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論　文

Heat Capacities of Aqueous 2-Butoxyethanol in the Water-rich Region by Adiabatic Calorimetry

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Heat capacities of aqueous 2-butoxyethanol at mole fraction, x_{BE} = 0.01702 and 0.01950, were measured from 271 to 313 K by adiabatic calorimetry. The data at x_{BE} = 0.01702 were compared with those at x_{BE} = 0.01703 obtained by differential scanning calorimetry in paper I [*Chem. Phys. Lett.* **217**, 245 (1994)]. They agreed within 0.2 %. The temperature dependence was not the same, but similar in that the temperature derivative, $\partial C_p/\partial T$, showed a step anomaly at the same temperature. The conclusion drawn in paper I is therefore correct. The observed small difference in the temperature dependence was attributed to the difference in thermal conductivity between the sample solution and pure water used as the reference in differential scanning calorimetry.

Introduction

Heat capacity, C_p, is the second derivative of Gibbs energy, G, with respect to T, and is proportional to the thermal fluctuation of the system, $<(\Delta H)^2>$. It is therefore powerful in providing a microscopic picture of the system in question. Across a phase transition, for example, C_p shows an anomaly, a variety of which depends crucially on the nature of the transition. We note that a phase transition involves a change of a long range order.

In a previous paper (called paper I)$^{1)}$, it was found that the C_p data of aqueous 2-butoxyethanol (BE) showed a bend at a temperature which depended on the composition of BE. For example, at x_{BE} = 0.01703, the C_p decreased slowly from 283 to 297 K, thereupon decreased much more rapidly up to 323 K. Such a bend in C_p, a second derivative, is naturally equivalent with a step anomaly in $(\partial C_p/\partial T)$, a third derivative. The loci of this kind of anomalies are plotted in **Fig. 1.** They all fall on the mixing scheme boundary as shown in Fig. 1, which separates two regions in the temperature-composition field. In each of these regions, the mixing scheme is qualitatively different from that in the other.$^{1)-7)}$ Here, by the mixing scheme we mean simply the way in which the solute and the solvent molecules mix with each other. We note that regions I and II are within a single phase domain, and the difference is only in their mixing scheme. Thus, the difference between regions I and II is much more subtle than an ordinary phase transition. Hence, the crossover from region I to II may involve a change in a short or medium range order in the system. It is noteworthy that such crossover is accomapanied by

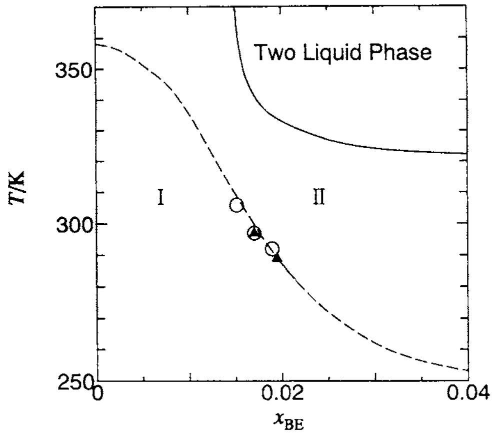

Fig.1 The mixing scheme boundary and the loci of step anomalies in $(\delta C_p/\delta T)$. ▲; this work, ○; paper I[1].

anomalies in the third derivative of Gibbs energy. In fact, the mixing scheme boundary shown in Fig. 1 was drawn through the anomalies in the other third derivatives of Gibbs energy: $(\partial H_m{}^E(BE)/\partial n_{BE})$[5,6], $(\partial S_m{}^E(BE)/\partial n_{BE})$[4], $(\partial V_m{}^E(BE)/\partial n_{BE})$[2], $C_p{}^E(BE)$[5,8], and $(\partial \alpha_p/\partial n_{BE})$[3]. Here, $H_m{}^E(BE)$, $S_m{}^E(BE)$, $V_m{}^E(BE)$, and $C_p{}^E(BE)$ are the excess partial molar enthalpy, entropy, volume and heat capacity respectively. α_p is thermal expansivity. Thus, in paper I,[1] another example was presented of an anomaly in a third derivative, $(\partial C_p/\partial T)$, at the mixing scheme boundary.

The C_p data in paper I were determined by high precision differential scanning calorimetry (DSC), and the uncertainty was estimated to be better than 0.2 %[1]. After all, a dynamic effect is inevitable in DSC technique. Recently, the thermal conductivity data were obtained in the water-rich region of BE-H_2O solutions by heat capacity spectroscopy[9]. The results indicated[9] that the thermal conductivities showed a bend at the mixing scheme boundary in a similar fashion as the C_p data determined by DSC[1]. Thus, the purpose of the present work is to determine C_p by adiabatic calorimetry, completely free from any dynamic effect.

