Short communication

Thermodynamic investigation on the azeotropic mixture composed of water + n-propanol + benzene

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Abstract

Molar heat capacity of the azeotropic mixture composed of water, n-propanol, and benzene was measured by an adiabatic calorimeter from 79 to 320 K. The glass transition and melting processes of the mixture were determined based on the curve of the heat capacity with respect to temperature. The glass transition occurred at 101.920 K. The melting processes took place in temperature ranges 258–268 and 268–279 K. The corresponding melting enthalpies and entropies were calculated to be 1.474 kJ mol^{-1}, 5.508 J K^{-1} mol^{-1}; 6.144 kJ mol^{-1}, 22.28 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.
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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 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 [9].

The ternary system of 0.257 M fraction of water, 0.102 M fraction of n-propanol, and 0.641 M fraction of benzene shows a minimum boiling point azeotrope at 340.1 K with

101.325 kPa [6]. The coexisting liquid splits into two liquid phases (upper layer: benzene and n-propanol; lower layer: water and n-propanol) in the system.

In this work, the molar heat capacity of the azeotropic mixture was measured by an adiabatic calorimeter in temperature range 79–320 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

2.1. Experimental materials

Commercially available n-propanol (Shenyang Chemical Agent Factory, normal mass fraction purity, 0.998) and benzene (Shenyang Chemical Agent Factory, normal mass fraction purity, 0.998) were distilled twice in a vacuum. The water used for calorimetric measurements was deionized and distilled twice. The ternary system is composed of 0.257 mol fraction of water, 0.102 mol fraction of n-propanol, and 0.641 mol fraction of benzene. The mean molecular weight of the sample is 60.83 and 0.6014 mol (36.5832 g) of the sample was used in the experiment.

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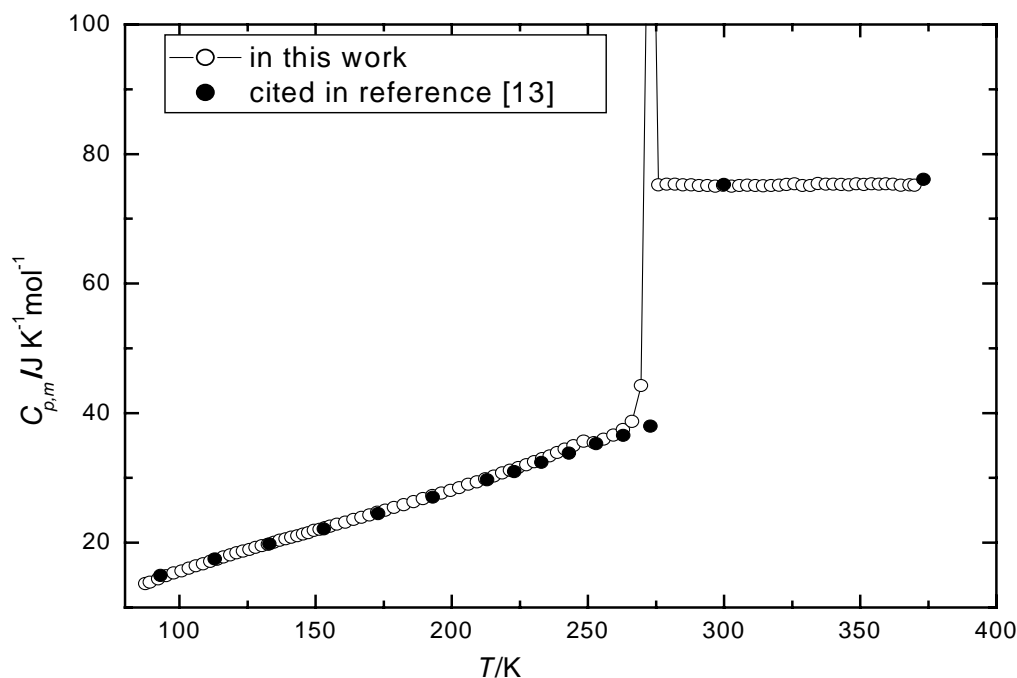*E-mail address:* zdnan65@hotmail.com (Z. Nan).

