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Thermodynamic investigation of the azeotropic system The binary system of (water + cyclohexane)

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Abstract

The molar heat capacities of the azeotropic system (0.30 mol water + 0.70 mol cyclohexane) were measured by an adiabatic calorimeter in temperature range of 78–320 K. The functions of the heat capacity with respect to thermodynamic temperature were established. The phase transition took place in temperature ranges of 184–190, 271–276 and 276–283 K corresponding to the solid–solid phase transition of cyclohexane, solid–liquid phase transition of water and solid–liquid phase transition of cyclohexane, respectively. The corresponding enthalpies and entropies of the phase transition were found to be 4.559 kJ mol^{-1}, 24.510 ± 0.065 J K^{-1} mol^{-1}; 2.576 kJ mol^{-1}, 9.454 ± 0.041 J K^{-1} mol^{-1}; and 2.040 kJ mol^{-1}, 7.296 ± 0.029 J K^{-1} mol^{-1}, respectively. The thermodynamic functions and the excess thermodynamic functions of the azeotrope were derived based on the relationships of the thermodynamic functions.

Keywords: Azeotropic system; Water; Cyclohexane; Heat capacity; Adiabatic calorimetry

1. Introduction

Behavior of the azeotropic systems 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 systems was extensively studied [2–8]. However, the heat capacities of azeotropic systems were not studied until recently. The system of water + cyclohexane shows a minimum boiling point azeotrope at 342.6 K with water mole fraction 0.30 at 1 atm [6].

In this study, the molar heat capacity of the azeotropic system of water and cyclohexane was measured by an adiabatic calorimeter in temperature range of 80–320 K at 1 atm. The thermodynamic functions of the azeotrope were derived based on the relationships of the thermodynamic functions.

2. Experimental

2.1. Experimental materials

The cyclohexane used for calorimetric study was purchased from Shenyang Chemical Agent Factory, and its purity was better than 99.8%. The purity of cyclohexane was determined to be 99.95 mol% from the observed melting-point curve [9,10]. The water used for preparing the azeotrope was deionized and distilled

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twice. The azeotropic system consists of 30 mol% water and 70 mol% cyclohexane and prepared by weighing method.

2.2. Adiabatic calorimeter

Heat-capacity measurements were carried out in a high-precision automatic adiabatic calorimeter described in detail elsewhere [11]. The principle of the calorimeter is based on the Nernst step-wise 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 6 cm^3. Four 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 at the bottom of the sample cell. The heater wire was wound on the surface of the cell. The lid of the cell with a copper capillary was sealed to the sample cell with cycleweld after the sample was loaded in it. 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 be 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 alternately measured. 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 picked up through a data acquisition/switch unit (model: 34970A, Aglient, USA) and processed by a computer. The heat capacities of the celll for an empty sample were shown in Fig. 1.

To verify the reliability of the adiabatic calorimeter, the molar heat capacities for the reference standard material α-Al_2O_3, water and cyclohexane were measured. The deviations of our experimental results from the recommended values of the National Bureau of Standards [12] 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 and cyclohexane as a function of temperature are given in Figs. 2 and 3.

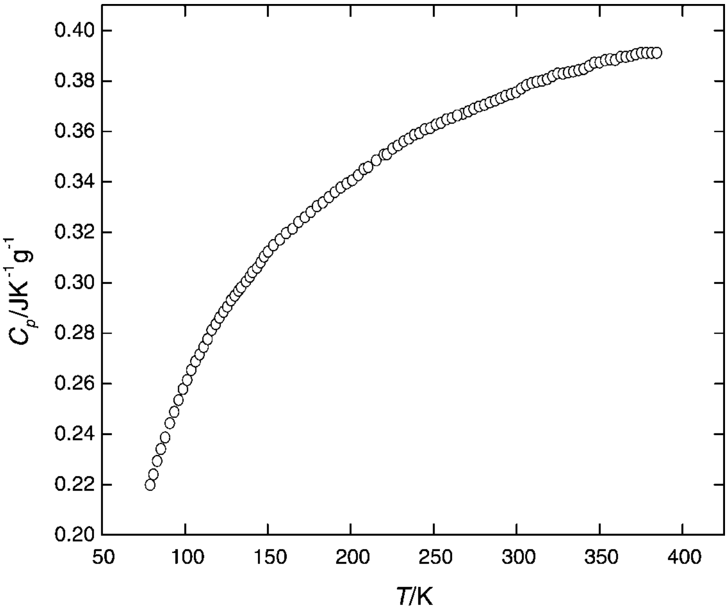

Fig. 1. Experimental heat capacities of the cell for an empty sample as a function of temperature.

