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Articles

Thermodynamic Investigation of the Azeotropic Binary Mixture Water + *n*-Propanol

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Molar heat capacities of the azeotropic mixture in the binary system {water ($x = 0.568$) + *n*-propanol ($x = 0.432$)}were measured with an adiabatic calorimeter in the temperature range from (80 to 320) K. The functions of the heat capacity with respect to the thermodynamic temperature were established. A glass transition was observed at 102.037 K. The solid−liquid-phase transition of the azeotropic mixture took place in the temperature range from (237.075 to 262.424) K. The corresponding enthalpy and entropy of the solid−liquid-phase transition were calculated to be 5.869 $\text{kJ}\cdot\text{mol}^{-1}$ and 22.73 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, respectively. The thermodynamic functions and the excess thermodynamic functions of the azeotropic mixture relative to a temperature of 298.15 K were derived on the basis of the relationships of the thermodynamic functions and the function of the measured heat capacity with respect to temperature.

Introduction

Extensive thermodynamic studies have been carried out on aqueous solutions of *n*-propanol.[1−3] However, the heat capacities of azeotropic mixtures were not studied until recently.

Heat capacity is one of the most 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 to establish energy balances, obtain entropy and enthalpy values, and study phase transitions. Moreover, the 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.[4]

The binary system water + *n*-propanol shows a minimum boiling point azeotropic mixture at 360.1 K with a water mole fraction of 0.568.[5] In this study, the molar heat capacity of the azeotropic mixture {(0.568)water + (0.432)-*n*-propanol} was measured by an adiabatic calorimeter in temperature range of (80 to 320) K. The thermodynamic functions of the azeotropic mixture were derived on the basis of the relationships of the thermodynamic functions and the function of the measured heat capacity with respect to temperature.

Experimental Section

Chemicals. The *n*-propanol used for the calorimetric study was purchased from Shenyang Chemical Agent Factory, and its purity was better than 99.8 wt %. The principal impurities were a carbonyl compound and an unsaturated compound, the contents of which were all smaller than 0.02%. The water used to prepare the azeotropic mixture was deionized and distilled twice. The azeotropic mixture consists of (0.568)water and (0.432)*n*-propanol and was prepared by a weighing method, in which 0.568 and 0.432 are the molar fractions of water and *n*-propanol in the azeotropic mixture, respectively.

Apparatus and Procedures. The mass of the azeotropic mixture used for heat capacity measurements was 29.7902 g. Heat capacity measurements were carried out in a high-precision automatic adiabatic calorimeter described in detail elsewhere.[6,7] 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 the sample cell and the inner shield was $\lesssim 0.5$ 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. The temperature increment in a heating

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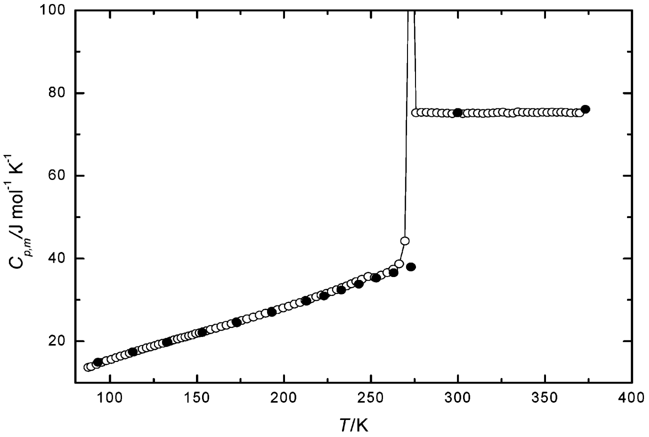

Figure 1. Molar heat capacities of water: ○, this work; ●, ref 9.