Fig. 1. Molar heat capacities of water.

2.2. Adiabatic calorimeter

Heat-capacity measurements were carried out in a high-precision automatic adiabatic calorimeter described in detail elsewhere [10,11]. 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
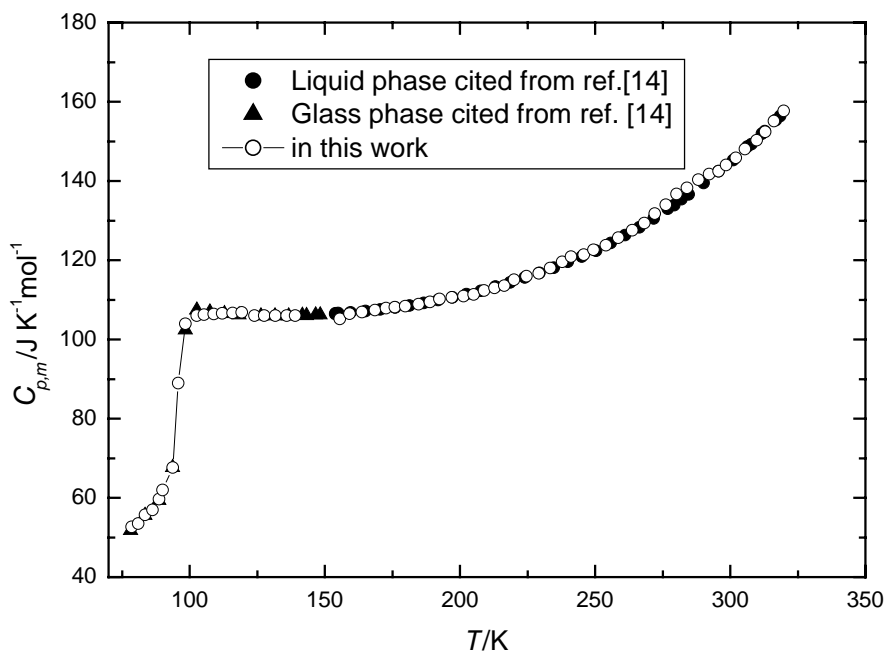
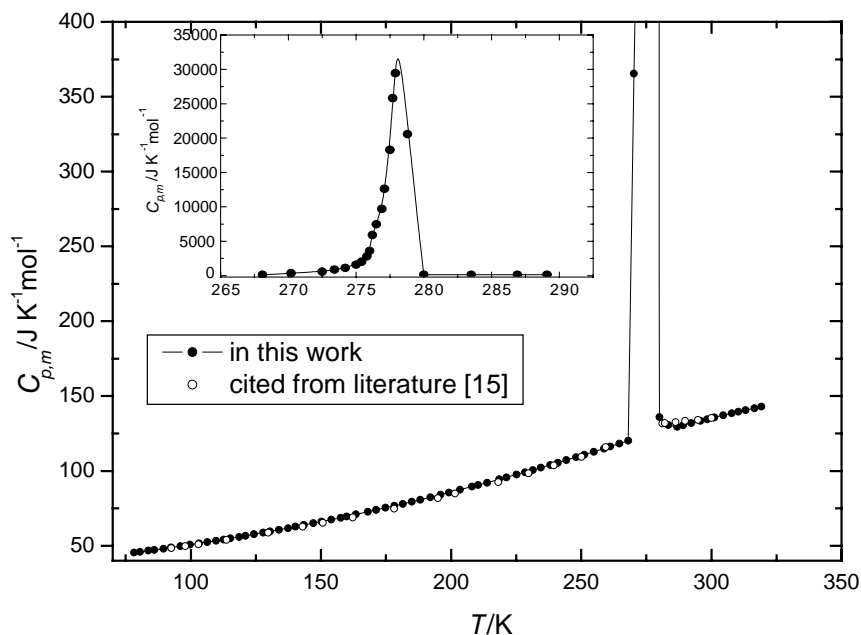Fig. 2. Molar heat capacities of n-propanol.

Fig. 3. Molar heat capacities of benzene. Inset shows solid–liquid phase transition of benzene.

