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Heat capacities and thermal conductivity of ternary mixtures of water+ethanol+1,2-ethanediol between 75 and 350 K

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Abstract

The heat capacities of two concentrations of the ternary systems of 1,2-ethanediol, ethanol and water have been measured with an adiabatic calorimeter in the temperature range 80–350 K. These mixtures exhibited complex phase transitions in the solid state. A very broad heat capacity anomaly starting from 130 to 240 K was observed in the heat capacity curves and three transition peaks were found in this temperature range in addition to the melting peak. Experiments have demonstrated that the cooling rates had no obvious influence on the heat capacity anomaly. The thermal conductivity of the ternary systems were measured with an instantaneous heating wire conductometer in the temperature range from 233.15 to 343.15 K. All of the heat capacity and thermal conductivity results in temperature range between 221 and 350 K were correlated with temperature for practical applications.

Keywords: Heat capacity; Phase transition; Thermal conductivity; 1,2-Ethanediol; Ethanol; Aqueous solution

1. Introduction

1,2-Ethanediol is an important chemical used in the petroleum and chemical industries. Its solutions are also an advanced working fluid in heat transfer equipment and widely used in the automobile, space and aviation industries. As a heat transfer medium, 1,2-ethanediol aqueous solutions may work at lower temperature with the addition of ethanol. Ethanol can also reduce the viscosity of 1,2-ethanediol in aqueous solution and improve its heat transfer performance.

Nikolaev and Rabinovich [1] and Knauth and Sabbah [2] have studied the low-temperature heat capacity and phase transition of pure 1,2-ethanediol by adiabatic calorimetry and DTA. One phase transition was observed for the solid–liquid phase change. No heat capacity anomaly was found in solid state. Zhi-cheng et al. [3,4] have investigated by adiabatic calorimetry heat capacities of 1,2-ethanediol aqueous solutions of different concentrations of 1,2-ethanediol in aqueous solutions over the temperature range between the melting and boiling point. They also measured the physical properties of 1,2-ethanediol aqueous solutions carefully, such as boiling point, melting point, viscosity and so on.

In this paper, the heat capacities of two ternary mixtures of 1,2-ethanediol, ethyl alcohol and water were measured with an adiabatic calorimeter in the temperature range from 80 to 350 K. The thermal conductivity of these mixtures were also determined with an instantaneous heating wire conductometer in the temperature range 233.15–343.15 K. All of the results of heat capacity and thermal conductivity in the

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liquid state were fitted to polynomial equations by least squares method so as to provide information for heat transfer design in a space project in China.

2. Experimental

2.1. Sample preparation

Commercial analytical purity grade 1,2-ethanediol (0.998 mass fraction), ethanol (0.997 mass fraction) and twice-distilled water were used to prepare the samples. The sample mixtures were prepared gravimetrically by mixing the guest liquid of 1,2-ethanediol with ethanol and distilled water. The concentrations of 1,2-ethanediol, ethanol and distilled water in sample I were 0.195, 0.132 and 0.673 molar fraction (i.e. 0.40, 0.20 and 0.40 mass fraction) and 0.144, 0.194 and 0.662 molar fraction (i.e. 0.30, 0.30 and 0.40 mass fraction) for sample II, respectively. The mean molecular weight of sample I is 30.02 and 1.168 mol (35.0539 g) of the sample was used in the experiment. The mean molecular weight of sample II is 29.80 and 1.2185 mol (36.3174 g) of the sample was used in the experiment.

2.2. Adiabatic calorimeter

A low-temperature adiabatic calorimeter was used to measure the heat capacity of the sample. The calorimetric apparatus and measuring technique have been described in detail [5]. Briefly, it is an adiabatic calorimeter with intermittent energy inputs and temperature equilibration after each input. The calorimeter cell, with an internal volume of 42 ml, was made of gold plated silver with eight fins, and was provided with a re-entrant well for locating the heater and platinum resistance thermometer assembly. The calorimeter cell was sealed with a silicon rubber or Pb–Sn alloy gasket by a screw cover. The details about the calorimeter can be referred to the relevant literature.

