

Fluctuations in Water, Aqueous tert-Butanol and 2-Butoxyethanol: Amplitude and Wavelength of Fluctuation

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We study fluctuations in liquid H₂O and aqueous solutions of tert-butanol and 2-butoxyethanol. We calculate the fluctuation density and the normalized fluctuation. The former shows the amplitude (or the intensity) of fluctuation, and the latter are indicative of the amplitude plus the wavelength (the extensity) of fluctuation. Three kinds of fluctuations are evaluated, the mean square volume fluctuation, the mean square entropy fluctuation, and the cross fluctuation between volume and entropy. They are calculated using respectively compressibility, heat capacity and thermal expansivity. Using these data, we discuss the peculiarity of liquid H₂O, and the details of the mixing schemes in aqueous tert-butanol and 2-butoxyethanol.

1. Introduction

In earlier publications,¹⁻⁴⁾ we introduced the normalized fluctuations denoted as ${}^q\Delta$, ($q = V, S$, or SV and their meanings are described in the next section), which turned out to give qualitative information about the amplitude (intensity) as well as the wavelength (extensity) of fluctuations. Using ${}^q\Delta$, we discussed the peculiarity of liquid H₂O in comparison with a typical van der Waals liquid, n-hexane in ref.(2) (we call paper A hereinafter). Similarly in ref. (4) (paper B) and ref. (3) (paper C) we also studied the nature of aqueous tert-butanol and 2-butoxyethanol respectively. In a recent paper (paper D),⁵⁾ we defined the fluctuation densities, ${}^q\delta$, which signifies strictly the amplitude of fluctuation, regardless of the wavelength of fluctuation. Hence, ${}^q\delta$ in addition of ${}^q\Delta$ will provide more detailed information about the fluctuations of the system. Indeed, we learned more about aqueous methanol, ethanol and 1-propanol using both ${}^q\delta$ and ${}^q\Delta$ in paper D.⁵⁾

This work supplements what were reported in papers A, B, and C, in that we calculate ${}^q\delta$ for liquid H₂O, and aqueous solutions of tert-butanol and 2-butoxyethanol, which were missing from papers A, B, and C. Together with ${}^q\Delta$ in the original papers, we

make an attempt at gaining deeper insight into the nature of liquid H₂O and aqueous solutions of tert-butanol and 2-butoxyethanol. Furthermore, we add the heat capacity data, C_p , necessary to calculate ${}^S\delta$ and ${}^{SV}\Delta$ for aqueous tert-butanol. In paper B,⁴⁾ we used the literature data for C_p ,^{6,7)} but the data points were scarce in the crucial range of our interest, i. e. the region where the transition of mixing scheme occurs (see below for more detail). We thus revise ${}^{SV}\Delta$ shown in paper B also.

Aqueous alcohols (abbreviated as AL) have been studied extensively in the past, and the papers up to the early 1980s have been comprehensively reviewed.⁸⁾ Our more recent studies⁹⁻¹²⁾ basically support earlier understandings that AL forms the so-called "iceberg". Our additional findings include (a) AL indeed enhances the hydrogen bond network in the immediate vicinity of solute, but the hydrogen bond probability of bulk H₂O away from AL is reduced. (b) Below a threshold value of the mole fraction of AL, however, the hydrogen bond probability of bulk H₂O is still high enough to retain the hydrogen bond connectivity throughout the entire bulk of H₂O, i. e., the hydrogen bond percolation is intact. We call this mode of mixing, "Mixing Scheme I". (c) Above the threshold, the percolation nature of H₂O is lost and the solution consists of two kinds of

clusters rich in AL and H₂O, respectively. This is called Mixing Scheme II. (d) The transition from Mixing Scheme I to II is associated with anomalies in the third derivatives of G, in particular the enthalpic interaction between solutes, H_{AL-AL}^E , as discussed below. It takes place in a small range of mole fraction. The starting point of transition is called point X, and the end point Y. Beyond point Y Mixing Scheme II is operative. We interpret the meanings of point X and point Y as follows. The bulk of H₂O away from solutes still retains the characteristics of liquid H₂O, except that the hydrogen bond probability is reduced, not yet to the percolation threshold, however. Thus, the bulk H₂O still undergoes a large and collective fluctuation in hydrogen bond strength, and there is a wide distribution (fluctuating) in hydrogen bond strength. At point X, the strongest hydrogen bonds reach the percolation threshold and lose their bond connectivity. As the mole fraction of AL increases, the bond probability of weaker hydrogen bonds reaches the bond percolation threshold. Finally at point Y, the weakest and all the hydrogen bonds lose their bond percolation nature. Hence, beyond point Y, there is no hydrogen bond connectivity and the solution consists of two kinds of clusters, each rich in AL and H₂O. We call this mode of mixing Mixing Scheme II. (e) The larger the hydrophobic moiety in AL, the stronger the effect of AL on H₂O, and the smaller the value of mole fraction at the mixing scheme boundary.

