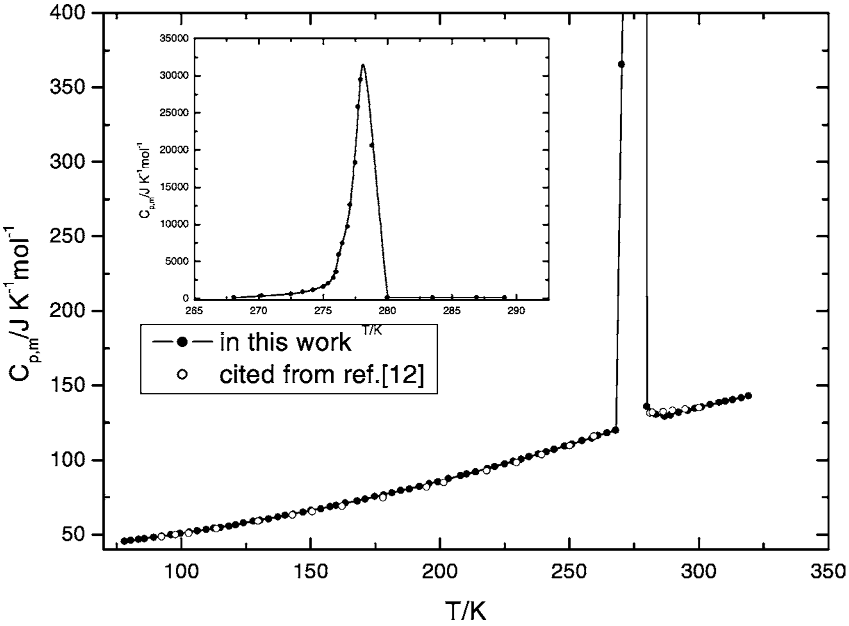

Fig. 2. Molar heat capacities of benzene as a function of temperature. Inset shows solid–liquid phase transition of benzene.

To verify the reliability of the adiabatic calorimeter, the molar heat capacities for the reference standard material α-Al_2O_3, ethanol and benzene were measured. The deviations of our experimental results from the values recommended by the National Bureau of Standards [11] were within ±0.2% in the temperature range of 80–400 K for α-Al_2O_3. The plots of molar heat capacities of ethanol and benzene as a function of temperature are given in Figs. 1 and 2. In order to compare the results of the heat capacities of ethanol and benzene measured in our laboratory with [12,13], the data of heat capacities gained from [12,13] are given in Figs. 1 and 2 as well. The enthalpy $\Delta_{\text{trans}}H_{\text{m}}$ and entropy $\Delta_{\text{trans}}S_{\text{m}}$ of the phase transition were calculated according to the relationship as follows [16]:

$$\Delta_{\text{trans}}H_{\text{m}} = \frac{\begin{array}{c} Q - n\int_{T_1}^{T_{\text{trans}}} C_{p,\text{m(S)}}\,\text{d}T \\ -n\int_{T_{\text{trans}}}^{T_2} C_{p,\text{m(L)}}\,\text{d}T - \int_{T_1}^{T_2} C_0\,\text{d}T \end{array}}{n} \tag{1}$$

$$\Delta_{\text{trans}}S_{\text{m}} = \frac{\Delta_{\text{trans}}H_{\text{m}}}{T_{\text{trans}}} \tag{2}$$

where Q is the total mount 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 above T_{trans}; $C_{p,\text{m(S)}}$, $C_{p,\text{m(L)}}$, C_0 the heat capacity in solid and liquid state and heat capacity of empty cell, respectively. The phase transition temperatures and enthalpies of ethanol and benzene are given in Table 1. Figs. 1 and 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 [12–14].

3. Results and discussion

3.1. 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 Fig. 3. No thermal anomaly was observed or no phase transition took place in the temperature range from 160 to 260 and 277 to 320 K, respectively.