2.3. Experimental procedures of heat capacity measurements

After filling the calorimeter cell with the sample, the cryostat was evacuated to a suitable vacuum. Cooling down the calorimeter from room temperature to liquid nitrogen at a desired cooling rate was controlled by adjusting the vacuum. In low-temperature region, the cooling rate decreased gradually and the liquid nitrogen temperature was obtained finally. From this temperature the calorimeter was ready for heat capacity measurements.

The heat capacity was measured by a step heating method that involved a determination of the heating energy and the corresponding temperature increment of the container with the specimen. In the first the calorimeter was heated to a desired temperature. After 5–10 min a steady temperature equilibration was attained and then the temperature and temperature drift rate of the calorimeter cell were recorded for 10 min with a 1 min interval. Next, another heating was carried out and the above steps were repeated until the upper limit of the temperature was reached.

In normal heat capacity region the temperature drift rate represents the native characteristics of a calorimeter. However in the phase transition from metastable state (e.g. glassy state) to an equilibrium state, the temperature drift rate (named spontaneous temperature drift rate due to an irreversible enthalpy relaxation from a frozen-in state that was disordered to an equilibrium state) may be significantly different from that in single phase region. In phase transition regions the $C_{p,m}$–T values may not be true equilibrium values if the equilibration period was not extended long enough.

After a series of heat capacity measurements were carried out, the sample was kept in the cell at room temperature for 2 days. Then the next series of measurements were conducted.

2.4. Thermal conductivity measurement

The thermal conductivity of the samples were measured with an instantaneous heating wire conductometer (Model KDR-1B, made by the Chinese University of Science and Technology) in the temperature ranging from 233.15 to 343.15 K. Prior to the thermal conductivity measurements of the sample, methylbenzene was used as standard reference material to verify the reliability of the apparatus. The deviations of the measured results from those of literatures were less than $\pm 3\%$.

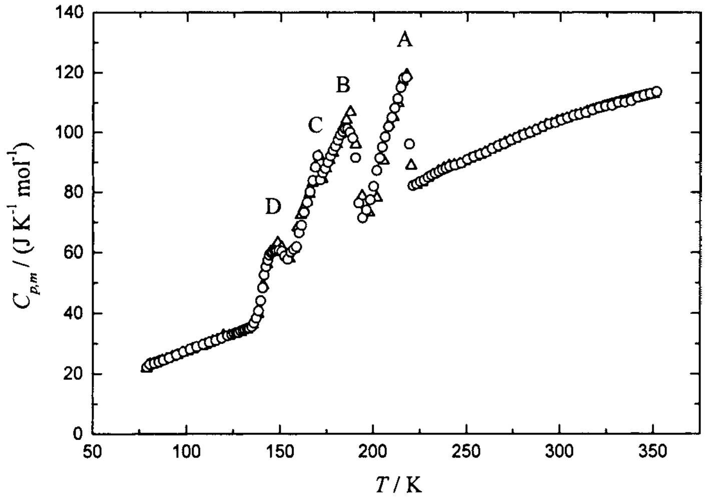

Fig. 1. Heat capacities of sample I (0.195 1,2-ethanediol+0.132 ethanol+0.673 water) at cooling rates of 0.1 K min^{-1} (o — series I) and 10 K min^{-1} (Δ — series II). (See text for discussion of peaks A, B, C and D.)

3. Results and discussion

3.1. Heat capacity

Two series of the experiments with different cooling rates of the sample were carried out to determine the heat capacities of the sample I in temperature range from 80 to 350 K. The cooling rate of series I was about 0.1 K min^{-1} and series II was about 10 K min^{-1}. The experimental results of the two series of measurements are shown in Fig. 1. The experimental molar heat capacities of the sample are listed in Table 1 in chronological order. One series of experiment was conducted for sample II. The result is shown in Fig. 2 and listed in Table 2.

