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Partial Molar Fluctuations in Aqueous 2-Butoxyethanol

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The normalized fluctuations were reformulated in a unified manner, keeping the number of molecules in each coarse grain fixed. The normalized fluctuations were evaluated for aqueous 2-butoxyethanol using the existing data of $\varkappa_T$, C_p, α_p, and V_m. The partial molar fluctuations of 2-butoxyethanol were then calculated. These quantities added some more evidences to the mixing schemes in aqueous 2-butoxyethanol conjectured earlier in this laboratory.

The purpose of this paper is two-fold:

Firstly, we introduce the "normalized fluctuation" in a unified manner. In the previous paper, (called paper I hereinafter),[1] fluctuations were normalized by the quantity representing the size of a coarse grain in which fluctuation is evaluated. Such quantities were shown to be useful in gaining some insight into the mixing scheme in aqueous solutions, the way in which the solute and H_2O molecules mix with each other. In evaluating a fluctuation, it is necessary to define coarse grains, in which the local, instantaneous value is determined. In paper I, however, the coarse grain was taken with a fixed number of molecules for entropy fluctuation, $\langle(\Delta S)^2\rangle$, while for number fluctuation, $\langle(\Delta N)^2\rangle$, the volume of the coarse grain was kept fixed. Although these quantities served to provide a new insight in paper I,[1] the cross fluctuation, $\langle(\Delta N)(\Delta S)\rangle$, was poorly defined as a result. In this work, we use coarse grains with a fixed number of molecules throughout. Instead of number fluctuation, therefore, volume fluctuation, $\langle(\Delta V)^2\rangle$, will be used. Thus, all three fluctuations are defined in a unified manner. We also point out that the statement made in paper I, that the normalized fluctuations are independent of the size of a coarse grain, is in error. This, however, does not affect the remainder of discussion.

Secondly, we calculate the "partial molar fluctuation of solute". By means of this quantity, we make an attempt at gaining a deeper insight into the mixing scheme of aqueous 2-butoxyethanol (abbreviated as BE).

A partial molar quantity of the *i*-th component for any thermodynamic function *F* is defined as,

$$F_i = (\partial F/\partial n_i)_{nj,p,T} \tag{1}$$

which signifies the actual contribution of the *i*-th component towards the value of *F* of the entire system. *F* can be an intensive as well as an extensive quantity. It is customary to obtain *F* as a function of the mole fraction x_i rather than n_i. Instead of Eq. 1, the following equations are then used,

$$F_i = F/N + \{(1-x_i)/N\}(\partial F/\partial x_i), \tag{2}$$

if *F* is extensive, and,

$$F_i = \{(1-x_i)/N\}(\partial F/\partial x_i), \tag{3}$$

if *F* is intensive. For example, the partial molar compressibility of the *i*-th component can be defined as,

$$\varkappa_T(i) = \{(1-x_i)/N\}(\partial \varkappa_T/\partial x_i). \tag{4}$$

Intuitively, however, it is somewhat difficult to attribute $\varkappa_T(i)$ to the contribution of the *i*-th species on $\varkappa_T$, since the latter is a response function rather than a description of the state.

On the other hand, $\varkappa_T$ is related to the volume fluctuation via rigorous statistical thermodynamic treatment[2—5] as,

$$\langle(\Delta V)^2\rangle_N = -kT(\partial\langle V\rangle/\partial p) = kT\langle V\rangle\varkappa_T. \tag{5}$$

The fluctuations related to the remaining response functions are,

$$\langle(\Delta S)^2\rangle_N = kT(\partial\langle S\rangle/\partial T) = k\langle c_p'\rangle, \tag{6}$$

$$\langle(\Delta S)(\Delta V)\rangle_N = kT(\partial\langle V\rangle/\partial T) = kT\langle V\rangle\alpha_p. \tag{7}$$

