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Low-temperature heat capacity of the azeotropic mixture composed of water + ethanol + benzene

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Abstract

Molar heat capacity of the azeotropic mixture composed of water, ethanol, and benzene was measured by an adiabatic calorimeter 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 102.850 K. The phase transitions took place in temperature ranges 140–155 K and 265–280 K corresponding to the solid–liquid phase transitions of ethanol, water and benzene, respectively. The corresponding enthalpies and entropies of the phase transition were calculated to be 0.4157 kJ mol^{-1}, 2.824 J K^{-1} mol^{-1}; 1.293 kJ mol^{-1}, 4.692 J K^{-1} mol^{-1}; 4.876 kJ mol^{-1}, 17.67 J K^{-1} mol^{-1}; respectively. The thermodynamic functions and the excess thermodynamic functions of the mixture relative to 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; Water; Ethanol; Benzene; Low temperature; Adiabatic calorimetry

1. Introduction

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 [1].

The behavior of azeotropic mixtures is of great interest as they are treated as pure substances. The behavior of the azeotropic mixtures was extensively studied [2–8]. We recently investigated the heat capacities of azeotropic systems composed of water + cyclohexane and ethanol + benzene [9,10]. Moving along these lines, the heat capacity of ternary system was studied.

The ternary system of 0.233 mol fraction of water, 0.228 mol fraction of ethanol, and 0.539 mol fraction of benzene shows a minimum boiling point azeotrope at 338.0 K with 101.325 kPa [6]. The coexisting liquid splits into two liquid phases (upper layer: ethanol and benzene; lower layer: ethanol and water) in the system [11].

In this work, 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.

2. Experimental

Commercially available ethanol (Shenyang Chemical Agent Factory, normal mass fraction purity, 0.998) and benzene (Shenyang Chemical Agent Factory, normal mass fraction purity, 0.998) were used to prepare the sample. The water used for calorimetric measurements was deionized and distilled twice. The ternary system is composed of 0.233 mol fraction of water, 0.228 mol fraction of ethanol,

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and 0.539 mol fraction of benzene. The mean molecular weight of the sample is 56.783 and 0.5242 mol (29.7648 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 the measurements.

Heat-capacity measurements were carried out in a high-precision automatic adiabatic calorimeter described in detail elsewhere [12,13]. 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–copper 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–copper 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} 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.

To verify the reliability of the adiabatic calorimeter, molar heat capacities for the reference standard material α-Al_2O_3, water, ethanol and benzene were measured. The deviations of our experimental results from the values [14] were within ±0.2% in the temperature range of 80–400 K for α-Al_2O_3. The plots of molar heat capacities of water, ethanol and benzene as a function of temperature are given in Figs. 1–3. In order to compare the results of the heat capacities of water, ethanol and benzene measured in our laboratory with literatures [15–18], the data of heat capacities gained from literatures [15–18] are given in Figs. 1–3 as well. The enthalpy $\Delta_{\mathrm{trans}}H_{\mathrm{m}}$ and entropy $\Delta_{\mathrm{trans}}S_{\mathrm{m}}$ of the phase transition were calculated according to the relationship as follows [19]:

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

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

where Q is the total mount of heat introduced into the sample cell; n the moles of substance of the sample; T_{trans} the phase transition temperature, T_1 slightly below T_{trans}; T_2 slightly above T_{trans}; $C_{p,\mathrm{m}(S)}$, $C_{p,\mathrm{m}(L)}$, C_0 are the heat capacity in solid and liquid state and heat capacity of empty cell, respectively; the subscript m stands for molar. The phase transition temperatures and enthalpies of ethanol and benzene are given in Table 1. Figs. 1–3 and Table 1 show that the molar heat capacities, the transition temperature and enthalpy