2. Fluctuation

The second derivatives of G with respect to p, T or their combination are related to fluctuations of the system. The mean square volume fluctuations, $\langle(\Delta V)^2\rangle$, the mean square entropy fluctuation, $\langle(\Delta S)^2\rangle$, and the cross fluctuation between volume and entropy, $\langle(\Delta V)(\Delta S)\rangle$, are written as,¹³⁻¹⁶⁾

$$\langle(\Delta V)^2\rangle = -kT(\partial^2\langle G\rangle/\partial p^2) = kT\langle V\rangle\kappa_T, \quad (1)$$

$$\langle(\Delta S)^2\rangle = -kT(\partial^2\langle G\rangle/\partial T^2) = k\langle C_p\rangle, \quad (2)$$

$$\langle(\Delta V)(\Delta S)\rangle = kT(\partial^2\langle G\rangle/\partial p\partial T) = kT\langle V\rangle\alpha_p, \quad (3)$$

where $\Delta V = V - \langle V\rangle$, $\Delta S = S - \langle S\rangle$. V or S is a local value and $\langle V\rangle$ or $\langle S\rangle$ is its global average. Since it is an extensive quantity, a local value must be evaluated in a coarse grain with a fixed number of molecules, N_L , which must be large enough for a thermodynamic quantity to be defined but small enough for fluctuation to be

detected. Namely, $\langle G\rangle$, $\langle V\rangle$, and $\langle C_p\rangle$ on the right hand sides of eqs.(1)-(3) are all evaluated for N_L molecules. Hence, each time eqs. (1)-(3) are calculated, the size of the coarse grain must be specified. The appropriate size of coarse grain may be best taken as a similar size to, if not the same as, the wavelength (the extent) of the fluctuation. However, it depends on the situation in question and is not universally constant. For example, as a critical point of demixing is approached from a super critical region, fluctuation becomes progressively more vigorous not only in amplitude but also in wavelength. And eventually at the critical point, the wavelength becomes of a macroscopic size. Another example may be seen in liquid H₂O. Molecular dynamic calculation showed collective fluctuations involving a large number of molecules.^{17,18)} An x-ray scattering study suggested that one of such collective motion is a cooperative flapping of a large number of six-member rings.¹⁹⁾ Thus, the wavelength of fluctuation in liquid H₂O could be quite large in comparison with that in normal liquids. The problem is, however, that we have no way of knowing the wavelength of fluctuation *a priori*, and hence the appropriate size of the coarse grain in calculating eqs. (1)-(3).

In paper D, we defined the fluctuation densities as,⁵⁾

$${}^v\delta \equiv \langle(\Delta V)^2\rangle/k\langle V\rangle = T\kappa_T, \quad (4)$$

$${}^s\delta \equiv \langle(\Delta S)^2\rangle/k\langle V\rangle = \langle C_p\rangle/\langle V\rangle = C_{pm}/V_m, \quad (5)$$

$${}^{sv}\delta \equiv \langle(\Delta V)(\Delta S)\rangle/k\langle V\rangle = T\alpha_p, \quad (6)$$

by dividing both sides of eq.(1)-(3) by $k\langle V\rangle$, the Boltzmann constant times the average volume of the coarse grain with N_L molecules. As a result, ${}^q\delta$ s are now independent of N_L . Hence, ${}^q\delta$ s provide the quantitative information about the amplitude of fluctuation regardless of the size of the coarse grain, or the wavelength of fluctuation.

On the other hand, we earlier introduced the normalized fluctuations.¹⁻⁴⁾ We used the variation normalized by the average volume of the coarse grain before taking average. Namely,

$$\langle(\Delta V/\langle V\rangle)^2\rangle = kT\kappa_T/\langle V\rangle = k{}^v\delta/\langle V\rangle, \quad (7)$$

$$\langle(\Delta S/\langle V\rangle)^2\rangle = k\langle C_p\rangle/\langle V\rangle^2 = k{}^s\delta/\langle V\rangle, \quad (8)$$

$$\langle(\Delta V/\langle V\rangle)(\Delta S/\langle V\rangle)\rangle = kT\alpha_p/\langle V\rangle = k{}^{sv}\delta/\langle V\rangle. \quad (9)$$

Furthermore, we defined the following quantities by

converting k to R , the gas constant, $\langle V \rangle$ to V_m , the molar volume, and $\langle C_p \rangle$ to C_{pm} , the molar heat capacity. Thus,

$${}^V\Delta \equiv RT\kappa_T/V_m = R^V\delta/V_m, \quad (10)$$

$${}^S\Delta \equiv RC_{pm}/V_m^2 = R^S\delta/V_m, \quad (11)$$

$${}^{SV}\Delta \equiv RT\alpha_p/V_m = R^{SV}\delta/V_m. \quad (12)$$

We call ${}^V\Delta$ the mean-square normalized volume fluctuation, ${}^S\Delta$ the mean square normalized entropy fluctuation, and ${}^{SV}\Delta$ the normalized cross fluctuation between volume and entropy. Since the right hand sides of eq. (7)-(9) contain $\langle V \rangle$ in the denominator, and since we converted $\langle V \rangle$ to the universal V_m in eq. (10)-(12), ${}^q\Delta$'s defined above provide some information about the size of the coarse grain, and hence the wavelength of fluctuation, in a relative and qualitative manner. Suppose we compare two situations with different sizes of the coarse grain, $N_{z1} > N_{z2}$. In calculating ${}^q\Delta$'s by eq. (10)-(12), we are forced to divide by the same volume, V_m , instead of the proper values, $\langle V \rangle_1$ which is proportional to N_{z1} and $\langle V \rangle_2$ proportional to N_{z2} , *i.e.* $\langle V \rangle_1 < \langle V \rangle_2$. As a result, ${}^q\Delta_1$ will become unduly larger than ${}^q\Delta_2$, if ${}^q\delta_1 = {}^q\delta_2$. Conversely, if ${}^q\Delta_1 > {}^q\Delta_2$ with ${}^q\delta_1 = {}^q\delta_2$, then $N_{z1} > N_{z2}$. Thus, ${}^q\delta$'s and ${}^q\Delta$'s together would provide some qualitative and relative information about the size of the coarse grain, or the wavelength of fluctuation. ${}^q\delta$'s, on the other hand give the amplitude of fluctuation regardless of the wavelength of fluctuation.

