

Heat Capacities of Isomeric 2-Butoxyethanols from 13 to 300 K: Fusion and Glass Transition

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We measured the heat capacities of 2-butoxyethanol (abbreviated as *n*BE), 2-isobutoxyethanol (*i*BE) and 2-*t*-butoxyethanol (*t*BE) from 13 to 300 K by adiabatic calorimetry, and glass transition was found for all three: 140 K (*n*BE), 146 K (*i*BE) and 150 K (*t*BE). We were successful in crystallizing *n*BE and *t*BE, and determined thermodynamic functions for fusion for the first time. The temperatures of fusion and their enthalpy changes are 199.53 K, 11.8 kJ mol^{-1} for *n*BE and 223.09 K, 11.4 kJ mol^{-1} for *t*BE. Where possible, we calculated thermodynamic functions. The total entropy in the liquid state at fusion is almost the same, within 1%, between *n*BE and *t*BE. However, the values of the liquid heat capacity are about 10% different at the melting point. This indicates that the entropy fluctuation is different while the global average of the entropy remains the same. We measured the density of the liquid and supercooled liquid states for all three samples, and calculated the amplitude, as well as the amplitude plus wavelength of the entropy fluctuation.

In our earlier attempt at completing liquid–solid phase diagram for system 2-butoxyethanol–H_2O,[1] no literature data was found for the melting point of pure 2-butoxyethanol (abbreviated as *n*BE hereinafter). It turned out that *n*BE liquid is readily super-cooled, and belongs to a class of materials that undergo a glass transition.[2–4] We thus studied the freezing behavior and glass transition of pure *n*BE by adiabatic calorimetry. As shown below, we successfully crystallized *n*BE in a vessel of an adiabatic calorimeter and determined its melting point and thermodynamic function for the first time. In the process we also determined the heat capacity of the glassy state and observed a glass transition. We report here on the results and those for other isomeric forms of 2-butoxyethanol, 2-isobutoxyethanol (*i*BE) and 2-*t*-butoxyethanol (*t*BE). In spite of our effort, we failed to crystallize *i*BE.

Experimental

2-Butoxyethanol (Wako Pure Chemicals, 99+%), 2-*t*-butoxyethanol (Tokyo Kasei Organic Chemicals, 99+%) and 2-isobutoxyethanol (Tokyo Kasei Organic Chemicals, 98+%) were dehumidified by Molecular Sieves 3A and 4A (G) overnight in vacuo. About 8 g (≈ 0.07 mol) of butoxyethanol was vacuum-distilled into the calorimeter vessel, taking only the middle 1/3 portion of the starting sample. The vessel was sealed in vacuo. The used adiabatic calorimeter was home-made, and the details of which are described elsewhere.[5,6] A platinum resistance thermometer (Tinsley, 5187L) was calibrated against ITS-90. The temperature range covered was from 13 to 300 K with increments of 1 to 2 K for each heat-capacity measurement.

To estimate the density of liquid below room temperature and that of super-cooled liquid, a homemade dilatometer was used. A calibrated burette of about 10 mL was glass-blown onto an Erlenmeyer flask of about 30 mL. The volume of the dilatometer was calibrated at room temperature using pure water. The correction for thermal expansion of the dilatometer (Pyrex glass) amounted to 0.003 mL for 100 K temperature change, and hence was neglected. The volume of the sample filled in the dilatometer was about 40 mL in total. The measurement was made by reading the meniscus of the liquid. It was filled in dry nitrogen atmosphere by a liquid sample at room temperature and cooled intermittently in a stirred alcohol bath of a Dewar flask by Dry Ice or liquid nitrogen. When the temperature remained constant within ± 0.3 °C for half an hour, the meniscus was read through a window of Dewar flask within ± 0.02 mL. The temperature of the bath was monitored by a plutinum–cobalt resistance thermometer. Through out the measurement, the sample was kept in dry nitrogen atmosphere.