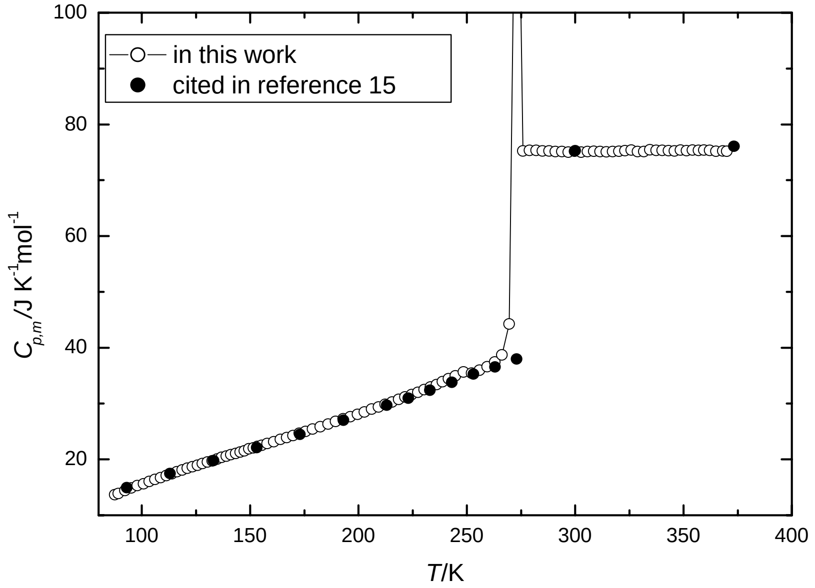

Fig. 1. Experimental molar heat capacities of water as a function of temperature.

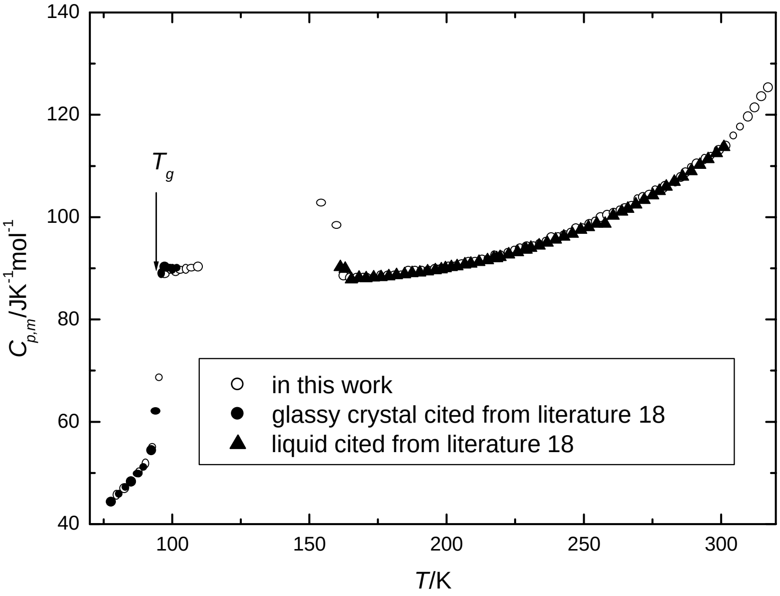

Fig. 2. Experimental molar heat capacities of ethanol as a function of temperature.

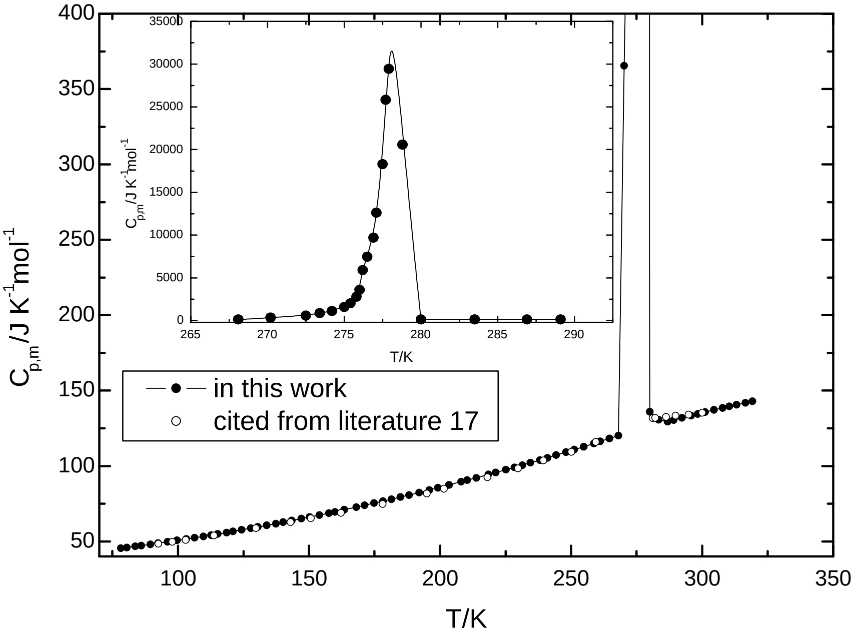

Fig. 3. Experimental molar heat capacities of benzene as a function of temperature. Inset shows solid–liquid phase transition of benzene.

determined in our laboratory are in excellent agreement with the data cited from [15–18].