Fig. 1 shows that the mixture of 1,2-ethanediol, ethanol and water exhibits complex phase transitions in solid state. A very broad heat capacity anomaly was

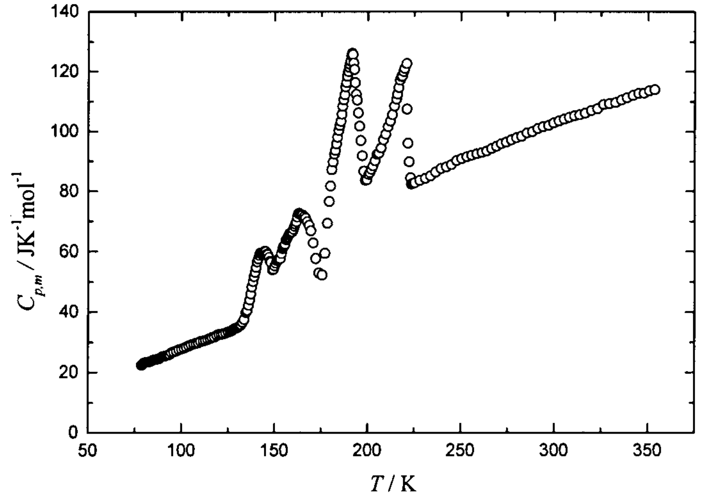

Fig. 2. Heat capacities of sample II (0.144 1,2-ethanediol+0.194 ethanol+0.662 water).

Table 1
Experimental molar heat capacities of the ternary mixture of sample I (0.195 1,2-ethanediol+0.132 ethanol+0.673 water)[a]

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	ΔT (K)
Series I (*cooling rate*: 0.1 K min^{-1})		
78.929	22.32	0.365
80.380	23.23	2.497
82.849	23.59	2.453
85.262	24.01	2.408
87.624	24.56	2.358
90.748	25.35	3.937
94.586	26.38	3.799
98.294	27.41	3.676
101.894	28.29	3.575
105.405	29.08	3.488
108.839	29.80	3.411
112.203	30.50	3.342
115.501	31.14	3.281
118.737	31.84	3.218
121.915	32.65	3.151
124.092	33.02	1.192
125.292	33.44	1.178
126.485	33.59	1.173
127.689	33.69	1.162
128.889	34.23	1.155
130.066	34.56	1.146
131.239	34.78	1.140
132.407	34.99	1.134
133.569	35.14	1.129
134.720	35.66	1.116
135.850	36.87	1.089
137.056	38.51	1.292
138.303	40.90	1.236
139.436	44.21	1.166
140.450	48.51	1.086
141.383	52.70	1.019
142.293	55.39	0.979
143.203	57.58	0.949
144.105	59.31	0.927
144.996	60.03	0.918
145.886	60.28	0.914
146.872	60.70	1.097
147.960	60.61	1.101
149.240	60.70	1.460
150.725	60.37	1.466
152.278	58.91	1.493
153.911	57.88	1.513
155.538	60.22	1.465
157.100	61.09	1.447
158.601	61.91	1.431
160.004	66.52	1.351
161.308	69.07	1.309
162.733	73.31	1.641
164.289	76.77	1.580
165.806	80.26	1.522
167.282	84.05	1.464
168.674	88.50	1.402
169.958	92.35	1.352
171.272	84.26	1.460
172.677	86.59	1.426
174.081	88.08	1.405
175.459	90.14	1.378
176.812	92.23	1.350
178.141	94.11	1.327
179.449	95.60	1.309
180.741	97.51	1.286
182.023	99.30	1.266
183.308	100.35	1.254
184.610	101.34	1.243
185.942	101.31	1.243
187.324	100.15	1.255
188.775	98.21	1.276
190.335	91.63	1.353
192.120	76.53	1.571
194.146	71.49	1.660
196.227	74.16	1.610
198.217	77.62	1.550
200.061	82.08	1.479
201.735	87.32	1.404
203.252	91.54	1.349
204.650	95.20	1.305
206.216	98.63	1.771
207.970	102.00	1.722
209.670	105.18	1.677
211.324	108.36	1.634
212.931	111.55	1.593
214.493	115.22	1.548
216.011	118.34	1.512
217.494	118.55	1.509
219.116	96.27	1.805
221.026	82.29	2.057
223.070	82.86	2.044
225.105	83.71	2.026
227.127	84.23	2.015
229.136	85.17	2.024
231.117	85.79	1.963
233.072	86.39	1.934
235.025	86.99	1.949
236.976	87.59	1.945
238.914	88.17	1.928
240.830	88.74	1.904
243.497	89.17	3.437
246.920	89.84	3.414
250.312	91.05	3.375
253.671	91.96	3.344
257.001	92.72	3.320
260.299	93.57	3.291
263.567	94.72	3.256
266.805	95.72	3.225
270.153	96.48	3.481