Experimental

2-Butoxyethanol (Wako, 99+ %) was used without further purification. H_2O was doubly distilled. The mixtures were made by weighing.

The adiabatic calorimeter was home-made, and the detail is described elsewhere[10,11]. About 12 g of solution (~ 0.6 mol) was sealed in the calorimeter vessel with about 0.7 cm^3 air space. The temperature increment for each measurement was about 0.7 K. The equilibrium freezing point being about 270 K[7], the calorimeter was cooled to about 271 K, thereupon the measurement was commenced and continued to about 313 K. The temperature scale of the Pt thermometer used has been calibrated to 302 K. The scale for $T < 302$ K was extended to 320 K.

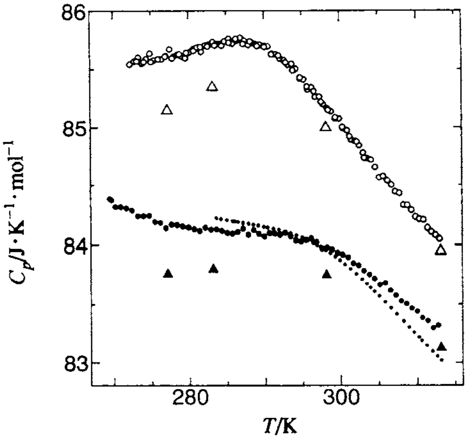

Fig.2 Heat capacities of aqueous 2-butoxyethanol. Open marks are for x_{BE} = 0.01950, and filled marks for x_{BE} = 0.01702. ○,●; by adiabatic calorimetry, this work. △,▲; by flow calorimetry, ref. (8).
●; by DSC, at x_{BE} = 0.01703, paper I[1].

Results and Discussion

The C_p data are plotted in **Fig. 2**. A reasonable estimate of uncertainty appears to be ± 0.3 J·K^{-1}·mol^{-1} (0.04 %). Smoothed values were read off from the graph at 1 K interval and listed in **Table 1**. Negligibly small corrections due to vapourization into a small air space in the vessel were made and the resulting values of corrected C_p are also listed in the table. Using the corrected values of C_p, the derivatives, $(\delta C_p/\delta T)$, were calculated and plotted in **Fig. 3**. The step anomalies are evident, similar to those found in paper I[1]. The point in the step where the slopes are the steepest were found to be 297 K for x_{BE} = 0.01702 and 289 K for x_{BE} = 0.01950. Both fall on the mixing scheme boundary as shown in Fig. 1. Thus,

Table 1 Smoothed values of heat capacities, C_p, of aqueous 2-butoxyerthanol.

T/K	C_p/J·K^{-1}·mol^{-1}			
	x_{BE} = 0.01702		x_{BE} = 0.01950	
	observed	corrected	observed	corrected
271	84.326	84.325		
272	84.290	84.289	85.592	85.591
273	84.260	84.259	85.586	85.585
274	84.234	84.233	85.584	85.583
275	84.211	84.210	85.587	85.586
276	84.192	84.191	85.590	85.589
277	84.176	84.175	85.601	85.600
278	84.163	84.162	85.615	85.614
279	84.152	84.151	85.634	85.633
280	84.143	84.141	85.656	85.654
281	84.135	84.133	85.680	85.679
282	84.128	84.127	85.702	85.701
283	84.121	84.119	85.723	85.721
284	84.116	84.114	85.740	85.738
285	84.112	84.110	85.752	85.750
286	84.110	84.108	85.756	85.754
287	84.108	84.106	85.754	85.752
288	84.106	84.104	85.742	85.740
289	84.104	84.102	85.723	85.721
290	84.100	84.097	85.693	85.691
291	84.094	84.091	85.655	85.652
292	84.088	84.085	85.606	85.603
293	84.076	84.073	85.547	85.544
294	84.064	84.061	85.483	85.480
295	84.049	84.046	85.416	85.413
296	84.030	84.026	85.346	85.343
297	84.008	84.004	85.276	85.273
298	83.981	83.977	85.200	85.196
299	83.951	83.947	85.121	85.117
300	83.916	83.912	85.040	85.036
301	83.877	83.873	84.955	84.951
302	83.833	83.828	84.872	84.868
303	83.787	83.782	84.789	84.784
304	83.738	83.733	84.707	84.702
305	83.688	83.683	84.625	84.620
306	83.637	83.631	84.546	84.541
307	83.584	83.578	84.466	84.461
308	83.530	83.524	84.389	84.383
309	83.477	83.471	84.315	84.309
310	83.426	83.419	84.242	84.236
311	83.379	83.372	84.176	84.170
312	83.333	83.326	84.111	84.104
313	83.288	83.280	84.048	84.041