3. Experimental and Data Analysis

tert-Butanol (Wako Pure Chemicals, Special Grade) was used as supplied. GLC analysis indicated its purity to be 99.96 mol %. H₂O was purified by means of a MilliQ Labo (Millipore) apparatus and its conductance was about 5×10^{-6} S. Heat capacity was measured by dilution method, mixing a dilute aqueous solution with H₂O. The details were described elsewhere.²⁰⁾ The precision in the excess heat capacity of the sample solution relative to that of pure H₂O was less than $\pm 0.02 \text{ J K}^{-1} \text{ mol}^{-1}$. Hence the values of C_p were obtained with at least 5 significant figures.

All the raw data used in this and the previous works, A,²⁾ B,⁴⁾ C,³⁾ and D⁵⁾ were all precisely determined with at least 5 mostly 6 significant figures. In the process of the following data analysis, we read a value off a smooth curve drawn through all the data points at a

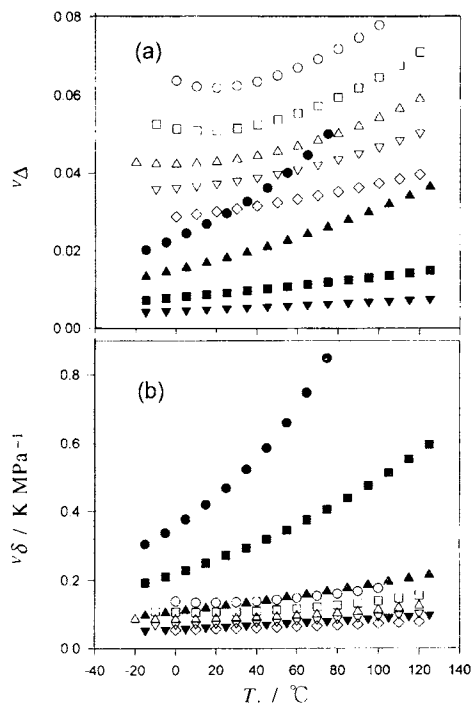


Fig.1 Volume fluctuations, H₂O vs. *n*-hexane. H₂O (open symbols): circle, 0.1 Mpa; square, 100 Mpa; uptriangle, 200 Mpa; downtriangle, 300 Mpa; diamond, 500 Mpa. *N*-hexane (filled symbols): circle, 0.1 Mpa; square, 50 Mpa; uptriangle, 200 Mpa; downtriangle, 500 Mpa. (a) Normalized volume fluctuation, ${}^V\Delta$, replotted using the data in paper A,²⁾ (b) Volume fluctuation densities, ${}^V\delta$.

prescribed interval. We used exactly the same method as described in detail in paper B⁴⁾ and D,⁵⁾ so as not to lose the number of significant figure much through reading off a graph. As a result, the final data shown in the Figures below have at least 3 significant figures, an uncertainty of a few per cent.

4. Results and discussion

4.1 H₂O vs. *n*-hexane

Fig.1 to **3** compare the pressure and the temperature dependence of ${}^q\Delta$'s and ${}^q\delta$'s ($q = V, S, \text{ or } SV$) between H₂O and *n*-hexane, a typical van der Waals liquid. The discussion given in paper A²⁾ remains qualitatively valid, with the additional information from ${}^q\delta$'s. Briefly, the volume fluctuations reflect the mixture model for liquid H₂O,²¹⁾ while in the entropy fluctuations the characteristics

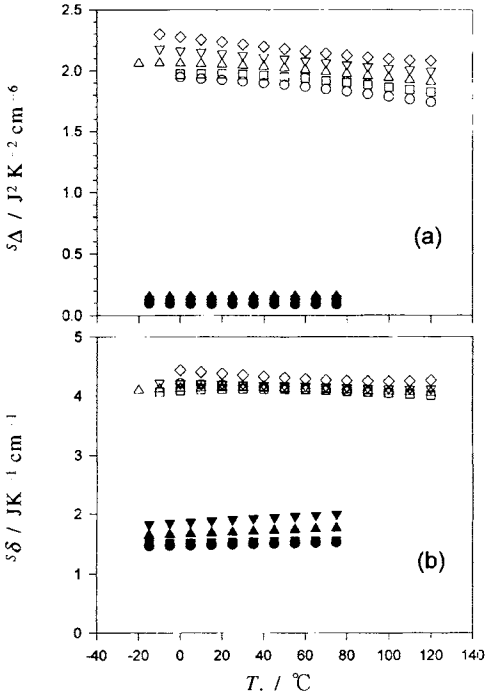


Fig.2 Entropy fluctuations, H₂O vs. *n*-hexane. The symbols are identical to Fig.1. (a) Normalized entropy fluctuation, ΔS , replotted using the data in paper A.²⁾ (b) Entropy fluctuation densities, $\Delta S\delta$.