Table 1 (*Continued*)

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	ΔT (K)
273.630	97.60	3.483
277.095	98.51	3.454
280.533	99.39	3.429
283.948	100.12	3.414
287.340	101.09	3.389
290.707	102.03	3.362
294.049	102.91	3.337
297.369	103.42	3.317
300.670	104.21	3.299
303.952	105.00	3.278
307.213	105.79	3.255
310.455	106.18	3.244
313.836	106.79	3.541
317.361	107.70	3.527
320.868	108.42	3.504
324.351	108.97	3.507
327.815	109.18	3.764
331.260	110.18	3.716
334.686	110.27	3.447
338.092	110.73	3.433
341.482	111.97	3.400
344.855	112.58	3.382
348.209	113.15	3.365
351.550	113.85	3.347
Series II (*cooling rate*: 10 K min^{-1})		
78.700	21.86	0.548
79.234	22.71	0.533
79.764	22.80	0.531
80.293	23.07	0.526
80.818	23.07	0.525
81.409	23.04	0.660
82.064	23.26	0.655
82.713	23.50	0.649
83.454	23.47	0.840
84.286	23.74	0.831
85.483	24.17	1.564
87.037	24.44	1.545
89.276	25.01	2.937
92.177	25.65	2.870
95.010	26.29	2.807
97.778	27.11	2.736
100.483	27.59	2.690
103.133	28.20	2.639
108.041	29.20	1.977
109.988	29.68	1.950
111.913	30.20	1.924
113.819	30.68	1.898
116.380	31.26	3.219
119.560	32.68	3.124
122.705	32.62	3.103
125.849	33.23	3.056
128.982	33.66	3.019
132.105	34.69	2.948
135.193	36.20	2.854
138.121	39.78	2.660
140.648	49.30	2.263
142.777	56.15	2.044
144.735	60.25	1.931
146.636	61.40	1.900
148.546	63.19	1.855
150.535	61.70	1.889
152.635	59.64	1.939
154.859	58.06	1.979
157.078	61.03	1.900
159.048	68.25	1.735
160.770	72.37	1.653
162.401	74.71	1.609
163.993	76.95	1.569
165.544	79.50	1.527
167.043	83.05	1.471
168.708	88.75	1.961
170.519	92.17	1.904
172.394	84.50	2.049
174.365	87.96	1.979
176.294	90.69	1.928
178.175	93.29	1.881
180.010	96.18	1.831
181.801	99.45	1.779
183.561	101.84	1.742
185.318	104.30	1.706
186.449	106.91	2.441
190.385	96.11	2.674
193.777	78.77	3.159
197.653	73.22	3.350
201.657	78.16	3.167
205.249	90.66	2.792
208.165	102.85	2.513
210.679	105.21	2.466
213.059	109.91	2.373
215.339	117.07	2.239
217.538	119.34	2.200
220.062	88.96	2.829
223.001	82.41	2.784
225.984	83.44	2.826
228.935	84.84	2.937
231.854	85.99	2.902
234.741	87.11	2.871
237.587	88.08	2.821
240.406	88.93	2.814
243.223	89.17	2.815
246.032	89.44	2.808
248.822	90.29	2.783
251.590	91.14	2.760
254.336	91.93	2.738
257.061	92.60	2.720
259.764	93.48	2.697
262.446	94.33	2.676
265.109	95.02	2.658