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

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

	T_{trans} (K)	$\Delta H_{\mathrm{trans}}$ (kJ mol^{-1})	$\Delta S_{\mathrm{trans}}$ (J K^{-1} mol^{-1})
Ethanol	111.40 ± 0.2 [15]	3.138 ± 0.03 [15]	
	159.00 ± 0.006 [14]	4.931 ± 0.007 [14]	
	158.5 [12]	5.021 [12]	
Benzene	278.2	9.818	35.291
	278.6 [13]	9.820 [13]	
The mixture	117.823	−1.266	−10.745
	156.746	2.166	13.818
	271.452	5.390	19.856

For 160–260 K

$$C_{p.\mathrm{m}} = 42.819X^4 + 32.287X^3 - 3.8507X^2 + 23.369X + 111.07 \qquad (3)$$

where $C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1}) is the molar heat capacity of the azeotropic mixture, T (K) thermodynamic temperature, reduced temperature $X = (T\,(\mathrm{K}) - 210)/50$, fitting coefficient $R^2 = 0.9925$.

In order to fit well, the temperature T was replaced by the reduced temperature X

$$X = \frac{T - ((T_{\max} + T_{\min})/2)}{(T_{\max} - T_{\min})/2} \qquad (4)$$

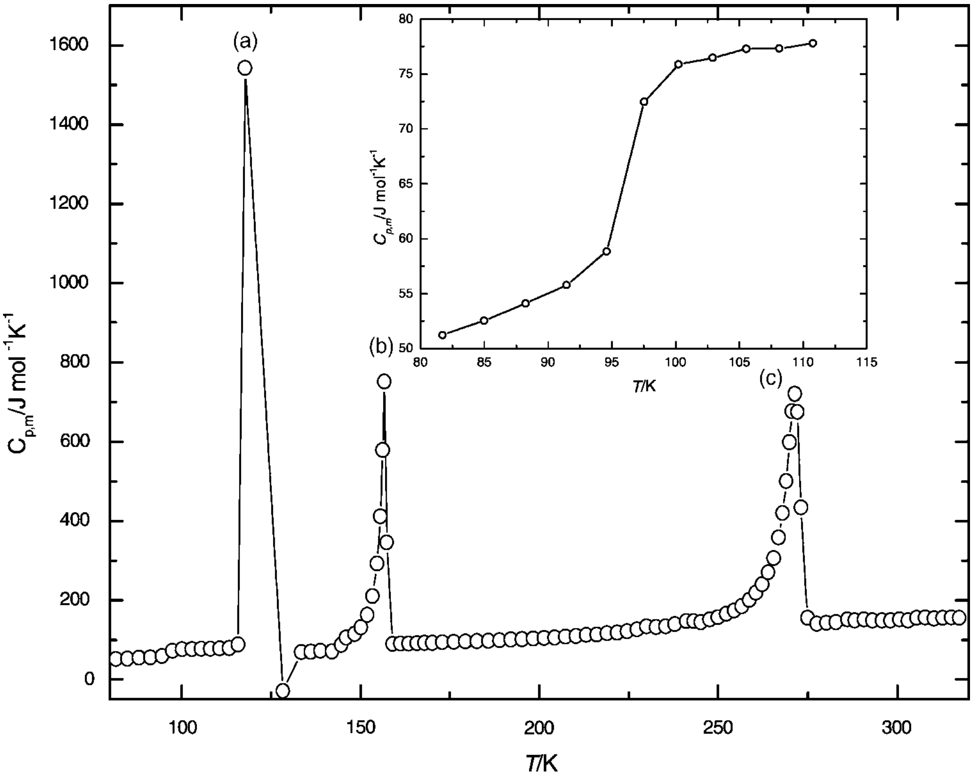

Fig. 3. Molar heat capacity of the mixture: "a", "b" and "c" degree the solid–solid and solid–liquid phase transitions of ethanol and solid–liquid phase transition of benzene, respectively. Inset shows glass phase transition of the mixture.