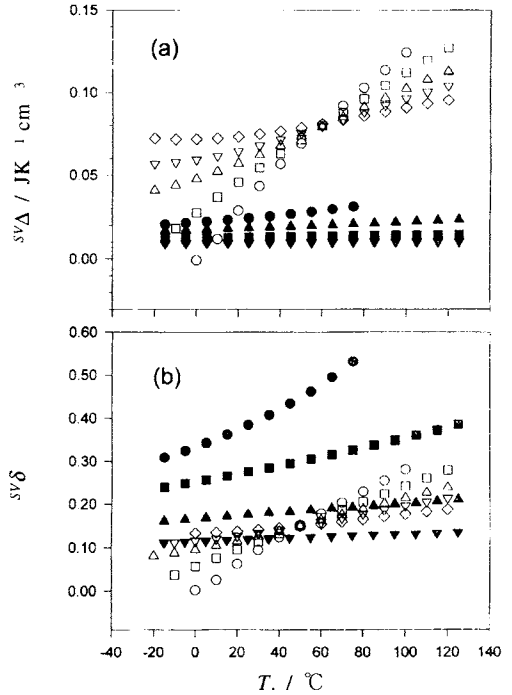


Fig.3 Cross fluctuations between volume and entropy, H₂O vs. *n*-hexane. The symbols are identical to Fig.1. (a) Normalized cross fluctuation, $\Delta S\Delta V$, replotted using the data in paper A.²⁾ (b) Cross fluctuation densities, $\Delta S\Delta V\delta$.

of the bent hydrogen bond model²²⁾ are more apparent. The most conspicuous feature of the peculiarity of H₂O is seen in the cross fluctuation between volume and entropy. Normally, the volume increase is associated with the entropy increase hence the product $(\Delta V)(\Delta S) > 0$. In H₂O, however, the putative appearance and disappearance of ice-like patches is accompanied by a negative contribution in the product $(\Delta V)(\Delta S)$ at low temperatures and pressures. Indeed, at 0.1 MPa and below 4 °C, both cross fluctuations are negative. As the temperature increases, the hydrogen bond probability decreases, and hence the tendency of formation of ice-like patches diminishes resulting in a rapid decrease in this negative contribution. The effect of pressure is not to directly reduce the hydrogen bond probability. Rather it hinders the formation of the ice-like patches via the Le Chatelier principle. The striking information given in Fig.1 to 3 is that the amplitudes of fluctuations are not that much larger for H₂O than those for *n*-hexane. In particular, the

volume fluctuation density, $\Delta V\delta$, the amplitude of volume fluctuation, is in fact several-fold smaller for H₂O, Fig.1(b). The entropy fluctuation density, $\Delta S\delta$, is larger for H₂O only by twice, Fig.2(b). On the other hand, $\Delta V\Delta S$, Fig.1(a), is much larger while $\Delta S\Delta V$, Fig.2(a), is some ten-fold larger for H₂O than *n*-hexane. It is therefore the wavelength of the fluctuation that is characteristically much larger for H₂O than that for *n*-hexane. Though qualitative in nature, such a conclusion is possible only when both ΔS and ΔV are compared between H₂O and *n*-hexane.

4.2 Aqueous tert-butanol and 2-butoxyethanol

We now turn to aqueous solutions of tert-butanol (abbreviated as TBA) and 2-butoxyethanol (BE). Our earlier thermodynamic studies⁹⁻¹²⁾ showed that the transition from Mixing Scheme I to II starts at point X and ends at point Y. Beyond point Y, Mixing Scheme II is operative. The loci of points X and Y are listed in Table 1.¹²⁾ The loci of points X and Y were obtained

Table 1 Loci in terms of mole fraction of the beginning (point X) and the end (Y) of the transition of Mixing Scheme I to II for aqueous solutions of tert-butanol and 2-butoxyethanol, at 25 °C. Ref. (12).

	TBA-H ₂ O	BE-H ₂ O
Point X	0.045	0.017
Point Y	0.065	0.021

as an anomalous behavior in the solute-solute interaction, H_{AL-AL}^E , defined as,⁹⁻¹²⁾

$$H_{AL-AL}^E \equiv N(\partial H_{AL}^E / \partial n_{AL}), \quad (13)$$

where,

$$H_{AL}^E \equiv (\partial H^E / \partial n_{AL}). \quad (14)$$

n_{AL} is the amount of AL in solution and N the total amount. Since the excess enthalpy, H^E , is the first derivative of G ,^{9,10)} the excess partial molar enthalpy of AL (TBA or BE), H_{AL}^E is the second derivative, and H_{AL-AL}^E is the third derivative of G . H_{AL}^E signifies the actual contribution of AL to the total excess enthalpy of the entire system, or the actual enthalpic situation of AL in the system. It follows then that H_{AL-AL}^E is the effect of additional AL on the actual enthalpic situation of AL in the system, or the AL-AL interaction in terms of enthalpy. Among other thermodynamic quantities, we used H_{AL}^E and H_{AL-AL}^E extensively to study aqueous alcohols.⁹⁻¹²⁾

Fluctuations defined above through eqs. (4)-(6) and (10)-(12), ${}^q\delta$ and ${}^q\Delta$, are related to the response functions which are the second derivative of G . We define the partial molar fluctuations of AL, the effect of AL on the respective fluctuations, as,³⁻⁵⁾

$${}^q\Delta_{AL} \equiv N(\partial {}^q\Delta / \partial n_{AL}) = (1 - x_{AL})(\partial {}^q\Delta / \partial x_{AL}), \quad (14)$$

$${}^q\delta_{AL} \equiv N(\partial {}^q\delta / \partial n_{AL}) = (1 - x_{AL})(\partial {}^q\delta / \partial x_{AL}), \quad (15)$$

in a binary system. x_{AL} is the mole fraction of AL. These quantities, being basically third derivatives of G , are expected to show some anomalies at the transition region from Mixing Scheme I to II, just as H_{AL-AL}^E .