Results and Discussion

The measured values of the heat capacity, C_p, are plotted in Fig. 1. Glass transitions are evident for all three isomers. As typical to glass transitions, there is a relaxation process near the glass transition temperature, T_g. After heat input corresponding to about a 2 K increase in the temperature of the system, prolonged temperature drifts, exothermic at first and then endothermic, were observed. Figure 2 shows plots of the temperature drift after 10 min of heat input. The glass transition temperatures, T_g, were determined to be 140, 146, and 150 K for *n*BE, *i*BE, and *t*BE, respectively. A further study on these glass transitions by means of heat-capacity spectroscopy[7–11] is now underway, and a more detailed discussion will be given in a future publication. In this paper, we limit ourselves to report on what was obtained by adiabatic

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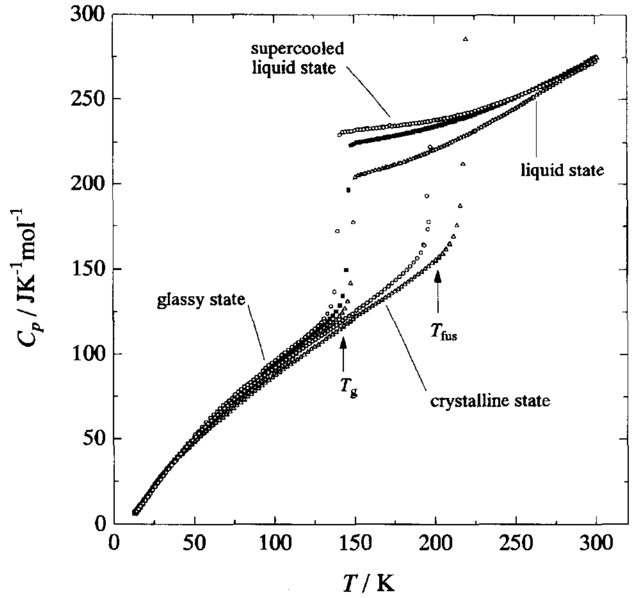

Fig. 1. Measured heat capacities, C_p, against temperature. ○, 2-butoxyethanol (*n*BE), ■, 2-isobutoxyethanol (*i*BE), △, 2-*t*-butoxyethanol (*t*BE).

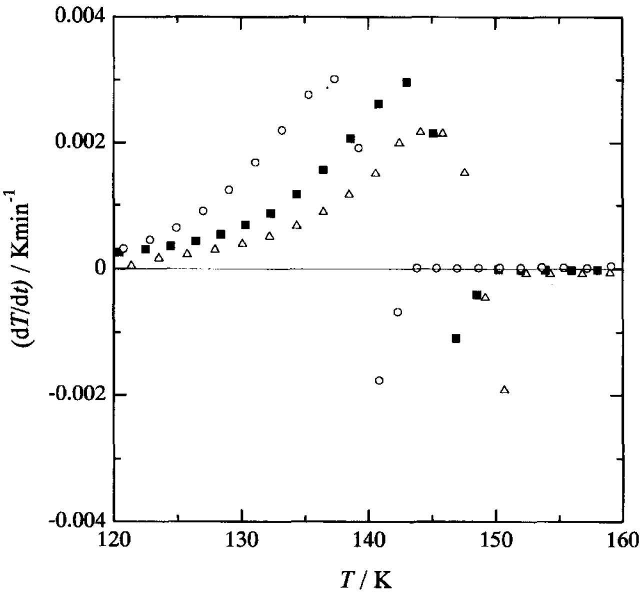

Fig. 2. Spontaneous thermal drifts, dT/dt, against temperature. ○, 2-butoxyethanol (*n*BE), ■, 2-isobutoxyethanol (*i*BE), △, 2-*t*-butoxyethanol (*t*BE).

calorimetry.

After several thermal cyclings in the super-cooled state, *n*BE and *t*BE underwent crystallization. We were thus able to determine C_p of the solid and liquid through the fusion process. The thermodynamic data for fusion are listed in Table 1. The temperature of fusion, T_{fus}, was corrected for impurities, which turned out to be 0.14 mol% for *n*BE and 0.37 mol% for *t*BE. An empirical rule is known such that $T_{fus}/T_g = 1.7$.[12] As shown in Table 2, however, we found the ratio to be 1.43 for *n*BE and 1.49 for *t*BE. If this ratio is similar for *i*BE, we could expect T_{fus} for *i*BE to be about 213 K.