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} 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$_2$O$_3$, water, n-propanol and benzene were measured. The deviations of our experimental results from the values recommended by the National Bureau of Standards [12] were within ±0.2% in the temperature range of 80–400 K for α-Al$_2$O$_3$. The plots of molar heat capacities of water, n-propanol 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, n-propanol and benzene measured in our laboratory with literatures [13–15], the data of heat capacities gained from literatures [13–15] are given in Figs. 1–3 as well. The melting enthalpy $\Delta_{\mathrm{melt}} H_{\mathrm{m}}$ and en-

tropy $\Delta_{\mathrm{melt}} S_{\mathrm{m}}$ were calculated according to the relationship as follows:

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

$$\Delta_{\mathrm{melt}} S_{\mathrm{m}} = \frac{\Delta_{\mathrm{melt}} H_{\mathrm{m}}}{T_{\mathrm{melt}}} \quad (2)$$

where Q is the total amount of heat introduced into the sample cell; n the moles of substance of the sample; T_{melt} melting temperature, T_1 slightly below T_{melt}; T_2 slightly above T_{melt}; $C_{p,\mathrm{m(S)}}$, $C_{p,\mathrm{m(L)}}$, C_0 the heat capacity in solid and liquid state and heat capacity of empty cell, respectively. The melting temperatures, enthalpies and entropies of water, n-propanol and benzene are given in Table 1. Figs. 1–3 and Table 1 show that the molar heat capacities, the melting temperature and enthalpy determined in our laboratory are

Table 1
Data of the melting temperature, enthalpy and entropy

	T_{trans} (K)	$\Delta H_{\mathrm{trans}}$ (kJ mol^{-1})	$\Delta S_{\mathrm{trans}}$ (J K^{-1} mol^{-1})
Water	273.104[a]	6.005[a]	21.99[a]
	273.15 [13]	6.010 [13]	
n-Propanol	148.75 ± 0.01 [14]	5.372 ± 0.004 [14]	
Benzene	278.325[a]	9.818[a]	35.28[a]
	278.6 [15]	9.820 [15]	
The azeotropic mixture	267.638	1.474	5.508
	275.745	6.144	22.28

[a] Determined in this work.

in excellent agreement with the data cited from literatures [13–15].

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 79 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 105 to 258 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 square method.

For 104–250 K

$$C_{p,m} = -0.6556X^5 - 1.1582X^4 + 1.2152X^3 + 1.5487X^2 + 2.9017X + 63.518 \quad (3)$$

where $C_{p,m}$ ($J\,K^{-1}\,mol^{-1}$) is the molar heat capacity of the azeotropic mixture, T (K) thermodynamic temperature, reduced temperature $X = (T\,(K) - 177)/73$, the standard error σ of this fit is $0.243\,J\,K^{-1}\,mol^{-1}$.

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

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

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

For 280–320 K

$$C_{p,m} = 1.0231X^3 - 1.5083X^2 + 2.4730X + 138.590 \quad (5)$$

where $X = (T\,(K) - 300)/20$, $\sigma = 0.074\,J\,K^{-1}\,mol^{-1}$.

3.2. Thermodynamic data of glass and melting processes

It can be seen from Fig. 4 that the heat capacity jump was found in the temperature range from 99 to 105 K. In order to see clearly the change of the heat capacities, the inset figure A was used in Fig. 4. The heat capacity changes