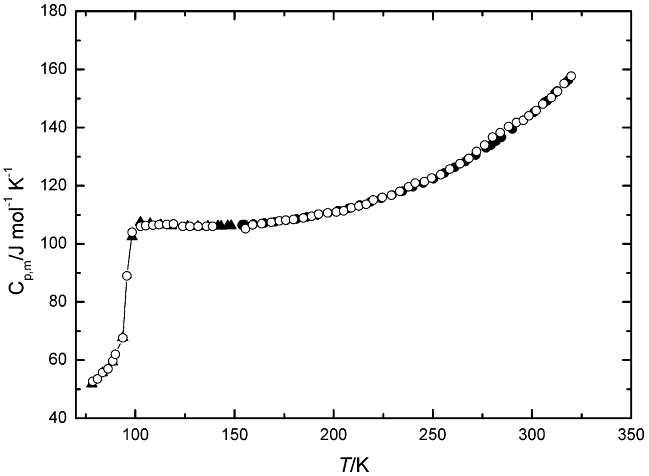

Figure 2. Molar heat capacities of n-propanol: ○, this work; ●, Counsell et al.[10] in the liquid phase; ▲, Counsell et al.[10] in the glass phase.

period was (2 to 4) K, and the temperature drift was maintained at about 10^{-3} K min^{-1} in the equilibrium period. All of the data were automatically picked up through a data acquisition/switch unit (model 34970A, Aglient) and processed by a computer.

Results and Discussion

Heat Capacities of **α*-Al_2O_3*, *Water, and n-Propanol.*** To verify the reliability of the adiabatic calorimeter, we measured the molar heat capacities for the reference standard material α-Al_2O_3, water, and n-propanol. The deviations of our experimental results from the values in ref 8 were within ±0.2% in a temperature range of (80 to 400) K for α-Al_2O_3. Plots of molar heat capacities of water and n-propanol as a function of temperature are given in Figures 1 and 2. To compare the results of the heat capacities of water and n-propanol measured in our laboratory with those in refs 10 and 11, we give, in Figures 1 and 2, the data from heat capacities obtained from refs 9 and 10. 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[11] given by

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

Table 1. Data of the Transition Temperature, Enthalpy, and Entropy of the Solid−Liquid Phase Transition Determined in this Work

	T_{trans}	ΔH_{trans}	ΔS_{trans}
	K	kJ·mol^{-1}	J·mol^{-1}·K^{-1}
water	273.10 ± 0.18 273.15[9]	6.005 6.010[9]	21.99 ± 0.01
n-propanol	148.75 ± 0.01[10]	5.372 ± 0.004[10]	
azeotropic mixture	258.16 ± 1.08	5.869	22.73 ± 0.09

and

$$\Delta_{\text{trans}}S_{\text{m}} = \frac{\Delta_{\text{trans}}H_{\text{m}}}{T_{\text{trans}}} \qquad (2)$$

where Q is the total amount of heat introduced into the sample cell; n the amount of the substance in the sample; T_{trans} is the phase-transition temperature, T_1 is slightly below T_{trans}; T_2 is slightly above T_{trans}; and $C_{p,\text{m(S)}}$, $C_{p,\text{m(L)}}$, and C_0 are the heat capacity in the solid and liquid states and heat capacity of the empty cell, respectively. The phase-transition temperatures and enthalpies of water and n-propanol are given in Table 1. For water, the overall measuring precision may be estimated to be ±0.3% by means of the deviations of the experimental data from the smoothed values of the polynomial equations. By comparing the results of this research with those of another investigation,[9] we have assessed the accuracy of the apparatus. The root-mean-square σ of the percentage deviation of the smoothed values from the reference[9] is used. The root-mean-square σ was calculated to be 0.4% for water from (80 to 370) K.[12] With the same method, the measuring precision may be estimated to be ±0.5% by means of the deviations of the experimental data from the smoothed values of the polynomial equations. The root-mean-square σ of the smoothed values from the reference results[10] was calculated to be 0.4% for n-propanol from (150 to 320) K.