$\langle\,\rangle$ means the ensemble average. Δ signifies the difference of the local, instantaneous value from the ensemble average of the quantity. For its evaluation, it is convenient to divide the system into coarse grains consisting of an equal number of molecules, *N*, and determine the quantity within each grain at a given instance. The size of coarse grain must be small enough for fluctuations to be detected, but large enough for thermodynamic quantities to be defined. An estimate indicated about 10^5 molecules.[5] Equations 5, 6, and 7 thus signify the average fluctuations in the coarse grain with a fixed number of *N*. The subscript *N* on the left-most side of above equations signifies this. $\langle V\rangle$, $\langle S\rangle$, and $\langle c_p'\rangle$ in the equations, being extensive quantities, are evaluated for *N* molecules. Thus, each time the value of fluctuation is quoted, the size of the coarse grain *N* must be specified. This causes inconvenience when the values of fluctuation are compared with those for other materials or under grossly different conditions. This point has not been explicitly noted

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in the past. To avoid this inconvenience, it was suggested to normalize the fluctuation with the average volume of the coarse grain.[1,6,7] Hence, instead of Eqs. 5, 6, and 7, the normalized fluctuations, $^{k}\Delta$, where $k=V$, S, or SV, may be written as,

$$^{V}\Delta \equiv \langle(\Delta V/V)^2\rangle_N = kT\varkappa_T/\langle V\rangle = RT\varkappa_T/V_m, \tag{8}$$

$$^{S}\Delta \equiv \langle(\Delta S/V)^2\rangle_N = k\langle c_p'\rangle/\langle V\rangle^2 = RC_p/V_m^2, \tag{9}$$

$$\begin{aligned} ^{SV}\Delta &\equiv \langle(\Delta S/V)(\Delta V/V)\rangle_N = kT\alpha_p/\langle V\rangle \\ &= RT\alpha_p/V_m. \end{aligned} \tag{10}$$

The last equality in each equation is performed for convenience by converting k to R and N to 1 mole, i.e. $\langle c_p'\rangle$ to C_p and $\langle V\rangle$ to V_m, where C_p and V_m are the molar quantities. We note that the right-most side of Eq. 8 is identical to that for $\langle(\Delta N/N)^2\rangle$ in paper I, while that of Eq. 10 has the opposite sign of $\langle(\Delta N/N)(\Delta S/V)\rangle$, which is reasonable since (ΔN) and (ΔV) have opposite signs. The volume fluctuation, $^{V}\Delta \equiv \langle(\Delta V/V)^2\rangle_N$, thus defined is the proper relative fluctuation and can now be subjected to comparison with other compounds or under grossly different conditions. By the same token, the entropy fluctuation should be normalized by $\langle S\rangle$ as $\langle(\Delta S/S)^2\rangle_N$. In the present work, however, $\langle V\rangle$ was used instead because evaluating $\langle S\rangle$ is a formidable task, $\langle V\rangle$ and $\langle S\rangle$ have generally the same trend, and, most importantly, the three normalized fluctuations above can thus be defined in a unified manner.

For concentration fluctuation, it is more convenient to use coarse grains with a fixed number of solvent molecules, n_w.[2,5] Thus, for solute B,

$$\begin{aligned} \langle(\Delta n_B)^2\rangle_{n_w} &= kT/(\partial\langle\mu_B'\rangle/\partial\langle n_B\rangle) \\ &= kT/\{(1-x_B)/\langle N\rangle\}(\partial\langle\mu_B'\rangle/\partial x_B), \end{aligned} \tag{11}$$

where $\langle\mu_\beta'\rangle$ is the chemical potential for one molecule of B. $\langle N\rangle = \langle n_B\rangle + n_w$, where n_w is fixed. Again to avoid the inconvenience of specifying the size of n_w, the number fluctuation is rewritten in terms of the mole fraction x_B. Since, $\Delta x_B = \{(1-x_B)/N\}\Delta n_B$,

$$\begin{aligned} ^{x_B}\Delta &\equiv \langle(\Delta x_B)^2\rangle \\ &= kT\{(1-x_B)/\langle N\rangle\}/(\partial\langle\mu_B'\rangle/\partial x_B) \\ &= RT(1-x_B)/(\partial\mu_B/\partial x_B), \end{aligned} \tag{12}$$

where μ_B is the chemical potential of B per mole of B, as normally determined experimentally.