4.2.1 Volume Fluctuation

Fig.4 shows the volume fluctuations, ${}^v\Delta$ and ${}^v\delta$. Both decrease on increasing x_{AL} . We recall that in evaluating the volume fluctuation, other extensive

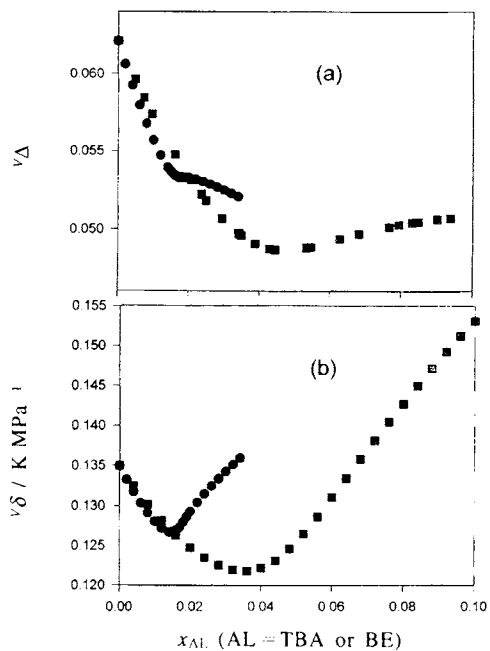


Fig.4 Volume fluctuations in TBA-H₂O and BE-H₂O at 25 °C. Square, TBA; circle, BE. (a) Normalized volume fluctuation, ${}^v\Delta$, replotted using the data in papers B⁴⁾ and C.³⁾ (b) Volume fluctuation density, ${}^v\delta$.

quantities are not allowed to fluctuate.¹³⁻¹⁶⁾ Accordingly, the mole fraction of AL in each coarse grain is the same as the global value. Thus, the initial decreases in ${}^v\Delta$ and ${}^v\delta$, **Fig.4**, suggest that the "iceberg" is rigid and is not involved in the fluctuation. As discussed in the introduction, the hydrogen bond probability of bulk H₂O away from the "iceberg" is progressively reduced. As a result, the amplitude and the wavelength of the volume fluctuation decrease as x_{AL} increases. This is the same for aqueous solutions of lower alcohols as discussed in paper D.⁵⁾ At the respective boundary from Mixing Scheme I to II for each solution, the mole fraction dependence of ${}^v\Delta$ and that of ${}^v\delta$ change the slope. This is more clearly seen in the partial molar volume fluctuations of AL (**Fig.5**). For BE-H₂O, anomalies at point X and point Y are both apparent. For TBA-H₂O, only point Y is conspicuous, while point X is debatable. This trend continues to lower alcohols in that aqueous 1-propanol had a reasonably conspicuous point Y in the analogue of **Fig.5** in paper D, while point X was

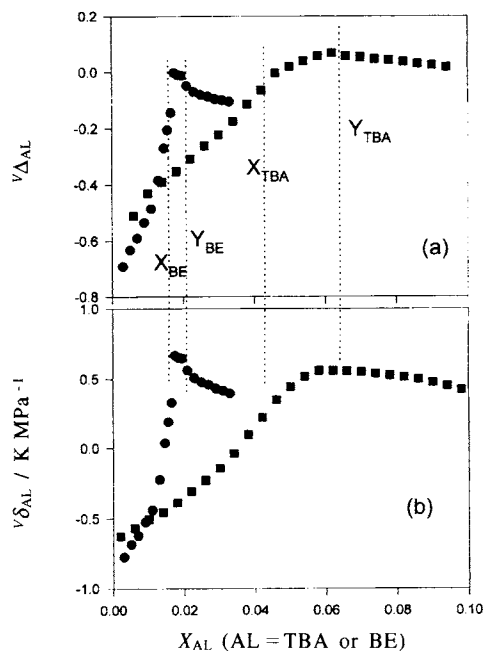


Fig.5 Partial molar volume fluctuations of AL (=TBA or BE). The symbols are identical to Fig.4. (a) Partial molar normalized volume fluctuation, $v\Delta_{AL}$, replotted using the data in papers B⁴⁾ and C.³⁾ (b) Partial molar volume fluctuation density, $v\delta_{AL}$. See text for X_{TBA} *etc.*

Table 2 Heat capacity of aqueous tert-butanol at 25.0 °C controlled within 0.0003 °C.

x_{TBA}	$C_p / JK^{-1} mol^{-1}$	x_{TBA}	$C_p / JK^{-1} mol^{-1}$
0	75.283	0.02808	86.847
0.00182	76.015	0.03260	88.775
0.00367	76.748	0.03726	90.701
0.00554	77.496	0.04207	92.472
0.00744	78.260	0.04705	93.973
0.00937	79.045	0.05219	95.565
0.01133	79.848	0.05751	97.181
0.01331	80.660	0.06301	98.666
0.01533	81.491	0.07461	101.164
0.01945	83.203	0.08708	103.088
0.02370	84.989	0.10053	104.761