Molar Heat Capacity of the Azeotropic 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 Figure 3. No thermal anomaly was observed and no phase transition took place in the temperature ranges from (110 to 235) K and (262 to 320) K, respectively.

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

For (110 to 235) K

$$C_{p,\text{m}} = 8.3558X^2 + 19.399X + 70.521 \qquad (3)$$

where $C_{p,\text{m}}$/(J·K^{-1}·mol^{-1}) is the molar heat capacity of the azeotropic mixture, T/K is thermodynamic temperature, $X = (T/\text{K} - 172.5)/62.5$ is the reduced temperature, and δ = 0.583 J·mol^{-1}·K^{-1} is the standard deviation.

To facilitate fitting, temperature T was replaced by reduced temperature X,

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

where T_{max} and T_{min} are the maximum and the minimum temperatures in the experiment. Thus, X is always in the range of $-1 \leq X \leq 1$.

Table 2. Molar Heat Capacity and Temperature Drift Rate of the Azeotropic Mixture

T	$C_{p,\mathrm{m}}$	$(\mathrm{d}T/\mathrm{d}t)$	T	$C_{p,\mathrm{m}}$	$(\mathrm{d}T/\mathrm{d}t)$
K	$\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$	$\mathrm{mK{\cdot}min^{-1}}$	K	$\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$	$\mathrm{mK{\cdot}min^{-1}}$
80.271	33.870	−1.42	192.065	76.697	−0.13
82.790	33.960	−2.14	193.497	77.401	−1.05
85.261	35.031	0.84	194.935	78.002	−0.98
87.677	36.125	1.36	196.340	78.303	0.98
90.044	37.194	0.87	197.752	78.798	0.98
92.365	38.528	1.05	199.707	79.707	0.62
94.654	39.654	−1.02	202.210	80.523	0.38
96.900	40.812	−0.78	204.697	81.873	−0.68
99.098	42.737	−1.44	207.142	83.191	−0.86
101.195	47.111	4.15	209.536	84.356	−0.98
103.092	55.027	−6.26	212.085	85.931	−0.72
104.883	57.436	−4.12	214.729	87.192	−0.98
106.661	57.958	−1.24	217.152	88.804	−0.92
108.421	58.191	0.64	219.241	89.501	0.02
110.177	58.452	−0.76	221.502	90.495	−1.02
111.923	58.765	0.88	223.763	91.798	−0.78
113.662	58.903	−0.17	225.638	93.203	−1.80
115.394	59.224	1.04	227.404	94.404	−0.78
117.123	59.372	−2.34	229.727	96.192	−1.32
118.844	59.548	−2.28	232.228	97.798	−1.50
120.556	60.000	−1.80	234.681	100.321	−1.32
122.267	60.188	−2.04	237.075	105.427	1.38
123.968	60.268	−2.22	239.391	110.404	−2.16
125.659	60.535	−1.98	241.572	115.293	−0.90
127.341	61.103	0.54	243.702	120.744	−1.50
129.037	61.192	1.14	245.785	126.903	−0.30
130.718	61.366	−0.78	247.786	133.498	−0.72
132.404	61.803	−0.78	249.675	144.582	−0.78
134.082	62.495	−0.12	251.441	159.139	−0.72
135.760	62.589	0.12	253.072	178.581	−3.01
137.432	62.936	0.42	254.556	202.474	−6.36
139.100	63.212	0.96	255.891	229.648	−7.48
140.773	63.311	1.26	257.085	260.744	−8.06
142.443	63.889	2.88	258.166	289.323	−10.66
144.126	64.300	−0.18	259.239	274.021	−5.08
145.834	64.546	0.28	260.547	177.555	−4.12
147.676	64.596	1.22	262.424	106.611	−0.42
149.612	65.002	−0.99	264.631	107.350	0.24
151.512	65.192	1.62	266.824	108.315	−1.88
153.221	65.495	1.08	269.021	109.169	0.96
154.844	65.707	−0.54	271.190	109.878	0.39
156.425	66.126	−2.01	273.354	110.578	−0.74
157.976	66.410	−1.68	275.499	111.101	−0.56
159.525	67.216	−1.80	277.637	111.891	0.56
161.063	67.494	1.98	279.757	112.628	0.62
162.592	67.873	−1.74	281.866	113.367	1.98
164.117	68.402	1.44	283.945	114.173	−0.68
165.640	68.757	−1.56	286.004	114.781	−0.38
167.152	69.298	1.14	288.064	115.381	−1.07
168.670	69.680	0.00	290.078	116.090	−1.48
170.164	70.289	−1.50	292.068	116.596	0.82
171.668	70.782	−1.14	294.062	117.181	−0.36
173.159	70.901	−1.54	296.025	117.949	−0.92
174.644	71.293	0.46	298.019	118.533	−1.44
176.114	71.798	−1.46	300.046	119.167	−1.56
177.622	72.358	0.38	302.068	119.939	−1.72
179.074	72.704	−0.12	304.118	120.614	−0.68
180.544	73.400	−2.37	306.151	121.223	−0.08
181.993	73.709	−2.44	308.184	121.921	−1.86
183.450	74.001	0.38	310.211	122.561	−0.44
184.892	74.293	1.20	312.236	123.003	−0.96
186.328	74.899	−1.38	314.262	123.589	0.44
187.757	75.202	−2.16	316.273	124.290	0.62
189.189	75.798	−1.56	318.277	124.811	0.86
190.624	76.101	−0.03			