Table 1 (*Continued*)

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	ΔT (K)
267.753	95.78	2.638
270.378	96.72	2.616
272.983	97.30	2.602
275.570	97.93	2.587
278.141	98.81	2.566
280.698	99.39	2.552
283.487	99.87	3.032
286.510	100.72	3.025
289.525	101.60	3.015
292.522	102.60	2.990
295.502	102.97	2.977
298.465	103.94	2.951
301.167	104.39	2.451
303.612	104.82	2.440
306.042	105.36	2.428
308.460	105.85	2.417
310.866	106.21	2.408
312.876	106.39	1.629
314.494	107.12	1.619
316.109	107.24	1.618
317.718	107.67	1.611
319.323	107.97	1.606
320.924	108.27	1.609
322.522	108.58	1.607
323.942	108.82	1.250
325.185	109.06	1.248
326.425	109.27	1.246
327.658	109.49	1.244
328.884	109.70	1.241
330.112	109.91	1.239
331.345	110.12	1.237
332.577	110.33	1.235
333.807	110.55	1.233
335.034	110.73	1.231
336.260	110.94	1.229
337.483	111.12	1.227
338.706	111.34	1.226
339.927	111.52	1.224
341.146	111.70	1.222
342.364	111.88	1.220
343.583	112.06	1.218
344.797	112.24	1.217
346.004	112.43	1.215
347.744	112.67	2.380
350.015	112.97	2.307

[a] Mean molecular weight $M = 30.32$.

Table 2
Experimental molar heat capacities of the ternary mixture of sample II (0.144 1,2-ethanediol+0.194 ethanol+0.662 water)[a]

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	ΔT (K)
78.512	22.45661	0.355
78.859	22.50	0.355
79.211	22.95	0.350
79.572	23.12	0.347
79.935	23.19	0.347
80.545	23.37	0.831
81.395	23.41	0.826
82.238	23.52	0.824
83.077	23.60	0.820
83.909	23.82	0.813
84.733	24.17	0.804
85.550	24.26	0.802
86.362	24.35	0.797
87.167	24.49	0.792
87.966	24.56	0.789
88.757	24.96	0.779
89.673	25.29	1.037
90.712	25.44	1.031
91.741	25.64	1.023
92.757	25.78	1.017
93.761	26.11	1.007
94.755	26.69	0.989
95.940	26.99	1.390
97.317	27.21	1.379
98.679	27.64	1.361
100.024	27.89	1.349
101.356	28.25	1.334
102.674	28.54	1.322
103.981	28.95	1.307
105.275	29.27	1.294
106.560	29.48	1.285
107.836	29.77	1.274
109.104	29.98	1.266
110.363	30.34	1.253
111.613	30.53	1.245
112.856	30.72	1.238
114.091	31.08	1.226
115.319	31.29	1.219
116.540	31.63	1.208
117.754	31.87	1.199
118.963	32.36	1.185
120.167	32.63	1.177
121.367	32.70	1.173
122.564	32.88	1.171
123.760	33.08	1.161
124.958	33.44	1.151
125.994	33.59	0.808
126.864	33.83	0.803
127.731	34.25	0.795
128.594	34.57	0.790
129.449	34.75	0.786
130.283	35.02	0.781

Table 2 (*Continued*)