Table 2 lists the values of thermodynamic functions, calculated by extrapolating C_p data between 13 K and 22 K to 0 K by a polynomial-containing terms of odd-number powers of T. A similar extrapolation of C_p of the glassy state yielded the residual entropy at 0 K, $S(0)$ to be 16.9 JK^{-1} mol^{-1} for *n*BE and 16.2 JK^{-1} mol^{-1} for *t*BE, also listed in Table 1. The values of the total entropy, $S(T)$, are plotted in Fig. 3 against T. The Kauzman temperatures, T_K, are estimated from Fig. 3 and are listed in Table 1. The ratio T_g/T_K is the same as the Adam-Gibbs value, 1.3.[13]

As is evident from Fig. 3, the entropy at T_{fus}, $S(T_{fus})$, takes almost the same value: 229 JK^{-1} mol^{-1} for *n*BE and 231 JK^{-1} mol^{-1} for *t*BE, indicating the same degree of randomness. Figure 1 shows, however, that the values of liquid C_p are different by about 10% at T_{fus}. This suggests that although the global averages of entropy are the same within 1%, those of the mean square entropy fluctuation are different. To see this more clearly, we calculated the mean square entropy fluctuation density and the mean square normalized entropy fluctuation.[14—18] As discussed earlier at some length,[14—18] a fluctuation in an extensive quantity, entropy, must be evaluated within a coarse grain, the size of which must be large enough for entropy to be defined, but small enough for a fluctuation to be detected. The problem is that the size of coarse grain is not known a priori, nor is it fixed universally. Depending on the mechanism of aggregation of the system in question, the size of a coarse grain could be different.[18] To circumvent this difficulty and ambiguity, one of us intro-

Table 1. Thermodynamic Functions of Fusion and Glass Transition

	2-Butoxyethanol	2-Isobutoxyethanol	2-*t*-Butoxyethanol
T_{fus} / K	199.53	213[c]	223.09
$\Delta_{fus}H$ / kJ mol^{-1}	11.8	—	11.4
$\Delta_{fus}S$ / JK^{-1} mol^{-1}	59.2	—	51.0
T_g / K	140	146	150
T_{fus} / T_g	1.43	—	1.49
$T_K^{a)}$ / K	110.2	—	116.7
T_g / T_K	1.27	—	1.29
ΔC_p / JK^{-1} mol^{-1}	101	94	73
$S(0)^{b)}$ / JK^{-1} mol^{-1}	16.9	—	16.2

a) Kauzmann temperature. b) Residual entropy of glass at T = 0 K. c) An estimate, see text.