3. Results and discussion

3.1. Molar heat capacity of the mixture

The molar heat capacities of the azeotropic 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. 4. No thermal anomaly was observed or no phase transition took place in the temperature ranges from 110 to 140 K, 155 to 265 K, and 280 to 320 K, respectively.

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

$$C_{p,\mathrm{m}} = \sum n_k X^k \tag{3}$$

where k is the number of adjustable coefficient. The fitting results were listed in Table 3.

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

	T_{trans} (K)	ΔH_{trans} (kJ mol^{-1})	ΔS_{trans} (J K^{-1} mol^{-1})
Water	273.104[a]	6.005[a]	21.99[a]
	273.15 [15]	6.010 [15]	
Ethanol	158.939[a]	4.928[a]	31.00[a]
	159.00 ± 0.006 [18]	4.931 ± 0.007 [18]	
	158.5 [16]	5.021 [16]	
Benzene	278.325[a]	9.818[a]	35.28[a]
	278.6 [17]	9.820 [17]	
The azeotropic mixture	147.212	0.4157	2.824
	275.591	1.293	4.692
	275.962	4.876	17.67

[a] Determined in this work.

Table 2
Experimental molar heat capacity of the azeotropic mixture

T (K)	$C_{p,\text{m}}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,\text{m}}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,\text{m}}$ (J K^{-1} mol^{-1})
79.427	41.401	183.583	81.364	273.393	245.612
83.267	42.562	186.047	82.206	274.684	531.582
87.121	44.204	188.474	83.622	275.267	992.367
90.884	45.609	190.900	83.293	275.526	1258.758
94.556	47.195	193.290	84.002	275.591	1647.875
98.159	48.890	195.662	84.603	275.807	1292.535
101.654	51.868	198.007	85.192	275.962	2712.216
104.942	58.150	200.317	85.798	276.110	1243.036
108.120	59.397	202.718	86.404	276.330	796.209
111.237	60.808	203.959	87.002	276.741	389.526
114.326	61.691	206.855	87.697	278.361	142.989
117.369	62.174	209.771	88.899	280.599	139.965
120.382	62.657	212.658	89.971	282.764	139.697
123.361	63.296	215.494	91.404	284.859	141.448
126.314	63.860	218.295	92.606	287.014	142.394
129.245	64.386	221.051	94.495	289.157	143.284
132.150	65.280	223.748	96.293	291.248	143.971
135.032	66.534	226.377	98.201	293.260	144.606
137.937	68.503	228.936	99.394	295.033	144.960
141.226	69.130	231.451	100.697	296.781	145.889
144.725	71.537	233.935	102.495	298.541	146.495
147.212	124.537	236.548	104.962	300.249	147.427
149.279	110.254	239.315	106.201	302.017	148.013
151.734	77.894	242.061	108.702	303.702	148.733
154.959	72.166	244.919	111.202	305.275	149.015
157.918	73.053	247.851	112.931	307.020	149.601
160.580	73.022	250.757	115.893	308.668	150.693
163.234	74.048	253.609	118.952	310.283	151.482
165.846	75.364	256.421	121.791	311.830	152.104
168.446	76.613	259.172	125.005	313.408	152.874
171.020	77.018	261.859	130.965	314.852	153.921
173.571	77.374	264.459	135.914	316.316	155.691
176.103	77.721	266.980	140.731	317.768	156.798
178.613	78.833	269.384	154.187		
181.110	79.979	271.577	177.389		

3.2. Thermodynamic data of glass and phase transitions

It can be seen from Fig. 4, that the heat-capacity jump was found in the temperature range from 98 to 104 K. In order to see clearly the change of the heat capacities, the inset figure B was used in Fig. 4. The heat capacity clearly changes before and after glass transition temperature [20]. The temperatures of the glass transition of the mixture were determined to be 102.850 K. The glass transition was found in the binary system composed of ethanol and benzene at