For (262 to 320) K,

$$C_{p,\mathrm{m}} = -0.3859X^2 + 9.4104X + 116.360 \qquad (5)$$

where $X = (T/\mathrm{K} - 291)/29$ and $\delta = 0.092\ \mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$.

Thermodynamic Data of Glass and Phase Transitions. It can be seen from Figure 3 that the heat capacity jump was found in the temperature range from (99.098 to 103.092) K. To see clearly the change in the heat capacities, the inset was used in Figure 3. The heat capacity changes clearly before and after the glass-transition temperature.[13] Then, the glass transition took place in the temperature range from (99.098 to 103.092) K. The curves of the temperature drift rate with respect to temperature were shown in Figure 4, and the values of the temperature drift rates were given in Table 2. Figure 4 shows that the temperature drift rate became larger during the glass transition. The temperature drift rates are determined to be less than ±2 $\mathrm{mK{\cdot}min^{-1}}$ at other temperatures, except that the temperature of the phase transition shows that the adiabatic conditions were better. Therefore, the experimental results are accurate and reliable. The temperature of the glass transition of the mixture was determined to be 102.037 K, which corresponds to the maximum of the molar heat capacity drift rate.

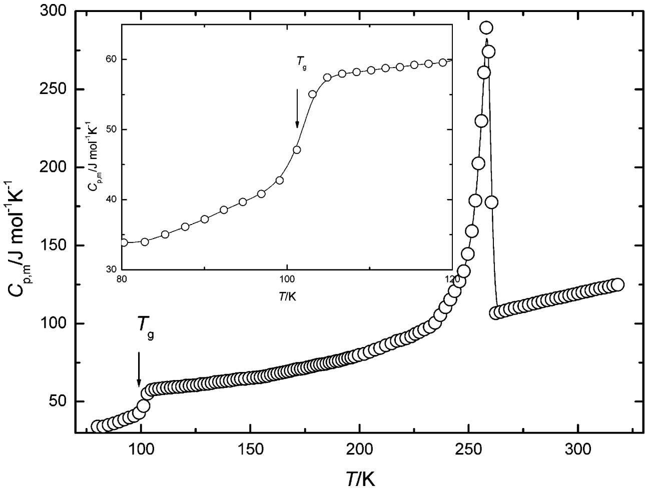

Figure 3. Molar heat capacities of (0.568)water + (0.432)*n*-propanol. The inset shows the glass transition of the azeotropic mixture.