The normalized fluctuations, $^{S}\Delta$, $^{V}\Delta$, $^{SV}\Delta$, and $^{x_B}\Delta$, intensive quantities, describe a property of the state with a fixed choice of the size of coarse grain. Thus, by virtue of Eqs. 1 and 3, one can formally define the "partial molar fluctuations of solute B" as,

$$^{k}\Delta_B = (\partial^{k}\Delta/\partial n_B)_{n_w,p,T}, \tag{13}$$

with $k=V$, S, SV, or x_B. They signify the effect of an additional B, or the actual contribution of B, on the respective normalized fluctuations of the system. We note that $^{k}\Delta_B$ is proportional to the third derivatives of Gibbs energy.

The normalized fluctuations, $^{k}\Delta$, for pure H_2O were shown together with those of benzene and ethanol in Fig. 1 of paper I as a function of temperature. Note that $^{V}\Delta$ is identical to $\langle(\Delta N/N)^2\rangle$, Fig. 1(b) of paper I, while $^{SV}\Delta$ has the opposite sign of $\langle(\Delta N/N)\rangle\langle(\Delta S/V)\rangle$, Fig. 1(c) of paper I. The behavior of $^{V}\Delta$ in comparison with those of benzene and ethanol indicated that at temperatures below 50 °C, $^{V}\Delta$ for H_2O has a positive contribution which diminishes rapidly on temperature increase. At higher temperatures (above 50 °C), however, $^{V}\Delta$ becomes almost identical to that of ethanol, showing increase which reflects the normal thermal fluctuation. This is not inconsistent with the "mixture model", in which small patches of bulky four hydrogen bonded molecules exist momentarily here and there, and the number of such patches decreases on temperature increase. The values of $^{V}\Delta$ for H_2O are only slightly larger than those of benzene and ethanol, at most twice. The values of $^{S}\Delta$ for H_2O, on the other hand, stay by an order of magnitude higher than those of others in the entire temperature range of the liquid state. As temperature increases, $^{S}\Delta$ for H_2O decreases, while those of others increases slightly, as it is expected for purely thermal fluctuations. This suggests that the "continuum, or bent hydrogen bond model" may be more appropriate. Namely, there is a wide distribution (fluctuating) of hydrogen bond strength and the hydrogen bond probability decreases as temperature increases. Thus, $^{V}\Delta$ and $^{S}\Delta$ appear to behave differently on temperature increase, although the origin of these peculiar behaviors of H_2O has been believed to be the existence of the hydrogen bond network.

We recall at this stage, the nature of the hydrogen bond connectivity in H_2O, pointed out by Stanley et al.[8,9] They considered the hydrogen bond connectivity allowing the wide distribution of hydrogen bond strength (continuum model).

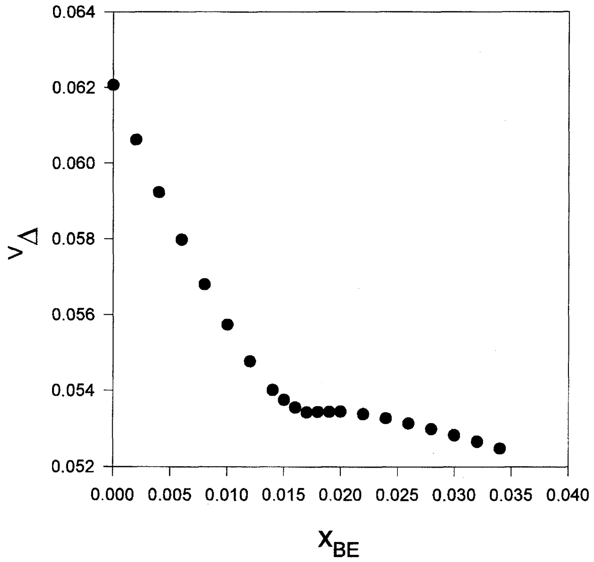

Fig. 1. The normalized volume fluctuation, $^{V}\Delta$, in aqueous 2-butoxyethanol at 25 °C, calculated by Eq. 8. The data of $\varkappa_T$ were taken from Ref. 10 and those of V_m from Ref. 11.