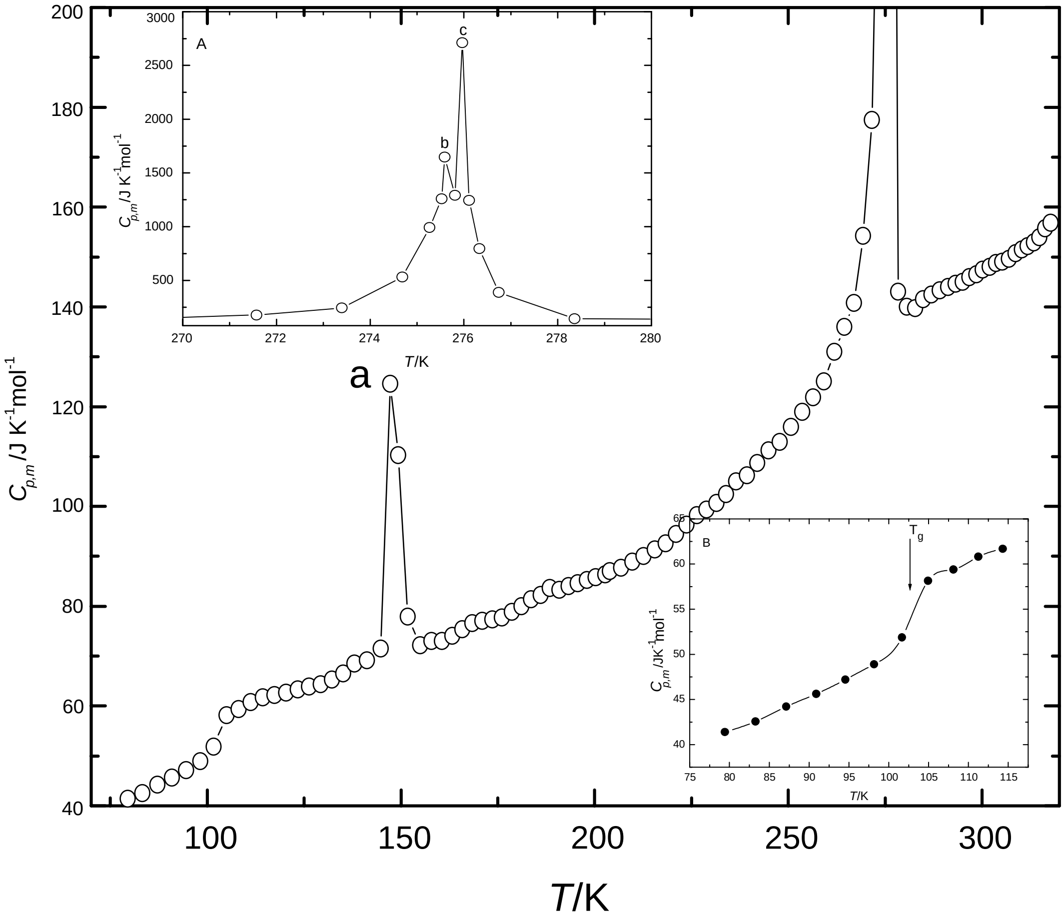

Fig. 4. Experimental molar heat capacity of the mixture. “a”, “b” and “c” degree the solid–liquid phase transitions of ethanol, water, and benzene, respectively. Inset A shows solid–liquid phase transitions of water (b), and benzene (c), respectively. Inset B shows glass phase transition of the mixture.

Table 3
Coefficients n_k and deviations δ

n_5	n_4	n_3	n_2	n_1	n_0	X	Ranges of temperature (K)	δ (J K^{-1} mol^{-1})
−0.6556	−1.1582	1.2152	1.5487	2.9017	63.518	$X = (T/K - 125)/15$	110–140	0.066
	5.7814	10.324	8.4372	21.978	89.121	$X = (T/K - 210)/55$	155–265	0.191
	1.3016	2.3116	0.8958	7.4035	147.130	$X = (T/K - 300)/20$	280–320	0.124

$\delta = \left(\sum(C_{p,\mathrm{m}}^{\mathrm{exp}} - C_{p,\mathrm{m}}^{\mathrm{fit}})^2/(s-1)\right)^{1/2}$, where $C_{p,\mathrm{m}}^{\mathrm{exp}}$ and $C_{p,\mathrm{m}}^{\mathrm{fit}}$ are experimental heat capacity values and fitted heat capacity values; s is the number of experimental points.

97.536 K [10]. Osamu et al. reported that the glass transition temperature (T_g), the heat-capacity jump at T_g, was found to be 97 K [18].

The glass transition temperature T_g of the azeotropic mixture is higher than that of pure ethanol, which is 97.46 K. T_g increases when the molecular structure becomes more rigid [21]. Glass transition temperature can be affected by the structure change of the system.