Table 2. Thermodynamic Functions

$\frac{T}{\mathrm{K}}$	$\frac{C_p}{\mathrm{JK^{-1}\,mol^{-1}}}$	$\frac{H(T)-H(0)}{\mathrm{J\,mol^{-1}}}$	$\frac{S(T)-S(0)}{\mathrm{JK^{-1}\,mol^{-1}}}$	$\frac{-\{G(T)-G(0)\}T^{-1}}{\mathrm{JK^{-1}\,mol^{-1}}}$
		a) 2-Butoxyethanol		
10	3.67	12.1	1.96	0.75
20	14.85	101	7.66	2.62
30	27.58	314	16.11	5.66
40	39.52	650	25.71	9.46
50	50.32	1100	35.70	13.70
60	60.18	1654	45.77	18.21
70	69.19	2301	55.73	22.86
80	77.39	3034	65.51	27.58
90	84.94	3847	75.07	32.32
100	92.05	4732	84.39	37.07
110	98.81	5687	93.48	41.78
120	105.4	6708	102.36	46.46
130	111.85	7794	111.05	51.10
140	118.39	8945	119.58	55.68
150	125.04	10162	127.97	60.22
160	131.98	11447	136.26	64.72
170	139.44	12804	144.48	69.17
180	147.59	14238	152.68	73.58
190	157.76	15761	160.91	77.96
		fusion		
210	240.06	31617	240.36	89.81
220	242.35	34029	251.58	96.91
230	244.97	36465	262.41	103.87
240	247.97	38929	272.90	110.69
250	251.33	41425	283.09	117.38
260	255.11	43958	293.02	123.95
270	259.21	46529	302.72	130.39
280	263.29	49141	312.22	136.72
290	267.77	51796	321.54	142.93
298.15	271.66	53994	329.01	147.91
300	272.58	54497	330.69	149.04
		b) 2-*t*-Butoxyethanol		
15	8.44	39.8	4.09	1.43
20	15.20	99.0	7.45	2.50
30	27.26	314	16.00	5.53
40	38.97	642	25.35	9.31
50	48.12	1079	35.08	13.49
60	56.84	1605	44.64	17.89
70	64.60	2213	53.99	22.38
80	72.27	2897	63.12	26.91
90	79.91	3658	72.07	31.43
100	87.28	4494	80.88	35.93
110	94.28	5402	89.53	40.41
120	101.06	6379	98.02	44.86
130	107.85	7424	106.38	49.27
140	114.71	8537	114.62	53.65
150	121.48	9718	122.77	57.99
160	127.87	10965	130.82	62.29
170	134.02	12274	138.75	66.55
180	140.58	13647	146.60	70.78
190	147.51	15087	154.38	74.98
200	154.87	16599	162.13	79.14
210	162.65	18186	169.88	83.28
220	170.85	19853	177.63	87.39
		fusion		
230	234.45	33348	238.03	93.04
240	239.53	35717	248.11	99.29
250	244.90	38139	258.00	105.44
260	250.56	40616	267.71	111.50
270	256.39	43151	277.28	117.46
280	262.31	45744	286.71	123.34
290	268.25	48397	296.02	129.13
298.15	273.45	50604	303.52	133.79
300	274.41	51110	305.21	134.85

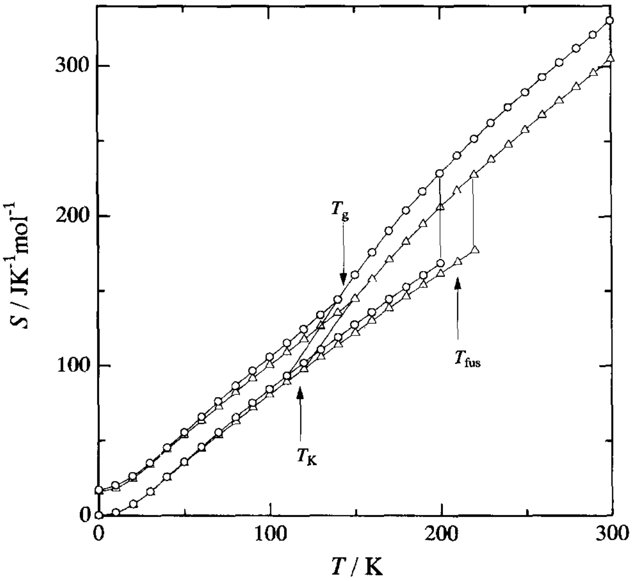

Fig. 3. Entropy, *S*, against temperature. ○, 2-butoxyethanol (*n*BE), △, 2-*t*-butoxyethanol (*t*BE).

duced two kinds of fluctuation function: (1) the mean square fluctuation density, ${}^{q}\delta$, and (2) the normalized fluctuation, ${}^{q}\Delta$, where $q = S$, V, or SV indicating entropy-, volume-, or cross between entropy and volume fluctuations.[18] The former, ${}^{q}\delta$, has no information about the size of a coarse grain, and hence it gives the amplitude of fluctuation. The latter, ${}^{q}\Delta$, on the other hand, contains qualitative information about the size of a coarse grain, or the wavelength of fluctuation as well as the amplitude of fluctuation.[18] Thus, the entropy fluctuation density, ${}^{S}\delta$, is written as[18]

$$ {}^{S}\delta \equiv \langle(\Delta S)^2\rangle/(k\langle V\rangle) = \langle C_p\rangle/\langle V\rangle = C_{pm}/V_{m}, $$

where C_{pm} signifies the molar heat capacity and V_m is the molar volume. $\langle C_p\rangle$ and $\langle V\rangle$ are the average heat capacity and the average volume of a coarse grain. The normalized entropy fluctuation is written as