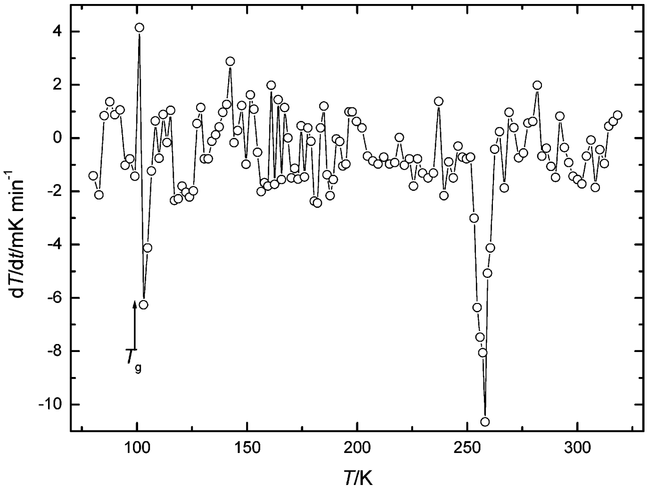

Figure 4. Temperature drift rate during the determination of the heat capacity of the azeotropic mixture.

The molar heat capacity reaches its maximum in the temperature range from (237.076 to 262.424) K, as shown in Figure 3. The phase transition took place in this temperature range. The temperature drift rate is given in Figure 4. The temperature drift rate reached its minimum in the same temperature range corresponding to that of the phase transition. This may be because the azeotropic mixture needed to absorb energy during the phase transition. Thus, the temperature drift rate became negative. The phase-transition temperatures were determined to be

Table 3. Data of the Thermodynamic Functions of the Azeotropic Mixture

T	$C_{p,\mathrm{m}}$	$[H_{(T)} - H_{(298.15\ \mathrm{K})}]$	$[S_{(T)} - S_{(298.15\ \mathrm{K})}]$
K	J·mol^{-1}·K^{-1}	kJ mol^{-1}	J·mol^{-1}·K^{-1}
110	59.478	−17.762	−71.10
120	60.122	−17.164	−66.49
130	61.193	−16.558	−62.25
140	62.693	−15.939	−58.35
150	64.620	−15.303	−54.75
160	66.975	−14.645	−51.43
170	69.758	−13.962	−48.36
180	72.969	−13.249	−45.51
190	76.608	−12.501	−42.86
200	80.674	−11.715	−40.37
210	85.168	−10.886	−38.04
220	90.091	−10.01	−35.82
230	95.440	−9.083	−33.71
240			
250		phase transition	
260			
270	109.343	−3.214	−10.98
280	112.735	−2.101	−7.05
290	116.035	−0.956	−3.15
300	119.243	0.220	0.71
310	122.360	1.428	4.55
320	125.385	2.667	8.35
298.15	118.657	0.000	0.00

258.166 K, which corresponds to the solid−liquid-phase transition of the azeotropic mixture.

Thermodynamic investigations have been carried out in our laboratory on azeotropic mixtures composed of water and cyclohexane[14] and ethanol and benzene.[15] The solid−liquid phase transitions, which correspond to pure compounds such as water and cyclohexane and ethanol and benzene, were found in the azeotropic systems, but in the binary system of water and n-propanol, only one kind of solid−liquid-phase transition was observed. The reason may be that the hydrogen bond of the bulk is strong enough to retain the hydrogen bond connectivity throughout the entire bulk, called the "mixing scheme" in the azeotropic mixture composed of water and n-propanol.[2] This leads the compounds composed of the azeotropic mixture to melt at the same temperature.

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 Azeotropic Mixture. The thermodynamic functions of the azeotropic mixture were calculated on the basis of the function of the molar heat capacity with respect to the thermodynamic temperature and the relationships of the thermodynamic functions. The results are given in Table 3.