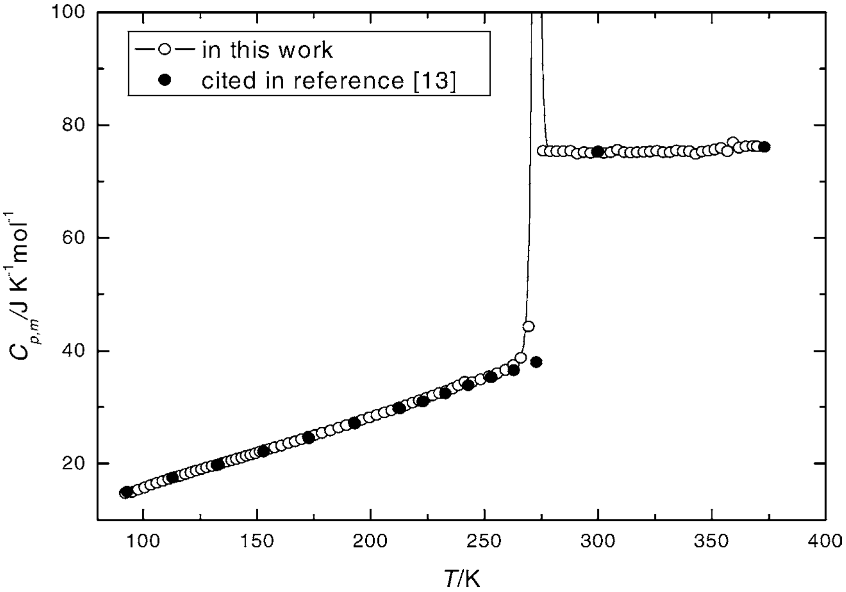

Fig. 2. Experimental molar heat capacities of H_2O as a function of temperature.

In order to compare the results of the heat capacities of water and cyclohexane measured in our laboratory with [13,14], the data of heat capacities gained from [13,14] are given in Figs. 2 and 3 as well. The enthalpy $\Delta_{\text{trans}}H_m$ and entropy $\Delta_{\text{trans}}S_m$ of the phase transition were calculated according to the relationship as follows [16]:

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

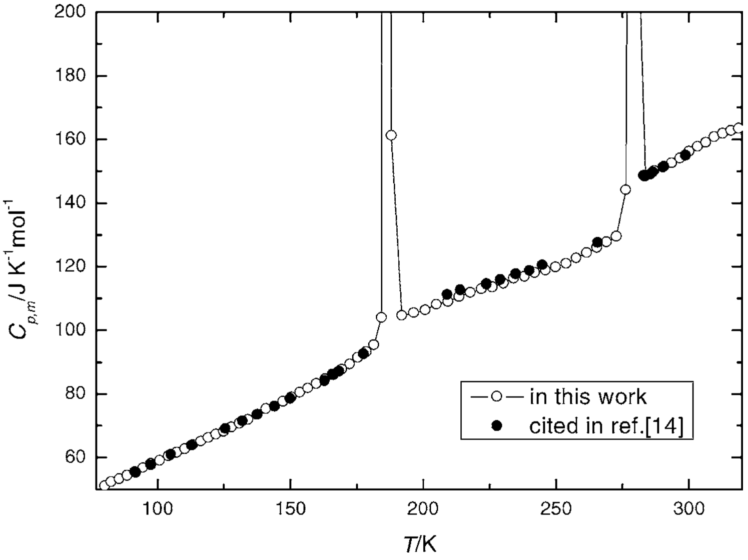

Fig. 3. Experimental molar heat capacities of C_6H_{12} as a function of temperature.

Table 1
Data of the 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})
Water	272.8 ± 0.7	5.927	21.720 ± 0.06
	273.15 [13]	6.012 [13]	
Cyclohexane	186.9 ± 1.1	6.694	35.820 ± 0.20
	185.9 [14]	6.714 [14]	
	186.1 [15]	6.735 [15]	
	279.6 ± 1.1	2.634	9.421 ± 0.036
Azeotrope	186.0 ± 0.5	4.589	24.510 ± 0.065
	272.5 ± 1.2	2.576	9.450 ± 0.04
	279.6 ± 1.1	2.040	7.296 ± 0.029

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

where Q is the total amount of heat introduced into the sample; n the amount of substance of the sample; T_{trans} the phase transition temperature; T_1 is below T_{trans}; T_2 is above T_{trans}; $C_{p,m(\mathrm{S})}$, $C_{p,m(\mathrm{L})}$ are the heat capacities in solid and liquid states; and C_0 is the heat capacity of empty cell. The phase transition temperatures and enthalpies of water and cyclohexane are given in Table 1. From Figs. 2 and 3 and Table 1, it can be shown that the molar heat capacities, the transition temperature and enthalpy determined in our laboratory are in excellent agreement with the data cited from [13–15].