Table 2
The molar heat capacity and temperature drift rate of the mixture

T (K)	$C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})	dT/dt (mK min^{-1})	T (K)	$C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})	dT/dt (mK min^{-1})
81.732	51.251	1.74	213.239	111.634	−1.62
85.012	52.554	2.06	216.139	113.416	−1.98
88.244	54.133	2.68	219.001	115.741	−1.50
91.463	55.788	2.60	221.834	118.071	−1.98
94.602	58.878	6.30	224.623	120.754	−2.28
97.536	72.446	−7.84	227.349	124.000	−1.26
100.263	75.889	−2.86	230.016	126.000	2.34
102.914	76.466	−1.72	232.706	128.000	−0.30
105.554	77.301	−1.60	235.343	132.000	−1.80
108.172	77.333	−2.26	237.913	135.200	−1.68
110.758	77.802	−3.00	240.391	138.100	−2.40
113.334	79.445	0.60	242.804	142.300	0.48
115.878	88.595	−23.04	245.224	145.800	1.34
117.823	1541.726	−68.44	247.652	151.372	1.52
128.401	−29.309	−4.62	250.015	157.371	1.18
133.465	69.189	−3.84	252.305	164.910	0.12
136.204	70.175	−4.74	254.526	173.092	0.32
139.045	59.849	−3.26	256.645	184.488	0.14
142.110	70.898	−4.20	258.670	199.937	−0.60
144.689	87.628	−0.24	260.588	218.732	−0.72
146.778	115.000	−2.74	262.384	240.624	−5.38
148.493	115.000	−3.50	264.039	269.612	−6.86
150.271	131.749	−4.26	265.536	305.250	−6.92
151.969	163.084	−5.58	266.873	357.660	−8.14
153.453	210.882	−5.90	268.053	419.111	−8.98
154.687	292.604	−6.00	269.057	500.780	−8.86
155.607	411.355	−7.74	269.915	598.933	−8.44
156.259	578.612	−8.32	270.700	676.515	−9.00
156.746	750.611	−10.54	271.452	720.316	−11.26
157.415	345.462	−5.40	272.219	674.909	−6.74
159.015	89.355	0.58	273.186	434.195	−5.48
161.279	90.016	−2.22	274.981	155.086	−0.86
163.535	90.910	−2.46	277.601	141.018	−0.80
165.771	91.874	−1.86	280.287	143.801	1.44
168.005	92.053	0.94	282.948	145.926	0.62
170.213	92.541	−2.16	285.583	147.607	−0.60
172.960	93.762	−2.16	288.163	149.034	−1.90
176.227	94.381	−2.76	290.712	150.406	−2.24
179.460	95.530	2.46	293.240	151.327	−1.36
182.671	96.630	1.30	295.754	152.804	−1.88
185.845	97.803	−2.70	298.208	153.721	−0.94
188.995	99.161	−2.58	300.647	154.614	−0.58
192.122	100.220	−2.70	303.092	155.602	0.62
195.220	101.410	−2.64	305.492	156.501	1.78
198.289	103.214	−1.80	307.874	157.316	1.96
201.340	104.897	−2.10	310.302	158.403	0.64
204.359	105.912	−2.46	312.693	158.901	−0.40
207.342	107.983	−1.38	315.079	159.212	−0.90
210.309	109.893	−1.74	317.449	159.715	0.80

