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Low-temperature thermal properties of the aqueous solutions of simple aminoalcohols: Finding of peculiarities in 1-amino-2-propanol solutions

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ABSTRACT

Low-temperature heat capacity (C_p) and glass-transition temperature (T_g) values of the aqueous solutions of three simple aminoalcohols (hereafter abbreviated as AA); *i.e.*, 2-aminoethanol (2AE), 3-amino-1-propanol (3A1P) and 1-amino-2-propanol (1A2P), were examined by differential scanning calorimetry (DSC). Both the 2AE and 3A1P aqueous solutions revealed gradual decrease of C_p values on cooling in an AA molar-fraction (x_{AA}) in the range of 0.2–0.7, while displaying no crystallization. On the other hand, the 1A2P aqueous solutions revealed a C_p hump at the temperature slightly above T_g on both cooling and heating curves when the x_{AA} approaches 0.19. The T_g values of the 1A2P solutions simultaneously displayed a maximum as a function of the x_{AA}, which suggests formation of an ordered aggregate structure with development of a certain hydrogen-bond network. We propose, as the origin of the anomalies, formation of a molecular-aggregate structure of nanometer-sized regions of two kinds; one region is composed of the hydrophilic groups of AA molecules and water molecules and the other of the hydrophobic groups of AA molecules.

1. Introduction

Water is one of the most mysterious liquids, although it exists abundantly and as an indispensable substance around us [1,2]. Liquid water reveals peculiar behaviors such as a volume minimum at 277.1 K and a specific heat-capacity minimum at around 308 K [1,2]; namely, the volume and heat capacity increase with decreasing temperature below the respective ones. The peculiarities are well known to become further striking with decreasing temperature in the supercooled liquid state [1–4]. They have been discussed to be associated with the potential existence of a liquid–liquid phase transition, which is one of the most attractive research subjects at present in the condensed-matter chemistry [1,2,5–10]. Angell pointed out that the substances forming a tetrahedrally networked structure potentially display the anomalous behaviors similar to those that water does [11,12]. The peculiarity of water is supported also by the fact that doping of second components of a small amount into water easily sweeps out the anomalies [13,14].

Unlike the liquids of pure substances, the solutions composed of plural components often reveal peculiar behaviors in their liquid states due to chemical-doping effects. Takeda and co-workers disclosed that the binary solutions between two compounds; one with dihydroxy and the other with diamino groups reveal a maximum in the glass-transition temperature (T_g) at an intermediate composition [15,16]. T_g is the characteristic temperature at which the relevant molecular rearrangement is frozen in on our experimental time scale and that is ordinarily in proportion to the activation energy against the rearrangement [17]. The formation of a network structure of hydrogen bonds between the hydroxy groups and amino groups increases the activation energy for the rearrangement in the binary solution and decreases the mobility of molecules most effectively at the composition of the T_g maximum. Therefore, the T_g can be a parameter providing the information not only about the dynamic properties but also the static molecular configurations realized in the liquid state.

A water molecule has two protons and two lone electron-pairs the combination of which enables a hydrogen-bond network to be formed neatly among the molecules [18–20]. In association with this, doping of ordinary second components commonly leads to

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Table 1
Data of aminoalcohol reagents used in this study.[a]

Reagent	Purity (w/w)	Methods for determination
2-Aminoethanol (2AE)	>98%	Gas chromatography and volumetric analysis
3-Amino-1-propanol (3A1P)	>98%	Gas chromatography and volumetric analysis
DL-1-amino-2-propanol (1A2P)	>98%	Gas chromatography and volumetric analysis

[a] The data were taken as provided by Tokyo Chemical Industry Co., Ltd.

depression of the water's T_g due to the collapse of the network structure [11,21,22]. In the meanwhile, we found the fact that doping of hydroxylamine (HA), the molecule of which has the same ratio between the numbers of protons and lone electron-pairs as water, causes no decrease in the T_g values [18]. This means that the HA doping brings no collapse of the hydrogen-bond network formed among water molecules, indicating that an HA molecule is accommodated snugly in the network structure. The HA solutions further revealed a peculiar increase of the specific heat capacity (C_p) at low temperatures in the same way as the pure water [19,20,23]. This fact also supports the above understanding of the snug accommodation of HA molecule into the network. We can thus expect that the presence of the same number of protons and lone electron-pairs in each molecule is relevant to the realization of the peculiar behaviors of liquid water. However, there have been no other studies reported about the aqueous solutions of the substances, but HA, with the same numbers of protons and lone electron-pairs as water.