The mass of the azeotrope used for heat-capacity measurements was 4.0020 g.

3. Result and discussion

3.1. Molar heat capacity of the azeotrope

The molar heat capacities of the azeotrope were determined by using the adiabatic calorimeter in the temperature range of 78–320 K. The results of the molar heat capacities are shown in Table 2 and Fig. 4. No thermal anomaly was observed or no phase transition took place in the temperature ranges of 78–181.5, 190–268 and 287–320 K, respectively.

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

$$78\text{–}182\,\mathrm{K} \quad C_{p,m} = 0.3204T + 12.585 \qquad (3)$$

$$190\text{–}268\,\mathrm{K} \quad C_{p,m} = 0.2392T + 35.083 \qquad (4)$$

$$287\text{–}320\,\mathrm{K} \quad C_{p,m} = 0.3146T + 36.842 \qquad (5)$$

where $C_{p,m}$ (J K^{-1} mol^{-1}) is the molar heat capacity of the azeotropic system and T (K) is the thermodynamic temperature.

3.2. Thermodynamic data of phase transition

The molar heat capacity reaches maxima in the temperature ranges of 184–190, 271–276 and 276–283 K as shown in Fig. 4. The azeotropic system took place phase transition in these temperature ranges. Insets 1 and 2 in Fig. 4 show clear change of the molar heat capacity of the azeotrope in the temperature ranges of the phase transitions. The temperature drift rate in the process of the determination of heat capacity is given in Fig. 5. The temperature drift rate reached the minima in the same temperature ranges corresponding to the phase transition. The reason is that the azeotrope needs to absorb energy during the phase transition. Thus, the temperature drift rate becomes negative. The phase transition temperatures were determined to be 186.0 ± 0.5 K, 272.5 ± 1.2 K and 279.6 ± 1.1 K which were corresponding to the solid–solid phase transition of cyclohexane, solid–liquid phase transition of water and solid–liquid phase transition of cyclohexane. Compared with the data of Table 1, the phase transition temperatures of water and cyclohexane were not affected by each other.

The enthalpies and entropies of the phase transition were calculated according to Eqs. (1) and (2). The data are given in Table 1. The ratios of $\Delta_{\mathrm{trans}} H_m$ of the azeotrope to the corresponding $\Delta_{\mathrm{trans}} H_m$ of pure cyclohexane and pure water were found to be $4.589/6.694 = 0.68$, $2.576/5.927 = 0.43$, $2.040/2.634 = 0.77$, respectively, in which 4.589, 2.576 and 2.040 J mol^{-1} are enthalpies of phase change of the azeotrope, and 6.694, 5.927 and 2.634 J mol^{-1} are enthalpies of phase change of pure cyclohexane and pure water determined in our laboratory, respectively. Compared with the composition of the azeotrope, these data of the ratios show that water content in the system affects little the solid–solid phase