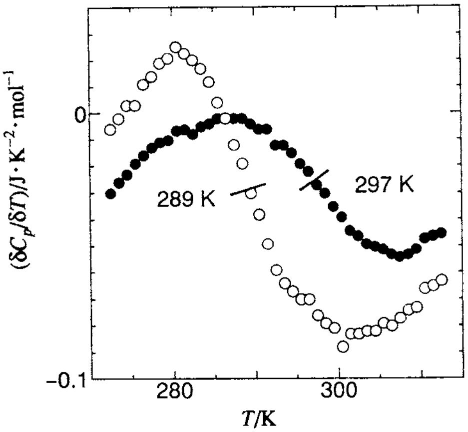

Fig.3 A third derivative of Gibbs energy, $\delta C_p/\delta T$. ●; x_{BE} = 0.01702. ○; x_{BE} = 0.01950.

the conclusion drawn in paper I remains correct.

In Fig. 2, the C_p data for x_{BE} = 0.01703 from paper I are also plotted. It is evident that the data are within 0.2 % of the present data for x_{BE} = 0.01702. However, their temperature dependence appears to be much sharper than that of C_p by adiabatic calorimetry. In DSC, the differential heat flow to the sample (BE-H_2O) and the reference (H_2O) necessary to keep the same temperature rise in the both cells is recorded. The thermal conductivities of BE-H_2O mixtures were found previously lower than that of pure H_2O, and much more so in region II, *i.e.* at higher temperatures above the mixing scheme boundary[9]. The temperature gradient in the cell, no matter how small it may be, will then be larger in the sample cell than that in the reference. The heat flow into the sample cell to keep up with the temperature rise of the reference will therefore be unduly less and less as the temperature increases. Thus, the C_p data tend to decrease faster than the case where there is no thermal gradient in the measuring cell. If the above interpretation is true, we may conclude that the DSC system used in paper I is not entirely free from a dynamic effect, while the values of C_p obtained by DSC are remarkably close to those by adiabatic calorimetry. Thus, the values of the their temperature derivative, ($\delta C_p/\delta T$), by DSC are systematically less than those by adiabatic calorimetry. However, the general feature of the temperature dependence of C_p remains the same, and in particular, the loci of the step anomalies in ($\delta C_p/\delta T$) evidently did not change. Thus, the conclusion drawn in paper I using the C_p date by DSC remains correct.

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Reference

1) P. Westh, Aa. Hvidt and Y. Koga, *Chem, Phys. Lett.* **217**, 245 (1994).
2) Y. Koga, *J. Phys. Chem.* **96**, 10466 (1992).
3) J. V. Davies, F. W. Lau, L. T. N. Le, J. T. W. Lai and Y. Koga, *Can. J. Chem.* **70**, 2659 (1992).
4) Y. Koga, *J. Phys. Chem.* 95, 4119 (1991).
5) Y. Koga, W. W. Y. Siu and T. Y. H. Wong, *J. Phys. Chem.* **94**, 3879 (1990).
6) W. Siu and Y. Koga, *Can. J. Chem.* **67**, 671 (1989).
7) Y. Koga, T. Tanaka, T. Atake, P. Westh and Aa. Hvidt, *Bull. Chem. Soc. Jpn.*, (in press).
8) G. Roux, G. Perron and J. E. Desnoyers, *J. Sol. Chem.* **7**, 639 (1978).
9) K. T. Puhacz, C. C. M. Hui, Y. Ootsuka, H. Kawaji, T. Atake and Y. Koga, *Rep. Res. Lab. Eng. Mater., Tokyo Inst. Tech.* **19**, 263 (1994).
10) T. Atake, Y. Takagi, T. Nakamura and Y. Saito, *Phys. Rev.* **B37**, 552 (1988).
11) T. Atake, H. Kawaji, A. Hamano and Y. Saito, *Rep. Res. Lab. Eng. Mater., Tokyo Inst. Tech.* **15**, 13 (1990).

要　旨

2-Butoxyethanolの希薄水溶液(モル分率0.01702および0.01950)の熱容量を断熱カロリメトリーにより271から313 Kの温度範囲で測定した。モル分率0.01702の試料のデータをDSCで得られたモル分率0.01703のもの[Paper I: *Chem. Phys. Lett.* **217**, 245 (1994)]と比較したところ, 0.2%で一致した。熱容量の温度依存性は, 全く同じではないがよく似ており, その温度微分($\partial C_p/\partial T$)はいずれも階段状の異常を示した。したがってPaper Iの結論は正しいと言える。DSCの結果との小さな違いは, DSCにおける試料と参照物質として用いた純水との熱伝導率の違いによる。