In this study, we chose 3 aminoalcohols as the second components; 2-aminoethanol (abbreviated as 2AE), 3-amino-1-propanol (3A1P), and DL-1-amino-2-propanol (1A2P). 2AE has a simple molecular structure next to HA. 3A1P was chosen to examine the effect of extending the alkyl-chain length, and 1A2P to examine the change of the probabilities for the amino and hydroxy groups to take their trans- and gauche-conformational interrelations due to the presence of a methyl group as compared with 2AE without the group.

2. Materials and methods

Reagent 2AE, 3A1P and 1A2P were purchased from Tokyo Chemical Industry Co., Ltd. and each as purchased was mixed with distilled water to prepare the solution samples with specified AA molar-fraction (x_{AA}). Data of all the reagents are summarized in Table 1.

Differential scanning calorimetry (DSC) was carried out with a PerkinElmer DSC-8500 immediately after preparation of the solution samples. The measurements were performed at a scanning speed of −10 or +10 K min^{-1} between 293 K and 123 K in the cooling and heating directions, respectively. Temperature scale was calibrated through measurements of fusion temperatures of *n*-heptane, water, and indium. Heat-flow rates were converted to C_p values by using liquid 2,3-dimethylpentane as a reference material for calibration of the C_p values as a function of temperature [24]. The T_g value of each sample was determined as a middle point of the C_p jump, due to the glass transition, on each heating curve [11]. No decomposition reaction of the samples with aluminum pans could be detected as confirmed from the reproduced DSC curves. After each sample had been sealed within a DSC pan at 295 K and 0.1 MPa, the measurements were performed while the pressure was not controlled.

3. Results

3.1. Specific heat capacity

First, we examined the molar-fraction range of the solutions that exhibited no crystallization on cooling at the speed of −10 K min^{-1} and therefore vitrified at low temperatures. The solutions with x_{AA} values ≥0.19, 0.19 and 0.15 for 2AE, 3A1P and 1A2P, respectively, exhibited no crystallization on cooling, while the pure liquids of the 3 aminoalcohols crystallized during the cooling.

Observed heat capacity values of 2AE aqueous solutions at 283 K on heating scans agreed with literature values [32] of the solutions of nearby composition within inaccuracy less than 1.0%, while those on cooling scans agreed with those [32] within inaccuracy of 5.0%. The imprecision of the measurement in each series was 0.3% and much less than the inaccuracy. Figs. 1–3 show C_p curves obtained for the 2AE, 3A1P and 1A2P aqueous solutions,

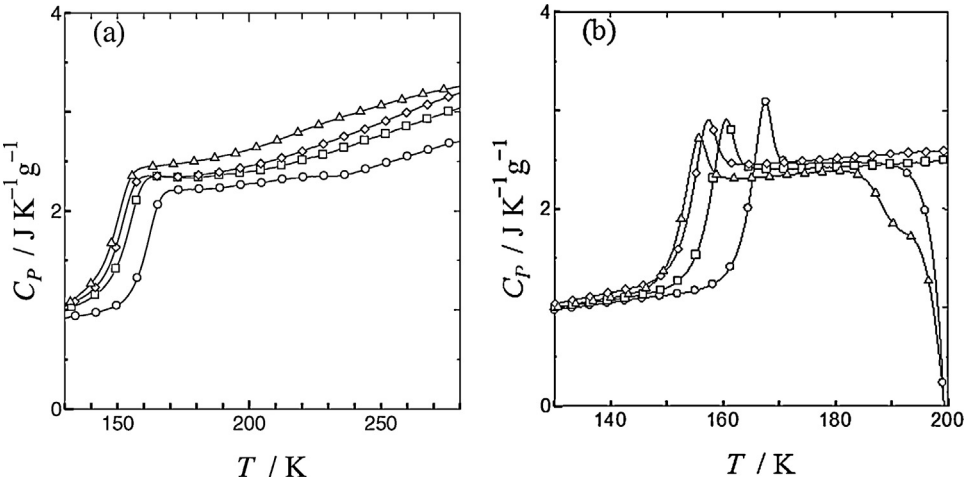

Fig. 1. Specific heat capacity curves of 2-aminoethanol (2AE) aqueous solutions measured by DSC on cooling (a) and on subsequent heating (b): open circles, x_{AA} = 0.73; open squares, 0.31; open diamonds, 0.23; open triangles, 0.19. Solid lines are the curves obtained.