They found that for any reasonable definition of a hydrogen bond, the hydrogen bond network in H_2O is percolated in the moderate temperature range. Moreover, the sites of four hydrogen bonded molecules are not distributed randomly, rather they are spatially correlated. As a result, there exist momentarily patches of four hydrogen bonded (ice-like) molecules. Thus, the basis for the "mixture model" is also supported. We note that an additional spatial correlation effect is required for the bulky ice-like patches to give rise to the volume fluctuation in addition to the normal thermal fluctuation. Thus, the fact that the dependencies of ${}^{S}\Delta$ and ${}^{V}\Delta$ are apparently different on temperature increase is the very nature of the hydrogen bond network of liquid H_2O. The cross fluctuation can then be understood as having a large negative contribution, (since ΔS and ΔV have the opposite signs in the hydrogen bonded system), which diminishes rapidly as ${}^{V}\Delta$ does on temperature increase. The peculiar nature of H_2O in terms of the normalized fluctuations, their temperature and pressure dependencies, will be discussed further in a forthcoming publication.

Figures 1, 2, and 3 show the plots of the normalized fluctuation, ${}^{k}\Delta$, for aqueous 2-butoxyethanol (BE) as a function of its mole fraction x_{BE}. Here, $k=V$, S, or SV. All show some anomalous behavior at $x_{\mathrm{BE}}\approx0.0175$, which has been discussed to be the transition point of the mixing scheme.[6,7] Namely, in region I, $x_{\mathrm{BE}}<0.0175$, the solute BE enhances the hydrogen bond network of H_2O in its immediate vicinity, while the hydrogen bond probability is reduced in the bulk away from the solute.[6,7] The percolation nature of H_2O is still retained. In region II, $0.0175<x_{\mathrm{BE}}<0.46$, the solution consists of two kinds of clusters, rich in each component. Thus the hydrogen bond network is no longer percolated. Figures 1 and 2 indicate that addition of BE in H_2O decreases both ${}^{S}\Delta$ and ${}^{V}\Delta$. The magnitudes of respective decrease, however, are different. As x_{BE} increases from 0 to 0.0175, ${}^{V}\Delta$ decreases from 0.062 to 0.053, to about the same value for pure ethanol, while ${}^{S}\Delta$ decreases from 1.9 at $x_{\mathrm{BE}}=0$ to 1.75 ($\mathrm{J}^2\ \mathrm{K}^{-2}\ \mathrm{cm}^{-6}$) to the level at 100 °C for pure H_2O, though remaining by an order of magnitude higher than that for ethanol. These facts suggest that BE reduces the positive contribution to ${}^{V}\Delta$, which is due to the putative formation of ice-like patches, down to zero or at least to the level in pure ethanol. The decrease of ${}^{S}\Delta$ by BE, on the other hand, is only marginal in comparison. As mentioned above, BE is believed to enhance the hydrogen bond network of H_2O in its immediate vicinity in terms of enthalpy and entropy.[6,7] By so doing, BE seems to make the hydrogen bond network in the immediate vicinity more rigid and hence the contributions to ${}^{S}\Delta$ and ${}^{V}\Delta$ from this part is almost null. In the bulk of solution away from solute BE, on the other hand, the hydrogen bond probability is reduced, and hence so be ${}^{S}\Delta$. At the same time, ${}^{V}\Delta$ becomes as low as that for pure ethanol, since the hydrogen bond probability becomes low enough to retard the formation of ice-like patches.

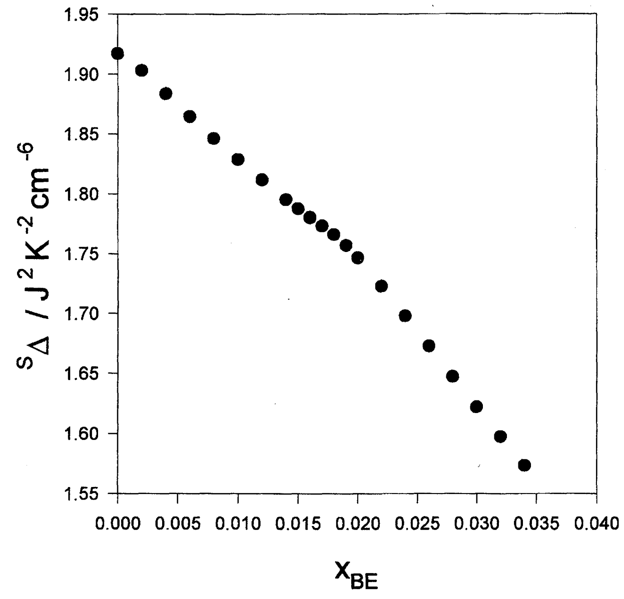

Fig. 2. The normalized entropy fluctuation, ${}^{S}\Delta$, in aqueous 2-butoxyethanol at 25 °C, calculated by Eq. 9. The data of C_{p} were taken from Ref. 12.