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	ΔT (K)
131.113	35.38	0.775
131.948	35.85	0.767
132.775	36.64	0.754
133.536	37.59	0.732
134.494	39.85	0.708
135.226	40.59	0.698
135.914	42.30	0.676
136.562	44.06	0.655
137.175	46.06	0.633
137.766	48.36	0.609
138.344	50.14	0.592
138.915	51.79	0.577
139.480	53.14	0.565
140.037	54.79	0.551
140.580	56.65	0.537
141.111	57.65	0.529
141.633	58.78	0.521
142.148	59.45	0.516
142.661	59.48	0.515
143.174	59.53	0.515
143.687	59.72	0.513
144.202	60.02	0.504
144.721	60.19	0.522
145.243	60.01	0.511
145.772	59.24	0.516
146.308	58.98	0.518
146.854	58.01	0.525
147.417	56.93	0.533
147.999	56.51	0.536
148.603	54.05	0.555
149.223	54.12	0.554
149.864	55.32	0.544
150.525	56.26	0.537
151.194	57.12	0.53
151.849	57.4	0.528
152.473	57.63	0.526
153.059	57.86	0.524
153.604	59.39	0.513
154.119	60.93	0.503
154.613	61.60	0.498
155.095	62.01	0.495
155.572	62.51	0.492
156.043	63.90	0.483
156.512	64.33	0.480
156.980	64.92	0.477
157.445	65.54	0.473
157.910	65.96	0.467
158.411	66.14	0.543
158.946	66.47	0.541
159.482	66.65	0.539
160.013	67.45	0.533
160.535	68.35	0.526
161.053	69.13	0.518
161.5662	69.97	0.511

Table 2 (*Continued*)

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	ΔT (K)
162.0778	71.52	0.504
162.5901	72.68	0.498
163.1035	72.80	0.496
163.6189	72.42	0.498
164.252	72.17	0.754
165.010	72.14	0.754
165.791	71.66	0.758
166.598	71.17	0.762
167.443	69.94	0.773
168.357	68.71	0.784
169.382	66.92	0.801
170.563	62.95	0.842
171.955	57.79	0.901
173.584	52.99	0.964
175.335	52.28	0.974
176.944	59.46	0.879
178.214	69.39	0.775
179.174	76.67	0.713
179.954	81.84	0.675
180.641	87.23	0.639
181.281	89.82	0.623
181.897	92.42	0.608
182.497	93.75	0.600
183.086	95.94	0.588
183.664	98.19	0.577
184.232	100.41	0.565
184.790	102.05	0.557
185.338	103.46	0.551
185.877	105.92	0.539
186.403	108.53	0.528
186.918	110.67	0.519
187.421	112.42	0.512
187.910	115.07	0.501
188.386	116.48	0.496
188.849	118.60	0.488
189.300	120.09	0.482
189.739	121.51	0.477
190.169	122.47	0.479
190.589	123.55	0.470
191.003	125.45	0.465
191.416	126.22	0.462
191.828	125.73	0.464
192.242	122.97	0.473
192.667	120.78	0.480
193.104	116.46	0.496
193.562	112.59	0.511
194.097	110.60	0.624
194.721	106.36	0.647
195.391	101.86	0.671
196.115	97.06	0.700
196.896	91.91	0.734
197.730	86.76	0.771
198.595	83.83	0.793
199.461	83.86	0.793

Table 2 (*Continued*)