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

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	dT/dt (mK min^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	dT/dt (mK min^{-1})
78.710	37.590	0.42	193.227	81.971	−0.30
81.033	38.691	0.36	196.320	82.482	−0.36
83.704	39.593	0.18	199.393	82.931	−0.48
86.922	40.689	0.06	202.443	83.667	0.12
90.252	41.759	0.06	205.477	84.430	0.18
93.555	42.836	0.02	208.492	84.870	0.06
96.654	43.911	0.00	211.486	85.516	0.36
99.725	44.831	−0.24	214.462	86.305	0.36
103.036	45.790	−0.54	217.416	86.949	0.36
106.578	46.942	−0.12	220.351	87.606	0.36
110.040	48.068	−0.18	223.268	88.300	0.30
113.424	49.032	−0.30	226.161	89.100	0.54
116.740	49.943	−0.42	229.022	89.800	1.92
119.992	50.855	−0.60	231.879	90.200	1.20
123.185	51.765	−0.60	234.716	91.000	0.72
126.324	52.711	−0.60	237.528	91.400	1.26
129.411	53.653	−0.54	240.310	92.000	0.54
133.029	54.719	−1.02	243.063	92.800	0.84
137.153	56.036	−0.66	245.829	93.557	0.72
141.202	57.349	−0.90	248.586	94.250	0.84
145.171	58.593	−1.02	251.327	94.968	0.72
149.067	59.832	−0.78	254.049	95.709	0.72
152.898	61.140	−0.48	256.753	96.559	1.08
156.669	62.383	−0.54	260.075	97.552	0.60
160.379	63.597	−0.66	263.994	98.735	0.54
164.029	64.936	−0.54	267.868	100.694	0.54
167.635	66.299	−0.54	271.283	149.696	−0.78
171.200	67.518	−1.14	272.800	8198.698	−1.08
174.704	68.901	−0.96	272.848	13207.000	−3.72
178.154	70.519	−0.84	273.671	5313.338	−4.90
181.549	72.177	−0.96	276.244	121.573	−5.60
184.549	108.130	−4.62	278.493	461.044	−7.14
185.508	124.025	−4.78	279.140	1941.865	−6.42
185.882	2455.006	−4.92	279.297	2844.097	−5.64
185.941	4940.514	−4.20	280.727	159.110	0.48
185.961	5455.634	−4.80	283.806	126.565	0.72
185.969	5527.408	−4.86	287.107	127.000	0.36
185.976	5497.093	−4.92	290.376	128.200	0.54
185.980	5755.098	−4.44	293.623	129.400	−0.36
185.988	5736.809	−4.44	296.843	130.300	0.42
185.998	5044.342	−4.68	300.058	131.430	−0.24
186.021	3730.913	−5.40	303.242	132.273	−0.12
186.296	647.715	−29.22	306.410	133.144	−0.48
186.498	124.642	−15.67	309.555	134.021	−0.42
187.328	117.043	−3.00	312.902	135.147	−0.36
190.107	80.722	−0.42	316.372	136.600	−0.40

transition of cyclohexane. However, the solid–liquid phase transition of water and cyclohexane are affected each other. The reason may be that the solid–solid phase transition of cyclohexane is influenced little by the ice in the azeotrope. The interval of the temperatures of the solid–liquid phase transitions of water and cyclohexane is about only 7 K. So that they may affect each other during the phase transition.

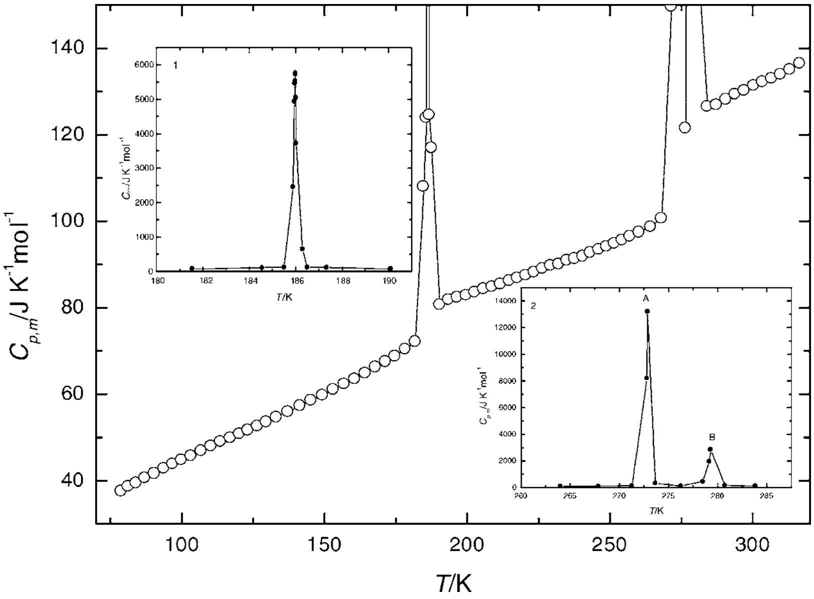

Fig. 4. Experimental molar heat capacity of 30 mol% water + 70 mol% cyclohexane. Insets 1 and 2 show solid–solid phase transition of cyclohexane and solid–liquid phase transition of water as A and solid–liquid phase transition of cyclohexane as B in inset 2, respectively.

3.3. Thermodynamic functions of the azeotrope

The thermodynamic functions of the azeotropic system 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 3. The values of $S_T - S_{298.15\,\mathrm{K}}$ are increasing with increasing temperature. These show that the molecules of the azeotropic system are becoming more active at higher temperature.