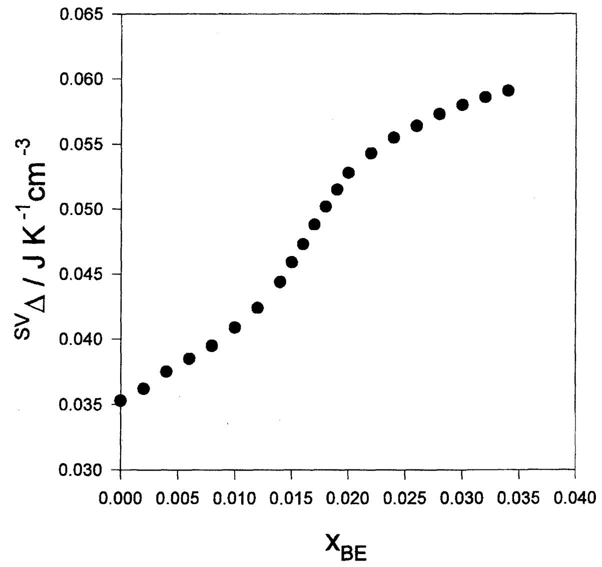

Fig. 3. The normalized cross fluctuation, ${}^{SV}\Delta$, in aqueous 2-butoxyethanol at 25 °C, calculated by Eq. 10. The data of α_{p} were taken from Ref. 13.

The discussion below using the partial molar fluctuations makes the above picture clearer. Figures 4, 5, and 6 show the partial molar fluctuations of BE, ${}^{k}\Delta_{\mathrm{BE}}$, where $k=V$, S, or SV, the actual contribution of BE on the respective normalized fluctuations. Reflecting the fact that BE reduces fluctuation, both ${}^{S}\Delta_{\mathrm{BE}}$ and ${}^{V}\Delta_{\mathrm{BE}}$ are negative. As x_{BE} increases within region I, the values of ${}^{S}\Delta_{\mathrm{BE}}$ and ${}^{V}\Delta_{\mathrm{BE}}$ becomes less negative. This may mean that the effect of the first BE on the fluctuations is transmitted over a long range, hence the second BE reduces the respective fluctuations to a lesser extent. This is also reflected in the fact that the slopes of ${}^{V}\Delta_{\mathrm{BE}}$ and ${}^{S}\Delta_{\mathrm{BE}}$ as a function of x_{BE} are positive, while the values of ${}^{S}\Delta_{\mathrm{BE}}$ and ${}^{V}\Delta_{\mathrm{BE}}$ themselves are negative; i.e. that the propensity of BE to damp fluctuations becomes less pronounced with increasing x_{BE}, similar to the explanation applied for the x_{BE}

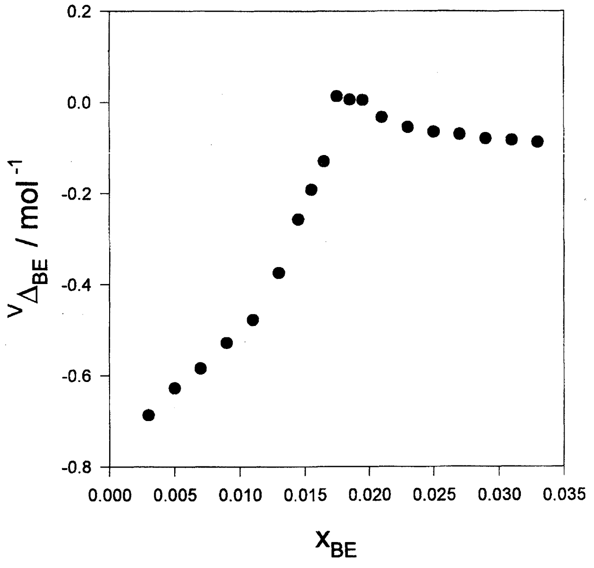

Fig. 4. The partial molar volume fluctuation of 2-butoxyethanol, $^{V}\Delta_{BE}$, in aqueous solution at 25 °C.