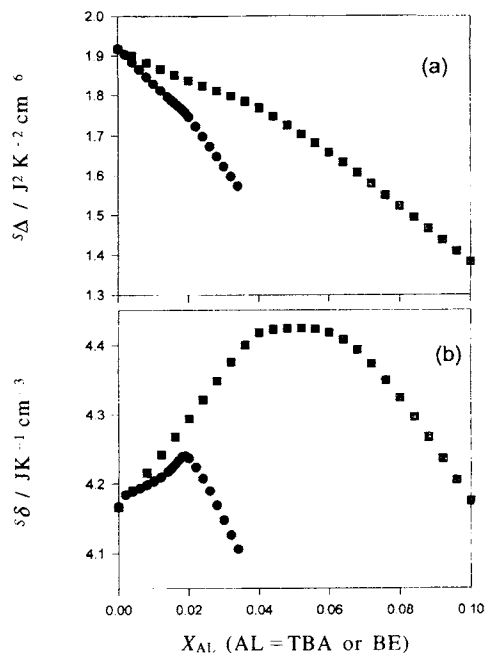


Fig.6 Entropy fluctuations in TBA-H₂O and BE-H₂O at 25 °C. The symbols are identical to Fig.4. (a) Normalized entropy fluctuation, $s\Delta$, replotted using the data in papers B⁴⁾ and C.³⁾ (b) Entropy fluctuation density, $s\delta$.

not clear at all. For ethanol, point Y is less clear, while that for methanol is completely obscure.

4.2.2 Entropy fluctuations

For TBA-H₂O, the normalized entropy fluctuation, $s\Delta$, reported in paper B⁴⁾ is revised using the heat capacity data that we measured. **Table 2** lists the C_p data. The method of graphical smoothing described in paper D was employed in calculating $s\Delta$ and $s\delta$. The results, $s\Delta$, are shown in **Fig.6(a)**, together with those of BE-H₂O from paper C.³⁾ The revision in $s\Delta$ for TBA-H₂O is too subtle to see in **Fig.6(a)**, but the partial molar normalized fluctuation of TBA, $s\Delta_{TBA}$, **Fig.7(a)**, now shows an anomaly at point X determined by that of $H_{TBA-TBA}^E$,^{12,23)} which was not the case in paper B.⁴⁾ Turning back to **Fig.6**, the amplitude of the entropy fluctuations, $s\delta$, increases as x_{AL} increases. Since the entropy fluctuation is related to the fluctuation in the hydrogen bond strength through $T^2\langle(\Delta S)^2\rangle = \langle(\Delta H)^2\rangle$, this initial increase in $s\delta$ indicates that the hydrogen bonds are forced to bend more perhaps due to the presence of icebergs that are

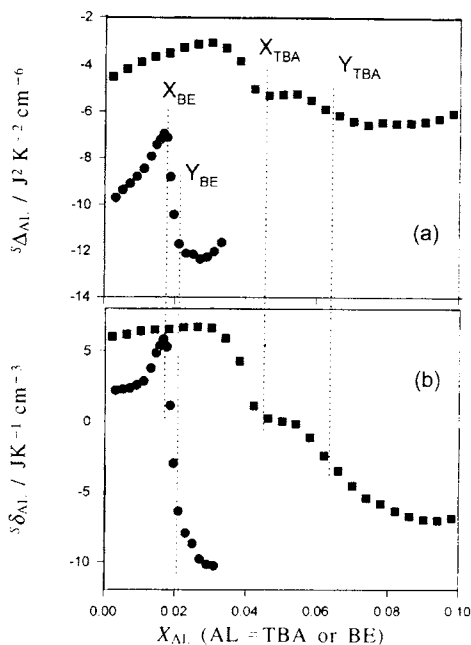


Fig.7 Partial molar entropy fluctuations of AL (• TBA or BE). The symbols are identical to Fig.4. (a) Partial molar normalized entropy fluctuation, ${}^s\Delta_{AL}$, replotted using the data in papers B⁴⁾ and C.³⁾ (b) Partial molar entropy fluctuation density, ${}^s\delta_{AL}$. See text for X_{TBA} etc.

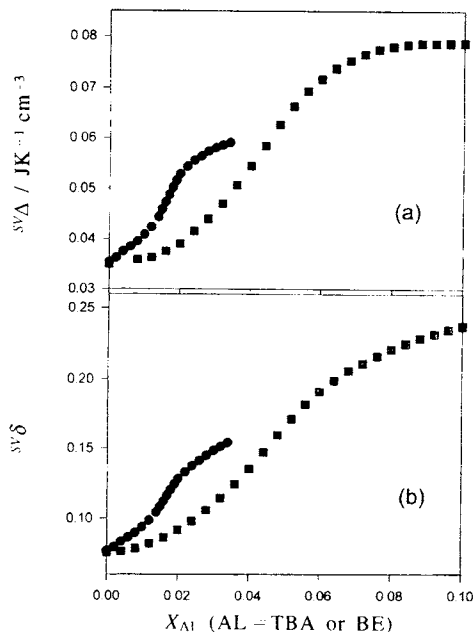


Fig.8 Cross fluctuations between volume and entropy in TBA-H₂O and BE-H₂O at 25 °C. The symbols are identical to Fig.4. (a) Normalized cross fluctuation, ${}^{sv}\Delta$, replotted using the data in papers B⁴⁾ and C.³⁾ (b) Cross fluctuation density, ${}^{sv}\delta$.

rigid, particularly in their vicinities. However, the amplitude and the wavelength of entropy fluctuation, ${}^s\Delta$, decrease in the same composition range, suggesting that the wavelength of fluctuation decreases more rapidly than the increase in amplitude.