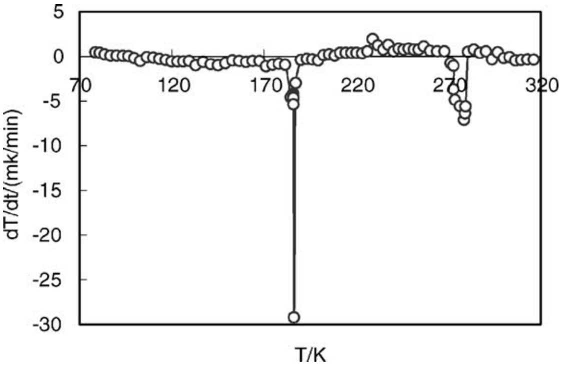

Fig. 5. Temperature drift rate of determination of heat capacity of the azeotrope.

3.4. Excess thermodynamic functions of the azeotrope

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

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

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

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

$$C^{\mathrm{E}}_{p,m} = 0.1286X^2 - 0.0878X + 0.0887 \qquad (7)$$

$$R^2 = 1, \quad X = \frac{T - 302.5}{17.5}$$

The temperature T was replaced by the reduced temperature X

$$X = \frac{T - (T_{\max} + T_{\min})/2}{(T_{\max} - T_{\min})/2} \qquad (8)$$

Table 3
The data of the thermodynamic functions of the azeotrope

T (K)	$C_{p,m}$ (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})	$-[G_T - G_{298.15\,\mathrm{K}}]$ (kJ mol^{-1})
80	38.217	−24.205	−119.728	14.627
90	41.421	−23.807	−115.041	13.453
100	44.625	−23.376	−110.511	12.325
110	47.829	−22.914	−106.108	11.242
120	51.033	−22.420	−101.809	10.203
130	54.237	−21.893	−97.598	9.206
140	57.441	−21.335	−93.461	8.251
150	60.645	−20.745	−89.389	7.336
160	63.849	−20.122	−85.372	6.463
170	67.053	−19.468	−81.405	5.629
180	70.257	−18.781	−77.482	4.834
190	80.531	−14.116	−52.387	4.163
200	82.923	−13.299	−48.195	3.660
210	85.315	−12.458	−44.092	3.199
220	87.707	−11.593	−40.067	2.778
230	90.099	−10.704	−36.116	2.397
240	92.491	−9.791	−32.231	2.055
250	94.883	−8.854	−28.407	1.752
260	97.275	−7.893	−24.639	1.487
270	Phase transition			
280	Phase transition			
290	128.076	−1.054	−3.585	0.015
300	131.222	0.242	0.810	0.001
310	134.368	1.570	5.164	0.031
320	137.514	2.930	9.480	0.104
298.15	130.640	0	0	0

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

From Eq. (7), it can be derived that the value of $C^{\mathrm{E}}_{p,m}$ of the azeotrope reaches the minimum 0.074 J K^{-1} mol^{-1} at $T = 308.5$ K. The larger the $C^{\mathrm{E}}_{p,m}$, the more different the interaction between the molecules in the system. The deviation of the solution from the ideal one is the smallest at 308.5 K.

The other excess thermodynamic functions of the system 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

Table 4
Excess thermodynamic functions of the azeotrope

T (K)	$C^{\mathrm{E}}_{p,m}$ (J K^{-1} mol^{-1})	$[H^{\mathrm{E}}_T - H^{\mathrm{E}}_{298.15\,\mathrm{K}}]$ (J mol^{-1})	$[S^{\mathrm{E}}_T - S^{\mathrm{E}}_{298.15\,\mathrm{K}}]$ (J K^{-1} mol^{-1})	$[G^{\mathrm{E}}_T - G^{\mathrm{E}}_{298.15\,\mathrm{K}}]$ (J mol^{-1})
285	0.305	−1.526	0.067	−20.728
290	0.217	−0.648	0.043	−13.187
295	0.150	−0.157	0.017	−5.232
300	0.104	0.051	−0.010	3.153
305	0.079	0.080	−0.039	11.978
310	0.075	0.037	−0.068	21.253
315	0.092	0.026	−0.098	30.985
320	0.130	0.152	−0.128	41.182
298.15	0.119	0	0	0

thermodynamic temperature. The results were listed in Table 4.

4. Conclusion

The temperatures of the phase transitions of the azeotrope were affected little compared with the pure water and cyclohexane. The enthalpies of the phase transitions of the azeotrope were affected because the interval of the temperatures of the solid–liquid phase transitions of water and cyclohexane is about only 7 K. The value of $C_{p,m}^{\mathrm{E}}$ of the azeotrope reaches the minimum $0.074\,\mathrm{J\,K^{-1}\,mol^{-1}}$ at $T = 308.5\,\mathrm{K}$.

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