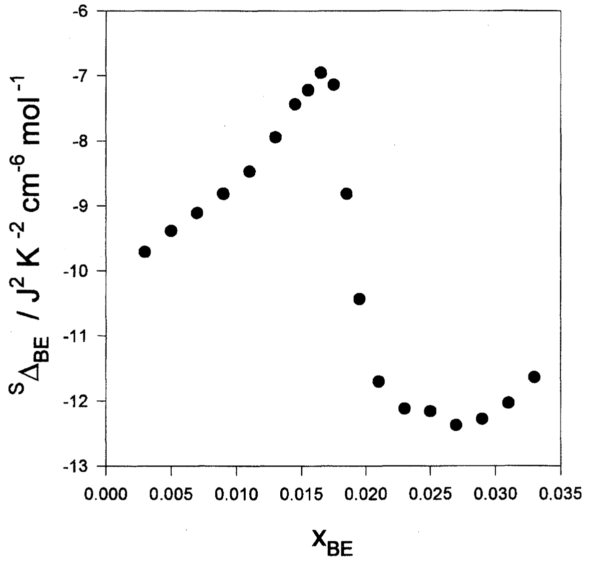

Fig. 5. The partial molar entropy fluctuation of 2-butoxyethanol, $^{S}\Delta_{BE}$, in aqueous solution at 25 °C.

dependence of the partial molar entropy of BE.[6,7] This trend continues up to the transition point to mixing scheme II. The partial molar volume fluctuation, $^{V}\Delta_{BE}$, reaches almost zero at the boundary $x_{BE}=0.0175$, and stays very small in region II. Since mixing scheme II is such that the solution consists of BE-rich and H_2O-rich clusters, i.e. the hydrogen bond connectivity is limited by the boundaries of the clusters, the chances of forming fluctuating ice-like patches are no longer high. The partial molar entropy fluctuations of BE, $^{S}\Delta_{BE}$, on the other hand, does not reach zero at the boundary, and moreover, the initial values in the region II are more negative. BE-rich clusters in region II may only contribute to the normal thermal fluctuation. H_2O-rich clusters, on the other hand, still contain hydrogen bonds among H_2O molecules, the strength of which is fluctuating. The effect of additional BE, $^{S}\Delta_{BE}$, is then more pronounced since the hydrogen bond connectivity is limited within the clusters.

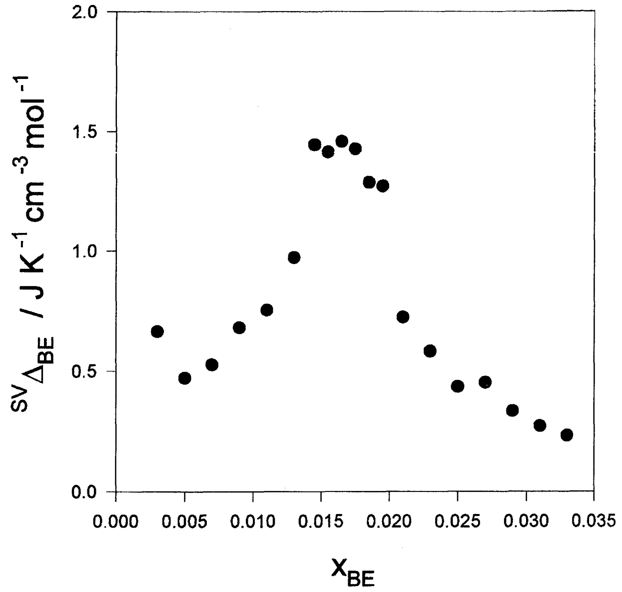

Fig. 6. The partial molar cross fluctuation of 2-butoxyethanol, $^{SV}\Delta_{BE}$, in aqueous solution at 25 °C.

Thus, the behaviors of properly normalized fluctuations and partial molar fluctuations of the solute add more evidence to the mixing schemes of this interesting BE–H_2O system. The same methodology could be very useful in studying various aqueous solutions including aqueous biopolymers.

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