$$ \langle(\Delta S/\langle V\rangle)^2\rangle = k\langle C_p\rangle/\langle V\rangle^2, $$

and by taking the size of coarse grain arbitrarily to 1 mol and converting k to R, ${}^{S}\Delta$ is defined as

$$ {}^{S}\Delta \equiv RC_{pm}/V_{m}^{2}. $$

The values of V_m measured by dilatometry are listed in Table 3. Using these and C_p data read off from Fig. 1, the values of ${}^{S}\delta$ and ${}^{S}\Delta$ were calculated by the above equations, and are plotted in Fig. 4. As is evident from the figure, at about 200 K, the amplitude of the entropy fluctuation, ${}^{S}\delta$, is by several percent larger for *n*BE than *t*BE. That for *i*BE lies in between the two. The difference, however, diminishes at room temperature. The wavelength and the amplitude of the entropy fluctuation, ${}^{S}\Delta$, shows the same general trend, except that the temperature dependence changes sign for *n*BE and *i*BE. This means that the wavelength of the entropy fluctuations for *n*BE and *i*BE increases upon cooling more rapidly than that for *t*BE. The difference in ${}^{S}\delta$ and ${}^{S}\Delta$ among three isomers may be attributed to the flexibility, and/or hindrance, of the hydrogen bond network by the alkyl moiety. The butyl group is more flexible than the isobutyl group, which in turn is more so than *t*-butyl. Hence, the entropy fluctuation could become smaller in this order. Alternatively, a possible hydrogen bond via -OH groups may be more hindered in the order of *t*-, isobutyl and butyl group, which gives rise to a lesser degree of hydrogen bonds. The greater number of hydrogen bonds, the larger on the entropy fluctuation, as in liquid H_2O.[15] The entropy fluctuation functions, Fig. 4, shows concavity upward upon cooling. In particular, ${}^{S}\Delta$ for *n*BE and *i*BE actually increases upon cooling. This increase, or at least the tendency of an increase (concavity), may be at least partially responsible for a triggering glass transition. In Fig. 5, are plotted ${}^{S}\delta$[##] and ${}^{S}\Delta$[15] in a comparison with H_2O and hexane. In terms of the amplitude of the entropy fluctuation, 2-butoxyethanol lies in between hexane, a typical van der Waals liquid, and H_2O with an extensive hydrogen-bond network. This indicates that isomeric 2-butoxyethanols have a property in between H_2O and hexane. Namely, there are some contributions of the hydrogen bond. Figure 5b indicates that the wavelength plus the amplitude of entropy fluctuation decreases almost to the level of hexane. This suggests that the wavelength of the entropy fluctuation is smaller than that of hexane, compensating the larger am-

Table 3. Entropy Fluctuations

T	V_m	${}^{S}\delta$	${}^{S}\Delta$
K	$cm^3\ mol^{-1}$	$JK^{-1}\ cm^{-3}$	$J^2K^{-2}\ cm^{-6}$
	2-Butoxyethanol		
200.8	121.4	1.963	0.1345
211.7	122.3	1.965	0.1335
219.7	123.2	1.967	0.1328
231.9	124.5	1.973	0.1318
244.9	125.9	1.983	0.1309
260.8	127.7	2.000	0.1302
276.2	129.4	2.022	0.1300
294.7	131.5	2.053	0.1298
	2-Isobutoxyethanol		
199.4	122.1	1.918	0.1305
207.4	122.9	1.922	0.1300
217.9	124.0	1.931	0.1295
232.2	125.6	1.945	0.1288
247.7	127.2	1.967	0.1286
260.6	128.8	1.985	0.1281
273.9	130.4	2.008	0.1280
292.2	132.5	2.046	0.1284
	2-*t*-Butoxyethanol		
200.3	121.2	1.823	0.1250
210.8	122.3	1.843	0.1253
219.2	123.2	1.861	0.1256
229.5	124.2	1.885	0.1262
242.4	125.6	1.918	0.1270
259.4	127.5	1.962	0.1280
295.4	131.3	2.069	0.1310

The data of Ref. 15 was used to calculate ${}^{S}\delta$ for H_2O and hexane.