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	ΔT (K)
200.293	85.66	0.779
201.083	86.30	0.774
201.852	87.38	0.765
202.736	88.52	1.006
203.734	90.19	0.990
204.718	92.44	0.969
205.852	92.81	1.292
207.128	94.59	1.271
208.377	97.36	1.239
209.601	99.18	1.219
210.801	101.68	1.193
211.973	103.60	1.173
213.123	105.72	1.152
214.250	108.67	1.124
215.355	110.98	1.104
215.895	112.70	0.702
216.577	114.91	0.689
217.229	117.25	0.675
217.860	118.48	0.668
218.478	118.70	0.667
219.083	120.13	0.659
219.678	121.17	0.655
220.832	122.75	0.653
220.864	107.63	0.683
221.494	96.19	0.729
222.175	89.85	0.772
222.913	84.58	0.813
223.414	82.55	0.923
224.527	82.76	0.961
225.313	82.97	0.825
227.895	83.69	2.935
230.874	84.39	2.896
233.635	85.21	2.871
236.444	86.46	2.836
239.255	87.65	2.809
242.152	88.19	2.792
244.947	88.93	2.771
247.635	90.33	2.733
250.394	91.03	2.714
253.142	91.62	2.697
255.722	92.08	2.684
258.521	92.59	2.670
261.181	93.03	2.657
263.818	93.60	2.641
266.436	94.42	2.620
269.034	95.17	2.601
271.610	96.02	2.577
274.246	96.56	2.726
276.948	97.34	2.712
279.628	97.99	2.691
282.430	98.57	2.960
285.352	99.69	2.930
288.249	100.08	2.917
291.120	101.11	2.889
293.968	101.71	2.874
296.801	102.16	2.860
299.616	103.00	2.837
302.407	103.66	2.821
305.174	104.27	2.806
307.921	104.86	2.791
310.647	105.37	2.779
313.356	105.70	2.771
316.358	106.36	3.380
319.650	107.16	3.367
322.918	107.82	3.349
326.150	109.19	3.313
329.349	109.50	3.305
332.520	109.83	3.293
335.654	110.69	3.271
338.753	111.50	3.251
341.826	112.25	3.245
344.861	112.90	3.218
347.801	113.01	3.167
350.649	113.79	3.148
353.517	114.21	3.185

[a] Mean molecular weight $M = 29.80$.

found from 130 to 240 K in solid state. Four peaks labelled A, B, C and D were observed at T=217.5, 186, 170 and 149 K, respectively. The peak temperatures were considered to be the corresponding phase transition temperatures or melting point.

Peak A was confirmed to be the melting peak from solid to liquid state. It was difficult to determine the structures of the solid at temperatures between peaks A and B, B and C, C and D and below peak D. The behaviour of four peaks in series I was similar to that in series II and they were not influenced by the cooling rate of the sample. However, the equilibration period had a little effect on the experiment results. The equilibration period was 7 min for series I and 5 min for series II. In phase transition regions, shorter equilibration period may cause false equilibration and the heat capacity values are likely not true equilibrium values.

From the above experimental results, at least three (A, B, C) of the peaks appeared in the present results should be attributed to the fusion of three phases, i.e. water, 1,2-ethanediol, and ethanol, respectively. Indeed, peak areas of these peaks seem to be proportional to the expected values (sample I for example) of enthalpy of fusion for each component material as follows:

Material	Expected value	Experimental value
Water	6.002 kJ mol^{-1} ×0.673 mol=4.039 kJ	3.975 kJ
1,2-Ethanediol	11.597 kJ mol^{-1}× 0.195 mol=2.261 kJ	2.304 kJ
Ethanol	4.814 kJ mol^{-1}× 0.132 mol=0.635 kJ	0.683 kJ

In addition, these peaks appeared near the melting point of these materials and expected depressions of freezing points.

Experimental heat capacity and corresponding temperature drift during equilibration period are shown in Fig. 3 for sample I in series I. Haida et al. [6] have reported plural glass-transition phenomena of ethanol in their study. Anomalous temperature drifts were observed in the measurement of heat capacities of hexagonal ice [7]. This is the characteristic of the enthalpy-relaxation phenomenon and implies that there is a glassy state in hexagonal ice. The above information reminded us that the mixture of 1,2-ethanediol, ethanol and water might exhibit glassy behaviour in the solid state. In Fig. 3 the spontaneous temperature drift rates of the sample are plotted against the temperature. The rates were observed during each equilibration period between each energy input. A series of exothermic followed by endothermic temperature drifts appeared in the temperature range 122–220 K. This type of relaxational heat capacity anomaly is one of the typical characteristic features of the glass transition. Accurate assignment of the peaks in the heat capacity curve should be established in the future.

Fig. 2 shows similar result to that of sample I. In the heat capacity measurements of sample II, the equilibration period was extended to 10 min. Also four transition peaks were observed at T=144, 163, 191 and 220.8 K.