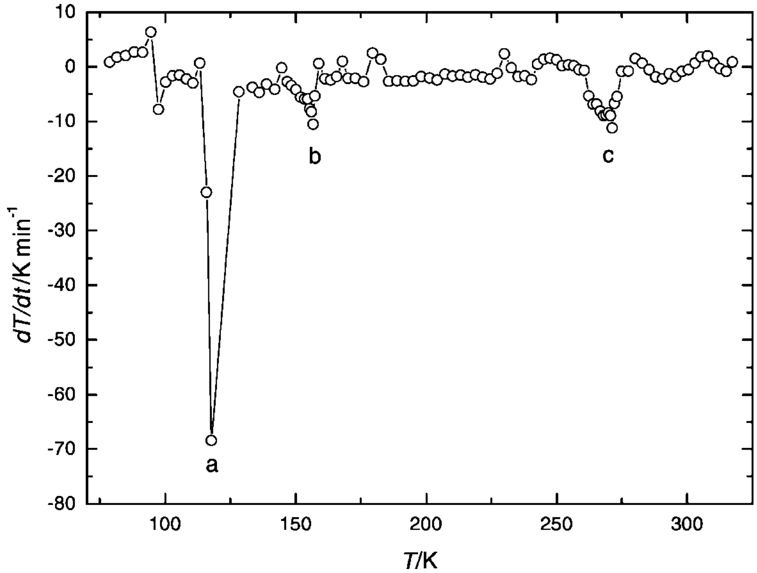

Fig. 4. Temperature drift rate during the determination of heat capacity of the mixture: “a”, “b” and “c” show the solid–solid and solid–liquid phase transitions of ethanol and solid–liquid phase transition of benzene, respectively.

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

For 277–320 K

$$C_{p,\mathrm{m}} = -2.5094X^2 + 8.1064X + 150.81 \qquad (5)$$

where $X = (T\ (\mathrm{K}) - 298.5)/21.5$, $R^2 = 0.9977$.

3.2. Thermodynamic data of glass and phase transitions

It can be seen from Fig. 3 that the heat capacity jump was found in the temperature range from 95 to 105 K. In order to see clearly the change of the heat capacities, the inset figure was used in Fig. 3. The heat capacity clearly changes before and after glass transition temperature [17]. Then, the glass transition took place in the temperature range. The curves of the temperature drift rates during the determination of the heat capacities of the system were shown in Fig. 4, and the values of the temperature drift rates were given in Table 2. Fig. 4 shows that the temperature drift rates become larger during the glass transition. Then, it can be demonstrated that the glass transition occurred in the temperature range according to the curve of the temperature drift rate with respect to temperature. This is agreement with literatures [18,19]. That the temperature drift rates are less than ±2 mK min^{-1} in other temperatures ranges except the temperature of the phase transition shows that the adiabatic conditions was better. So the experimental results are accurate and reliable. The temperatures of the glass transition of the mixture were determined to be 97.536 K, which is corresponding to the maximum of the molar heat capacity drift rate.

Fig. 3 shows that the molar heat capacity reaches maxima in temperature ranges from 115.875 to 128.400, 146.778 to 159.015 and 256.645 to 274.981 K corresponding to “a”, “b” and “c”, respectively. The phase transitions took place in these temperature ranges. The temperature drift rate reaches the minima in the same temperature ranges corresponding to the phase transition degreed as “a”, “b” and “c”, respectively. This may be that the mixture needed to absorb energy during the phase transition. Thus, the temperature drift rate became negative. The phase transition temperatures were determined to be 117.823, 156.746 and 271.452 K, which were corresponding to the solid–solid phase transition of ethanol, solid–liquid phase transition of ethanol and solid–liquid phase transition of benzene. Compared the data in Table 1, the phase transition temperatures

Table 3
Data of the thermodynamic functions of the mixture

T (K)	$C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})	$[H_{(T)} - H_{(298.15\,\mathrm{K})}]$ (kJ mol^{-1})	$[S_{(T)} - S_{(298.15\,\mathrm{K})}]$ (J K^{-1} mol^{-1})
160	84.728	−11.826	−241.790
170	93.668	−11.267	−228.914
180	98.365	−10.740	−213.718
190	100.271	−10.300	−196.921
200	101.089	−9.991	−178.917
210	102.780	−9.838	−159.836
220	107.558	−9.851	−139.595
230	117.895	−10.017	−117.935
240	136.516	−10.304	−94.451
250	166.403	−10.650	−68.616
260	210.792	−10.968	−39.801
270	Phase transition		
280	142.772	−2.692	−9.312
290	149.036	−1.232	−4.188
300	153.840	0.284	0.949
310	157.184	1.840	6.052
320	159.068	3.423	11.076
298.15	153.061	0.000	0.000