What is puzzling, however, is that the extent of ${}^s\delta$ is larger for TBA than that of BE at each maximum. It was shown in paper D that the extent of increase in ${}^s\delta$ is in the order of methanol, ethanol and 1-propanol. This appears natural since the size of the hydrophobic moiety dictates the size of the iceberg. **Fig.6(b)** is contrary to this trend. Clearly BE has a larger hydrophobic moiety than TBA as a single molecule, and indeed the loci of the transition from Mixing Scheme I to II are in the proper order; the mole fraction values at point X and Y for BE-H₂O are smaller than those for TBA-H₂O, (**Table 1**).

As discussed at some length earlier,^{9,10)} in the Mixing Scheme I the solution is preparing for an addition compound of the type $AL(H_2O)_m$ on freezing. For AL

BE, $m = 38$, which is a reasonable number of H₂O molecules sufficient to surround a BE molecule.²⁴⁾ The mixing scheme boundary for BE-H₂O hits the incongruent melting point, 269.5 K, of the addition compound $BE(H_2O)_{38}$, corresponding to $X_{BE} = 0.0260$.²⁴⁾ For TBA-H₂O, the relation between the mixing scheme boundary and the liquid-solid phase diagram has not been studied. However, as shown in Table 1, the locus of point X is at $X_{TBA} = 0.045$ at 25 °C, and as the temperature decreases the boundary value of X_{TBA} increases.^{9,10)} This means that at freezing the boundary value could be larger, hence the value of m in a possible addition compound of the type $TBA(H_2O)_m$ could at the very most be $0.955/0.045 = 21$, and most likely is much less. Would this number be sufficient to form an addition compound with a TBA molecule? If, however, TBA forms an oligomer, just as the case for aqueous dimethyl sulfoxide (DMSO) via direct dipole attraction between S=O groups,²⁵⁾ then a possible addition compound could be of the type $(TBA)_k(H_2O)_{km}$ instead. A few (k) of TBA molecules cluster together perhaps via -OH groups. Then k ter-

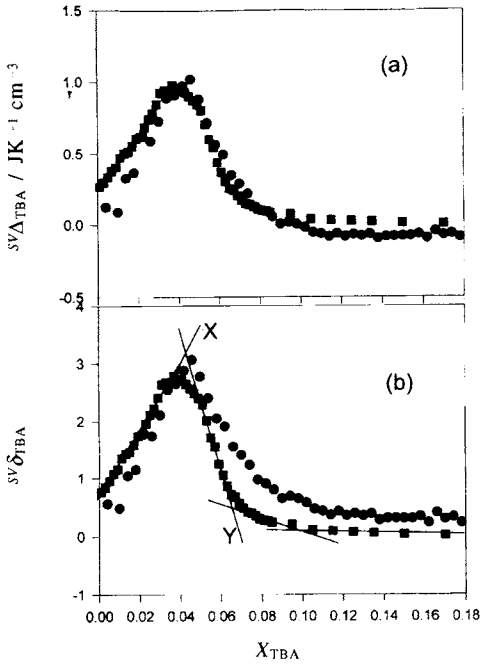


Fig.9 Partial molar cross fluctuations of TBA. Circle, partial molar cross fluctuation of TBA; square, the enthalpic TBA-TBA interaction, $H_{TBA-TBA}^E$. (a) Partial molar normalized cross fluctuation, $^{SV}\Delta_{TBA}$, replotted using the data in paper B.⁴⁾ (b) Partial molar cross fluctuation density, $^{SV}\delta_{TBA}$. See text for X and Y.

butyl groups point outward of such a cluster surrounded by km H₂O molecules as an iceberg. If this scenario is a possibility, then the observation of Fig.6 that the maximum value of $^{SV}\delta$ is larger for TBA than BE becomes explicable.

Turning to Fig.7, we note that $^{S}\Delta_{TBA}$ and $^{S}\delta_{TBA}$ show a different x_{AL} -dependence from the counterparts for BE, which are in turn similar to that of the lower alcohols shown in paper D.⁵⁾ This may hint that TBA could be a unique alcohol in interacting with H₂O in Mixing Scheme I.

4.2.3 Cross Fluctuation

The special nature of liquid H₂O is most conspicuous in the cross fluctuation between volume and entropy. Namely, there is a negative contribution in $(\Delta V)(\Delta S)$ due to the putative presence of ice-like patches, where an increase in volume is accompanied by an entropy decrease. Fig.8 shows that both $^{SV}\Delta$ and $^{SV}\delta$ increase