Table 2
Experimental molar heat capacity of the azeotropic mixture

| T (K)	$C_{p,m}$ ($J\,K^{-1}\,mol^{-1}$)	T (K)	$C_{p,m}$ ($J\,K^{-1}\,mol^{-1}$)	T (K)	$C_{p,m}$ ($J\,K^{-1}\,mol^{-1}$)
79.661	41.500	176.336	74.185	266.486	521.000
82.802	42.521	179.694	75.500	267.638	727.000
86.211	43.928	183.030	76.717	268.935	241.265
89.522	45.126	186.332	77.771	270.524	262.059
92.745	46.118	189.606	78.813	271.868	346.993
95.911	47.238	192.846	80.035	272.973	504.463
99.016	48.450	196.060	81.093	273.843	735.070
102.036	51.277	199.241	82.500	274.459	996.691
104.962	53.690	202.422	83.700	274.904	1295.279
107.819	54.501	205.585	85.200	275.236	1590.426
110.650	55.176	208.633	86.500	275.502	1876.126
113.444	55.747	211.574	87.700	275.745	1973.693
116.201	56.500	214.537	89.200	276.018	1695.702
118.961	57.600	217.544	90.481	276.332	1462.999
121.519	58.400	220.509	92.258	277.054	436.394
123.927	58.748	223.448	93.760	279.003	134.269
126.334	59.695	226.333	95.936	281.732	134.204
128.913	60.475	229.156	97.753	284.455	135.352
131.360	61.300	231.989	99.200	287.166	136.100
133.943	61.800	234.791	101.000	289.861	136.948
136.408	62.353	237.550	102.600	292.533	137.438
138.855	63.106	240.800	104.500	295.206	137.874
141.294	64.046	242.809	105.944	297.878	138.219
143.764	64.467	245.453	107.312	300.544	138.610
146.235	65.038	248.114	109.510	303.199	138.910
148.706	65.600	250.730	112.596	305.849	139.140
151.758	66.200	253.310	115.949	308.904	139.541
155.378	67.300	255.836	119.662	311.534	139.842
158.971	68.200	258.298	125.598	315.071	140.037
162.541	69.259	260.679	136.827	317.806	140.350
166.044	70.360	262.736	207.896	319.997	140.510
169.517	71.844	264.108	298.000		
172.945	72.889	265.226	376.000		
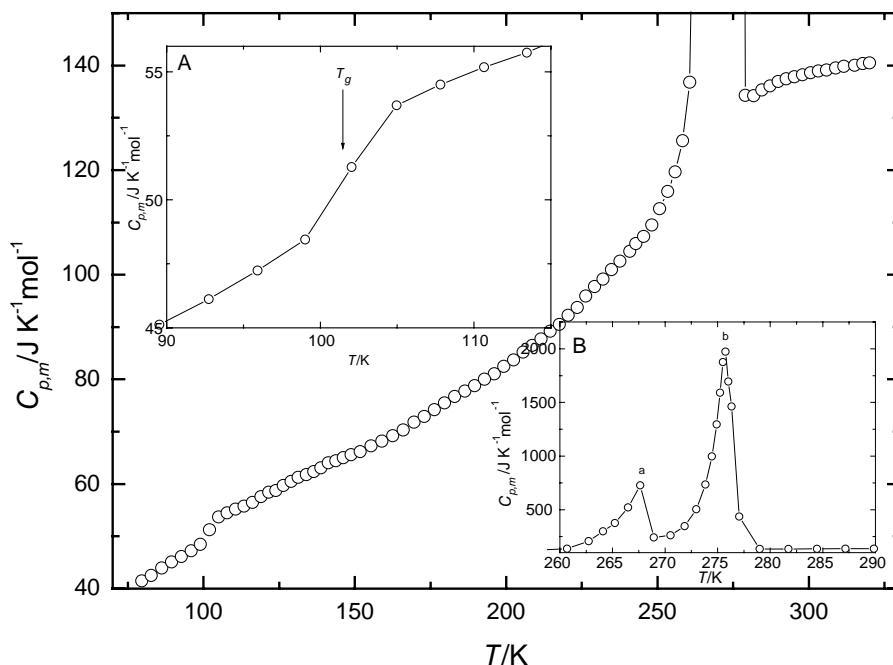
Fig. 4. Molar heat capacities of the azeotropic mixture. Inset A shows glass phase transition of the mixture. Inset B shows melting processes of the azeotropic mixture.

clearly before and after glass transition temperature [16]. The temperatures of the glass transition of the mixture were determined to be 101.920 K.

The glass transition temperature T_g of the azeotropic mixture is higher than that of pure n-propanol, which is about 96.4 K [14].