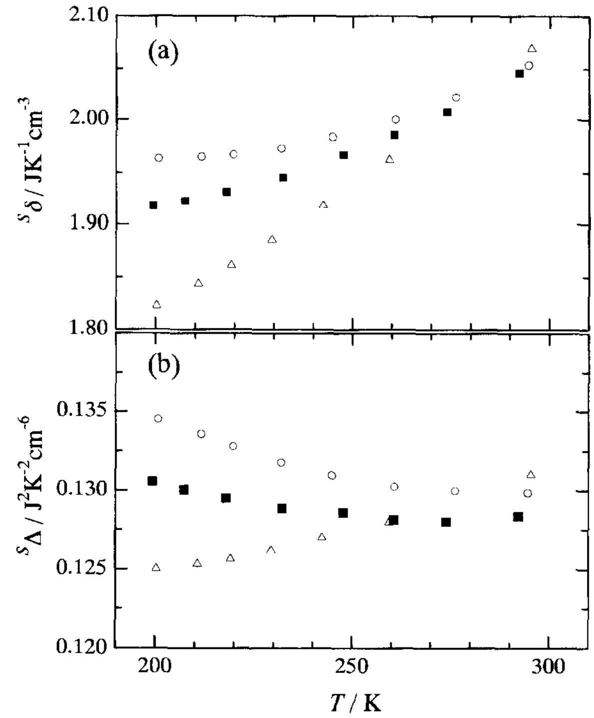

Fig. 4. Entropy fluctuations of liquid (including supercooled liquid) of 2-butoxyethanols. ○, 2-butoxyethanol (*n*BE), ■, 2-isobutoxyethanol (*i*BE), △,2-*t*-butoxyethanol (*t*BE), (a) Amplitude of entropy fluctuation, $^S\delta$, (b) Amplitude plus wavelength of entropy fluctuation, $^S\Delta$.

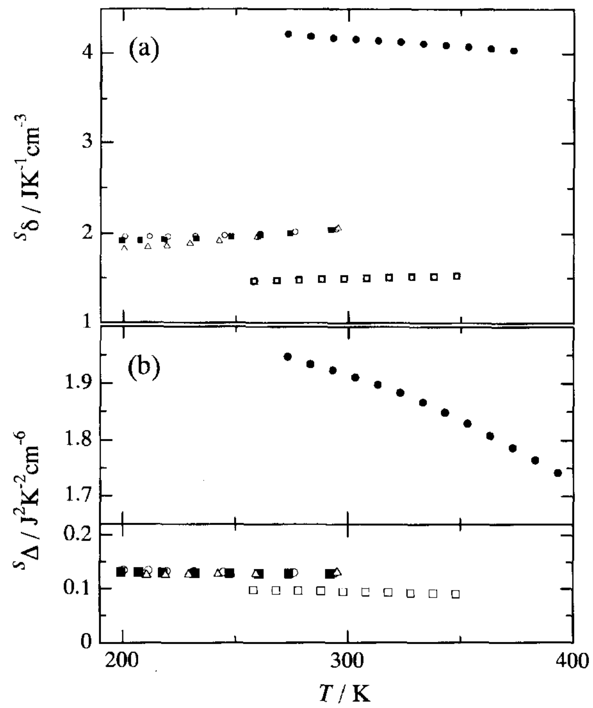

Fig. 5. Comparison of entropy fluctuations among 2-butoxyethanol, hexane and H_2O. ●, H_2O, □, hexane, ○, 2-butoxyethanol (*n*BE), ■, 2-isobutoxyethanol (*i*BE), △, 2-*t*-butoxyethanol (*t*BE), (a) Amplitude of entropy fluctuation, $^S\delta$, (b) Amplitude plus wavelength of entropy fluctuation, $^S\Delta$.

plitude of 2-butoxyethanols than that of hexane. However, caution should be exercised in any comparison with $^q\Delta$, in that the information contained in $^q\Delta$ is qualitative in nature, as compared with $^q\delta$ which gives strictly the amplitude of fluctuation.[18] Nevertheless, we might add in closing that these fluctuations could lead to a better understanding of the nature of the liquid state.

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