Excess Thermodynamic Functions of the Azeotropic Mixture. The excess molar heat capacity of the binary system of (x)water + (1 − x)n-propanol was calculated by the following equation

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

where $C^{*}_{p,\mathrm{m},1}$ and $C^{*}_{p,\mathrm{m},2}$ are the molar heat capacities of water and n-propanol, respectively, and $C_{p,\mathrm{m}}$ is the molar heat capacity of a mixture at the mole fraction of water x. The values of $C^{\mathrm{E}}_{p,\mathrm{m}}$ were calculated in the liquid phase and are listed in Table 4 and shown in Figure 5. Positive $C^{\mathrm{E}}_{p,\mathrm{m}}$ indicates more structure in the solution.[16]

Our present result of $C^{\mathrm{E}}_{p,\mathrm{m}}$ = 13.685 J·mol^{-1}·K^{-1} is roughly in agreement with $C^{\mathrm{E}}_{p,\mathrm{m}}$ = 13.580 J·mol^{-1}·K^{-1} at 298.15 K, which was calculated from the literature.[1]

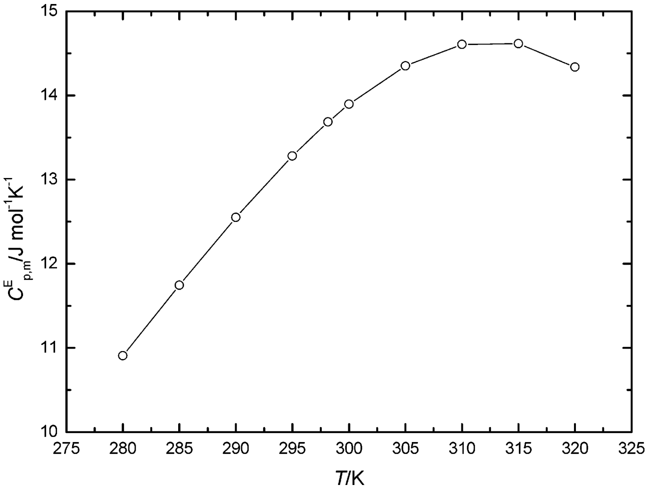

Figure 5. Excess molar heat capacities of the azeotropic mixture.

Table 4. Excess Thermodynamic Functions of the Azeotropic Mixture

T	$C^{\mathrm{E}}_{p,\mathrm{m}}$	$[H^{\mathrm{E}}_{\mathrm{m}}(T) - H^{\mathrm{E}}_{298.15\ \mathrm{K}}]$	$[S^{\mathrm{E}}_{\mathrm{m}}(T) - S^{\mathrm{E}}_{298.15\ \mathrm{K}}]$
K	J·mol^{-1}·K^{-1}	J·mol^{-1}	J·mol^{-1}·K^{-1}
280	10.908	−224.49	−0.583
285	11.745	−167.86	−0.436
290	12.550	−107.10	−0.277
295	13.281	−42.48	−0.109
300	13.896	25.52	0.065
305	14.352	96.21	0.241
310	14.606	168.70	0.418
315	14.615	241.86	0.592
320	14.338	314.37	0.762
298.15	13.685	0	0

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

$$C^{\mathrm{E}}_{p,\mathrm{m}} = -0.4546X^3 - 1.2734X^2 + 2.1696X + 13.896 \quad (7)$$

where $X = (T/\mathrm{K} - 300)/20$ and $\delta = 0.000$ J·mol^{-1}·K^{-1}.

From eq 7, it can be derived that $C^{\mathrm{E}}_{p,\mathrm{m}}$ reaches a maximum value of 14.644 J·mol^{-1}·K^{-1} at T = 312.719 K. The larger value of $C^{\mathrm{E}}_{p,\mathrm{m}}$ shows that there are more interactions 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 azeotropic mixture such as the 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 the thermodynamic temperature. The results are listed in Table 4.

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