of ethanol and benzene in the mixture were lower than those of pure ethanol 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 unusual phenomenon is that the mixture absorbed energy firstly at about 117 K and then released energy. As [14,15] reported, the metastable crystal and stable crystal exist in solid phases of ethanol. The phase transition of metastable crystal into stable crystal occurs at 111.40 ± 0.2 K. Then, the phase transition of metastable crystal of ethanol in the mixture into crystal took place at 117.823 K. The mainly reason of released energy may be that the hydrogen bond was formed during the phase transition. So that the order of molecular collocation was promoted and the change of the entropy of the system became negative.

The melting temperatures of the mixture are lower than those of the corresponding pure samples as listed in Table 1. This may be that the interaction between molecules of benzene and ethanol exists in the mixture. The result of the interaction causes the lower melting temperature.

3.3. Thermodynamic functions of the mixture

The thermodynamic functions of the mixture were calculated based on the function of the molar heat

Table 4
Excess thermodynamic functions of the mixture

T (K)	$C^{\mathrm{E}}_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})	$[H^{\mathrm{E}}_{\mathrm{m}}(T) - H^{\mathrm{E}}_{298.15\,\mathrm{K}}]$ (J mol^{-1})	$[S^{\mathrm{E}}_{\mathrm{m}}(T) - S^{\mathrm{E}}_{298.15\,\mathrm{K}}]$ (J K^{-1} mol^{-1})
280	25.744	−536.265	−1.855
285	27.092	−394.703	−1.354
290	27.983	−247.213	−0.841
295	28.419	−96.071	−0.324
300	28.398	56.449	0.189
305	27.921	208.071	0.690
310	26.987	356.520	1.173
315	25.598	499.522	1.630
320	23.752	634.802	2.057
298.15	28.459	0.000	0.000

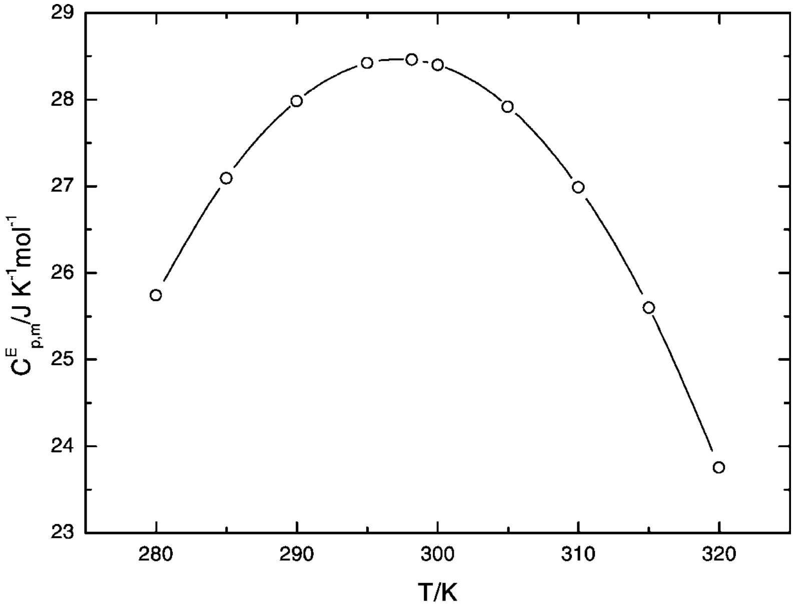

Fig. 5. Excess molar heat capacity of the mixture.

capacity with respect to thermodynamic temperature and the relationships of the thermodynamic functions. The results are given in Table 3.