Fig. 4 shows that the molar heat capacity reaches maxima in temperature ranges from 140 to 155 K and 265 to 280 K corresponding to “a”, “b”, and “c”, respectively. The phase transition temperatures were determined to be 147.212, 275.591 and 275.962 K, which were corresponding to the solid–liquid phase transitions of ethanol, water, and benzene, respectively. Compared the data in Table 1, the phase transition temperatures of ethanol and benzene in the mixture are lower than those of pure ethanol and benzene. The addition of alcohol to water decrease both the freezing points [22]. But the phase transition temperature of water in the mixture is higher than that of pure water. This may be that the difference between the melting temperatures of water and benzene is only 5.45 K. The melting processes of water and benzene can be affected each other. The effect induces that the melting temperature

Table 4
Data of the thermodynamic functions of the azeotropic mixture

T (K)	$C_{p,\mathrm{m}}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	$H_{(T)} - H_{298.15\,\mathrm{K}}$ ($\mathrm{kJ\,mol^{-1}}$)	$S_{(T)} - S_{298.15\,\mathrm{K}}$ ($\mathrm{kJ\,mol^{-1}}$)
110	60.447	−22.042	−357.2
120	62.666	−21.425	−327.4
130	64.685	−20.789	−291.6
140	67.37	−20.128	−248.7
150	Phase transition		
160	72.306	−19.713	−245.9
170	75.246	−18.976	−236.8
180	78.48	−18.207	−227.2
190	81.849	−17.406	−216.9
200	85.348	−16.57	−206
210	89.121	−15.698	−194.4
220	93.464	−14.786	−182
230	98.826	−13.825	−168.7
240	105.806	−12.804	−154.5
250	115.156	−11.702	−139.1
260	127.779	−10.49	−122.6
270	Phase transition		
280	139.612	−3.663	−91.38
290	143.445	−1.617	−43.07
300	147.13	0.3608	10.26
310	151.426	2.273	68.89
320	159.043	4.125	133.1
298.15	146.451	0	0

of water increases and the melting temperature of benzene decreases.

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

3.3. *Thermodynamic functions of the mixture*

The thermodynamic functions of the mixture 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.

3.4. *Excess thermodynamic functions of the azeotrope*

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

$$C_{p,\mathrm{m}}^{\mathrm{E}} = C_{p,\mathrm{m}} - x\,C_{p,\mathrm{m},1}^{*} - y\,C_{p,\mathrm{m},2}^{*} - (1-x-y)C_{p,\mathrm{m},3}^{*} \tag{4}$$

where $C_{p,\mathrm{m},1}^{*}$, $C_{p,\mathrm{m},2}^{*}$, and $C_{p,\mathrm{m},3}^{*}$ are the molar heat capacities for water, ethanol and benzene, respectively, and $C_{p,\mathrm{m}}$ the molar heat capacity of a mixture at the mole fraction of water x, ethanol y, and benzene $(1-x-y)$. The values of $C_{p,\mathrm{m}}^{\mathrm{E}}$ were calculated in the liquid phase and listed in Table 5.

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

Table 5
Excess thermodynamic functions of the azeotropic mixture

T (K)	$C_{p,\mathrm{m}}^{\mathrm{E}}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	$H_{\mathrm{m}(T)}^{\mathrm{E}} - H_{298.15\,\mathrm{K}}^{\mathrm{E}}$ ($\mathrm{kJ\,mol^{-1}}$)	$S_{\mathrm{m}(T)}^{\mathrm{E}} - S_{298.15\,\mathrm{K}}^{\mathrm{E}}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)
280	29.994	−4.172	−14.42
285	30.272	−3.091	−10.6
290	30.546	−1.959	−6.661
295	30.727	−0.774	−2.61
300	30.849	0.4648	1.554
305	31.068	1.76	5.836
310	31.660	3.115	10.24
315	33.026	4.535	14.79
320	35.689	6.026	19.48
298.15	30.804	0	0

$$C_{p,\mathrm{m}}^{\mathrm{E}} = 2.3339X^{3} + 1.9877X^{2} + 0.5165X + 30.721 \tag{5}$$

where $\delta = 0.137\,\mathrm{J\,K^{-1}\,mol^{-1}}$, $X = (T/K - 300)/20$.

From Eq. (5), it can be derived that the value of $C_{p,\mathrm{m}}^{\mathrm{E}}$ increases with temperature increasing in the temperature range from 280 to 320 K. The larger the $C_{p,\mathrm{m}}^{\mathrm{E}}$, the more different the interaction between the molecules in the system. Positive $C_{p,\mathrm{m}}^{\mathrm{E}}$ indicates more structure in the solution [23].

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 5.

4. Conclusions

The molar heat capacity of the azeotropic mixture composed of water, ethanol, and benzene were measured from 80 to 320 K. The glass transition temperature and phase transition temperatures were determined to be 102.850, 147.212, 275.591 and 275.962 K, respectively. The enthalpies and entropies of phase transitions were derived.

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