The experimental results of heat capacity of the specimens in temperature range between 221 and 350 K (liquid state) resulted in the following correlation equations.

$$C_{p,m} = -23.194 + 0.626T - 6.761 \times 10^{-4}T^2 \quad \text{(for sample I)},$$

$$C_{p,m} = -5.625 + 0.491T - 4.298 \times 10^{-4}T^2 \quad \text{(for sample II)},$$

where, T (K) is the temperature and $C_{p,m}$ ($\text{J K}^{-1}\,\text{mol}^{-1}$) is the heat capacity.

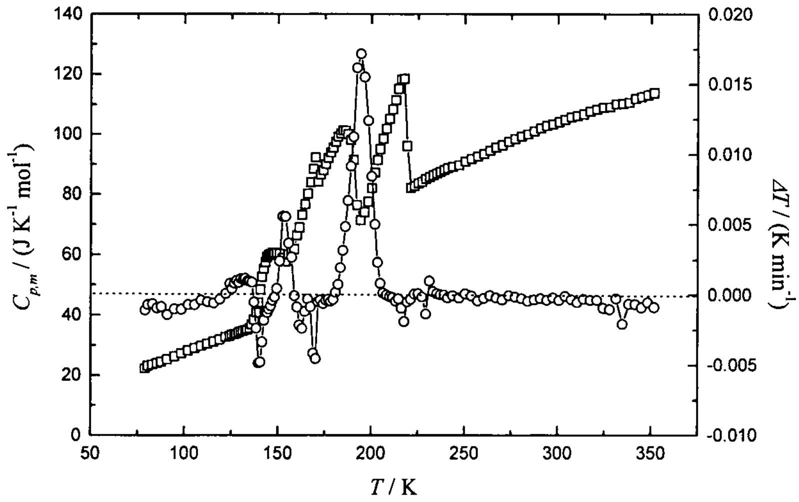

Fig. 3. Heat capacities (— □ —) of sample I (0.195 1,2-ethanediol+0.132 ethanol+0.673 water) in series I and corresponding spontaneous temperature drift rates (— o —).

Table 3
Thermal conductivity of the ternary mixture of sample I (0.195 1,2-ethanediol+0.132 ethanol+0.673 water) and sample II (0.144 1,2-ethanediol+0.194 ethanol+0.662 water)

T (K)	λ (W m^{-1} K^{-1})
Sample I	
233.15	0.291
238.15	0.298
243.15	0.305
248.15	0.312
253.15	0.320
258.15	0.327
263.15	0.334
268.15	0.341
273.15	0.349
283.15	0.363 (0.460)[a]
303.15	0.392 (0.490)[a]
323.15	0.421 (0.511)[a]
343.15	0.450 (0.524)[a]
Sample II	
233.15	0.276
238.15	0.284
243.15	0.291
248.15	0.298
253.15	0.306
258.15	0.313
263.15	0.320
268.15	0.328
273.15	0.335
283.15	0.350 (0.452)[a]
303.15	0.379 (0.481)[a]
323.15	0.409 (0.501)[a]
343.15	0.438 (0.514)[a]

[a] The values given in brackets are theoretical values.

3.2. Thermal conductivity

The thermal conductivity λ of the mixture of 1,2-ethanediol, ethanol and water was measured in temperature range from 233.15 to 343.15 K. The experimental results are listed in Table 3 and the equations to correlate the experimental results may be expressed as

$$\lambda = -4.679 \times 10^{-2} + 1.450 \times 10^{-3} T \quad \text{(for sample I)},$$

$$\lambda = -6.687 \times 10^{-2} + 1.470 \times 10^{-3} T \quad \text{(for sample II)},$$

where, T (K) is the temperature and λ (W m^{-1} K^{-1}) is the thermal conductivity. These equations can be extrapolated down to T=221 K or up to 350 K.

Usually the conductivity of a ideal mixture can be derived from its pure components. The theoretical values of the sample conductivity are also listed in Table 3 for comparison. It is obvious that the theoretical values are higher about 22.6–14.1% than the experimental results and the data below 273.15 K are difficult to obtain theoretically. Therefore, the present experiment has provided an important information about the sample conductivity for practical application.

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