Fig. 4 shows that the molar heat capacity reaches maxima in temperature ranges from 258 to 280 K corresponding to "a" and "b", respectively. The melting temperatures were determined to be 267.638 and 275.745 K. Compared the data in Table 1, the melting temperatures of the azeotropic mixture are different from the pure compounds. The melting temperature decreases because the random mixing of the components decreases the free energy of the liquid phase relative to the pure solid phase.

The enthalpies and entropies of the melting processes 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 3.

3.4. Excess thermodynamic functions of the azeotrope

The excess molar heat capacity for the ternary system of x water + y n-propanol + $(1 - x - y)$ benzene was calculated

by the following equation:

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

(6)

where $C_{p,\mathrm{m},1}^{*}$, $C_{p,\mathrm{m},2}^{*}$, and $C_{p,\mathrm{m},3}^{*}$ are the molar heat capacities for water, n-propanol and benzene, respectively, and

Table 3
Data of the thermodynamic functions of the azeotropic mixture

T (K)	$C_{p,\mathrm{m}}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	$[H_{(T)} - H_{(298.15\,\mathrm{K})}]$ ($\mathrm{kJ\,mol^{-1}}$)	$[S_{(T)} - S_{(298.15\,\mathrm{K})}]$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)
110	55.042	−10.221	−146.3
120	57.873	−10.212	−141.5
130	60.605	−10.204	−136.8
140	63.308	−10.195	−132.3
150	66.051	−10.186	−127.9
160	68.905	−10.177	−123.7
170	71.937	−10.167	−119.5
180	75.217	−10.157	−115.4
190	78.816	−10.146	−111.4
200	82.801	−10.135	−107.4
210	87.242	−10.124	−103.5
220	92.210	−10.111	−99.50
230	97.772	−10.098	−95.49
240	103.999	−10.084	−91.43
250	110.959	−10.07	−87.30
260	Melting process		
270	Melting process		
280	133.586	−2.451	−59.51
290	136.849	−1.116	−27.63
300	138.590	0.256	6.482
310	139.577	1.653	42.90
320	140.578	3.072	81.76
298.15	138.348	0	0

Table 4
Excess thermodynamic functions of the azeotropic mixture

T (K)	$C_{p,m}^{E}$ (J K^{-1} mol^{-1})	$[H_m^E(T) - H_{298.15\,K}^E]$ (J mol^{-1})	$[S_m^E(T) - S_{298.15\,K}^E]$ (J K^{-1} mol^{-1})	$[G_m^E(T) - G_{298.15\,K}^E]$ (kJ mol^{-1})
280	19.506	−348.6	35.31	−10.24
285	19.626	−250.6	26.08	−7.685
290	19.320	−153.1	16.48	−4.933
295	18.672	−57.98	6.496	−1.974
300	17.769	33.21	−3.890	1.200
305	16.697	119.4	−14.69	4.599
310	15.541	200.0	−25.90	8.23
315	14.387	274.8	−37.55	12.1
320	13.322	344.1	−49.62	16.22
298.15	18.128	0	0	0

$C_{p,m}$ is the molar heat capacity of a mixture at the mole fraction of water x, n-propanol y, and benzene $(1 - x - y)$. The values of $C_{p,m}^{E}$ were calculated in the liquid phase and listed in Table 4. Positive $C_{p,m}^{E}$ indicates more structure in the solution [17].

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

$$C_{p,m}^{E} = 0.9158X^3 - 1.3555X^2 - 4.0079X + 17.769 \quad (7)$$

where $\sigma = 0.001$ J K^{-1} mol^{-1}, $X = (T\,(\text{K}) - 300)/20$.

From Eq. (7), it can be derived that the value of $C_{p,m}^{E}$ reaches the maximum 19.639 J K^{-1} mol^{-1} at 283.774 K. The larger the $C_{p,m}^{E}$, the more different the interaction between the molecules in the mixture from that in the pure samples.

The other excess thermodynamic functions of the mixture such as excess enthalpy, excess entropy, and excess free energy 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.

4. Conclusions

The molar heat capacity of the azeotropic mixture composed of water, n-propanol, and benzene were measured from 79 to 320 K. The glass transition temperature and melting temperatures were determined based on the curve of heat capacity with respect to temperature. The enthalpies and entropies of glass transition and melting process were derived.

Acknowledgements

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