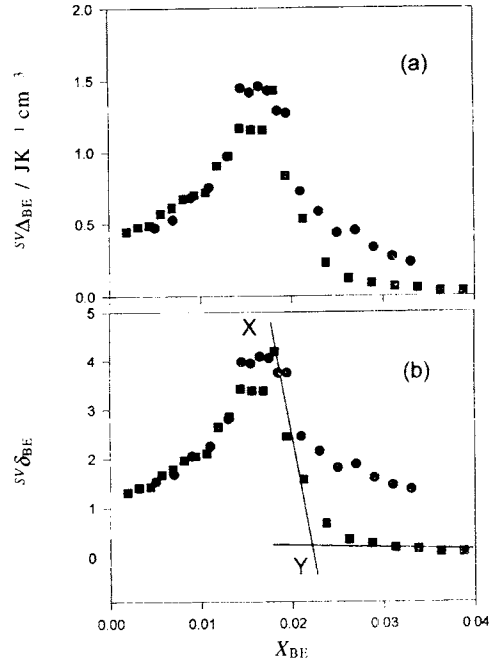


Fig.10 Partial molar cross fluctuations of BE. Circle, partial molar cross fluctuation of BE; square, the enthalpic BE-BE interaction, H_{BE-BE}^E . (a) Partial molar normalized cross fluctuation, $^{SV}\Delta_{BE}$, replotted using the data in papers C.³⁾ (b) Partial molar cross fluctuation density, $^{SV}\delta_{BE}$. See text for X and Y.

progressively as x_{AL} increases. Or the negative contribution characteristic of liquid H₂O diminishes progressively on addition of AL. At about the mixing scheme boundary from I to II, such effect of AL slows down. The partial molar cross fluctuations of AL, $^{SV}\Delta_{AL}$ and $^{SV}\delta_{AL}$, Fig.9 and 10, show this trend more clearly. $^{SV}\Delta_{AL}$ and $^{SV}\delta_{AL}$ increases sharply to point X and decreases rapidly to point Y. In the figures, the enthalpic interactions, $H_{TBA-TBA}^E$ for TBA-H₂O,^{12,23)} and H_{BE-BE}^E for BE-H₂O,^{12,26)} are also plotted with an arbitrary scaling factor on the ordinate. It is striking that the x_{AL} -dependence of $^{SV}\Delta_{AL}$ and $^{SV}\delta_{AL}$ is similar to H_{AL-AL}^E . Thus, the enthalpic interaction and the AL's effect on the cross fluctuation share the same fundamental cause. We suggest therefore that the interaction between the iceberg-clad AL's is operative via bulk H₂O in solution where the putative presence of the ice-like patches causes the negative contribution to $^{SV}\Delta$ and $^{SV}\delta$.

5. Summary

We introduced ${}^q\delta$ and ${}^q\Delta$. The former indicates the amplitude (intensity) of fluctuation while the latter provides the amplitude and the wavelength (extensity) of fluctuation in a qualitative manner. $q = V, S$, or SV signifies the fluctuation in volume, entropy or the cross fluctuation between volume and entropy.

5.1 H₂O

Using the data of ${}^q\delta$ and ${}^q\Delta$, it was shown that H₂O has a much larger wavelength of fluctuation than a typical van der Waals liquid, n-hexane. The volume fluctuation supports the mixture model of H₂O²¹⁾ clearly. The entropy fluctuation, on the other hand, reflects the bent hydrogen bond model.²²⁾ A striking feature of H₂O is most conspicuous in the entropy volume cross fluctuation, in that there is a large negative contribution at low temperature due to the putative occurrence of the ice-like patches in H₂O. This negative contribution diminishes rapidly as temperature is increased.

5.2 Aqueous TBA and BE

In the most water-rich region, where Mixing Scheme I is operative, it was shown from the mole fraction dependence of the volume fluctuations, ${}^V\delta$ and ${}^V\Delta$, that the "icebergs" are rigid and do not participate in fluctuation and the hydrogen bond probability of bulk H₂O away from "icebergs" is progressively reduced on addition of TBA or BE. The amplitude of the entropy fluctuation, ${}^S\delta$ suggests that more bending of the hydrogen bonds is induced by addition of TBA and BE, perhaps in the vicinity of the "icebergs". However, the amplitude plus the wavelength of entropy fluctuation, ${}^S\Delta$, indicates that the wavelength of the entropy fluctuation diminishes on addition of the solutes much more rapidly than the increase in the amplitude. The partial molar volume and entropy fluctuations of the solute, ${}^q\delta_i$ and ${}^q\Delta_i$, ($q = V$ or S and $i = \text{TBA or BE}$), show anomalies more clearly for BE than TBA at point X, the onset, and point Y, the end point of the transition from Mixing Scheme I to II. The volume-entropy cross fluctuations, ${}^{SV}\delta$ and ${}^{SV}\Delta$, show disappearance of the negative contribution characteristic of H₂O on addition of TBA or BE. The mole fraction dependence of the partial molar cross fluctuations, ${}^{SV}\delta_i$ and ${}^{SV}\Delta_i$, ($i = \text{TBA or BE}$) is strikingly similar to that of the enthalpic solute-solute interaction, H_i ,¹⁵⁾ This could mean that the solute-solute interaction

and the solute's effect on the volume-entropy cross fluctuation share the same fundamental cause. We suggest that the solute-solute interaction is water-mediated and operative via the bulk H₂O.

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要 旨

水, *tert*-butanol および, 2-butoxyethanol の水溶液内での揺らぎについてしらべる。揺らぎ密度と, 規格化揺らぎを計算する。前者は, 揺らぎの振幅を与え, 後者は揺らぎの振幅と波長を, 定性的にあらわす。これらを, 体積揺らぎ, エントロピー揺らぎ, および, 体積とエントロピーの相互揺らぎについて, 計算する。それぞれ, 圧縮率, 熱容量, および, 体膨張率を使って計算できる。これら, 揺らぎのデータをつかって, 液体の水の特殊性を議論する。また, *tert*-butanol および, 2-butoxyethanol の水溶液内での混ざり方の詳細, さらに, 混ざり方の転移について議論する。



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