3.4. Excess thermodynamic functions of the azeotrope

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

$$C^{\mathrm{E}}_{p,\mathrm{m}} = C_{p,\mathrm{m}} - xC^{*}_{p,\mathrm{m},2} - (1-x)C^{*}_{p,\mathrm{m},1} \qquad (6)$$

where $C^{*}_{p,\mathrm{m},2}$ and $C^{*}_{p,\mathrm{m},1}$ are the molar heat capacities for ethanol and benzene, respectively, and $C_{p,\mathrm{m}}$ is the molar heat capacity of a mixture at the mole fraction of benzene x. The values of $C^{\mathrm{E}}_{p,\mathrm{m}}$ were calculated in the liquid phase and listed in Table 4 and shown in Fig. 5.

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

$$C^{\mathrm{E}}_{p,\mathrm{m}} = -3.6492X^2 - 0.996X + 28.398 \qquad (7)$$

where $R^2 = 1$, $X = (T\,(\mathrm{K}) - 300)/20$.

From Eq. (7), it can be derived that the value of $C^{\mathrm{E}}_{p,\mathrm{m}}$ reaches the maximum 28.466 J K^{-1} mol^{-1} at $T = 297.270$ K. The larger the $C^{\mathrm{E}}_{p,\mathrm{m}}$, 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 according to 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.

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References

[1] Y. Demirel, Fluid Phase Equilib. 86 (1993) 1.
[2] C. González, J.M. Resa, J. Lanz, J.A.M. Ilarduya, Fluid Phase Equilib. 137 (1993) 141.
[3] J.M. Resa, C. González, M.A. Betolaza, A. Ruiz, Fluid Phase Equilib. 156 (1999) 89.

[4] J.M. Resa, C. González, S.O. Landaluce, J. Lanz, M. Fanega, Fluid Phase Equilib. 182 (2001) 177.

[5] J.M. Resa, C. González, A. Ruiz, Sep. Purification Technol. 18 (2000) 103.

[6] Y. Demirel, Thermochim. Acta 339 (1999) 79.

[7] K.L. Carter, G.G. Haselden, Int. J. Refrig. 22 (1999) 442.

[8] I. Rodriguez-Donis, E. Pardillo-Fontdevila, V. Gerbaud, X. Joulia, Comput. Chem. Eng. 25 (2001) 799.

[9] Z.C. Tan, G.Y. Sun, Y. Sun, A.X. Yin, W.B. Wang, J.C. Ye, L.X. Zhou, J. Thermal. Anal. 45 (1995) 59.

[10] Z.C. Tan, L.X. Zhou, S.X. Chen, A.X. Yin, Y. Sun, J.C. Ye, X.K. Wang, Sci. Sin. Ser. B 26 (1983) 1014.

[11] D.A. Ditmars, S. Ishihara, S.S. Chang, G. Bernstein, E.D. West, J. Res. Natl. Bur. Stands. 87 (1982) 159.

[12] K.K. Kenneth, J. Am. Chem. Soc. 51 (1929) 779.

[13] M.H. Hugh, S.P. George, C.D. Albert, J. Am. Chem. Soc. 52 (1930) 1547.

[14] H. Osamu, S. Hiroshi, S. Syuzo, J. Chem. Thermodynamics 9 (1977) 1133.

[15] P.N. Nikolaev, I.B. Rebinovich, Russ. J. Phys. Chem. 688 (1967) 41.

[16] Z.C. Tan, B. Xue, S.W. Lu, S.H. Meng, X.H. Yuan, Y.J. Song, J. Thermal. Anal. Catal. 63 (2001) 297.

[17] Z.H. Liu, T. Hatakeyama, Handbook of Analytical Chemistry, second ed., Chemical Industry Press, Beijing, 2000, p. 64.

[18] I. Tsukushi, O. Yamamuro, T. Ohta, T. Matsuo, H. Nakano, Y. Shirota, J. Phys. 8 (1996) 245.