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Mixture-Model Approach to the Theory of Classical Fluids. III. Application to Aqueous Solutions of Nonelectrolytes

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An extension of the mixture-model approach to the theory of liquid water is developed to include aqueous solutions of nonelectrolytes. The Kirkwood–Buff theory of solution is employed to obtain a general and exact expression for the "stabilization effect" induced by the solute. This relation is applied, in the framework of a two-structure model, to obtain further insight into the molecular origin of some anomalous thermodynamic properties of aqueous solutions. The generalized continuous mixture-model formalism is also extended to solutions. It is demonstrated that current concepts such as "structural changes" in the solvent are strongly dependent on the particular classification procedure adopted to construct the mixture model.

KEY WORDS: Statistical mechanics; aqueous solutions; solutions; structure of water; mixture-model theory of fluids.

1. INTRODUCTION

In the previous articles(1,2) of this series a mixture-model approach has been developed and applied to the theory of liquid water. This paper

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extends the application of this approach to aqueous solutions of nonelectrolytes.

It is now well known that aqueous solutions of nonelectrolytes reveal some outstanding properties in comparison with the corresponding nonaqueous solutions.[2] For example, the entropy and the enthalpy of solution of argon in water are distinctly more negative than the corresponding values in other fluids for which data are available.(3)

It has long been postulated that "structural changes" in water should hold the clues for this apparently anomalous behavior. An earlier example of application of the mixture-model idea to explain a puzzling observation is following.(5) Addition of some solutes such as ether or methyl acetate to water was known to *decrease* the compressibility of the system in spite of the fact that the compressibility of these pure liquids is a few times *larger* than that of pure water. It has been postulated that water is "built up" of at least two species (say, monomers and polymers of water molecules, the latter species supposedly having higher compressibility). Addition of solute causes a shift toward that component which has lower compressibility—hence a qualitative explanation of the observable effect was provided.[3]

So far concepts like the "structure of water" and "structural changes" induced by a solute were used either within the framework of an *ad hoc* mixture model for water or in connection with some experimental observation. The latter has been interpreted in terms of these concepts although precise definitions have been lacking. Bernal and Fowler(6) have introduced the concept of "structural temperatures" which, although not providing a definition of the "structure," gives a useful qualitative way of correlating changes of structure due to the addition of solute with changes of structure caused by changes of temperature. Such a correlation is based on the premise that we "know" that any reasonable quantity defining the "structure of water" would probably decrease upon increasing the temperature.[4]

Frank and Evans,(8) in an effort to explain the anomalous thermodynamic behavior of aqueous solutions, have introduced the idea of an "iceberg formation" around the solute. Further research in this field has been concentrated on the following two main questions: (1) What is the structure of the immediate environment of a solute molecule in water? (2) What are the molecular reasons for the phenomena of "structural changes" if any?

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[2] For a review mainly concerned with the experimental aspects of this topic see Ref. 3. For a review of some theoretical aspects see Ref. 4.

[3] This "explanation" is not satisfactory, however, even on qualitative grounds. For, suppose that we knew that the solute has shifted the equilibrium toward the component with lower compressibility; there is still an unknown effect on the relaxation term [see Eq. (2.16) of Ref. 2] that we cannot predict even in a qualitative manner.

[4] A more detailed discussion of this subject is given in Ref. 7.

This paper is concerned with the second question. One should bear in mind that almost all theories of "structural changes" are deeply anchored in some specific *ad hoc* mixture model for water.[5] It is therefore no wonder that some serious doubts have been cast upon their validity. Moreover, even the very application of the mixture-model idea has been called in question and vigorously criticized as being unsupported on experimental grounds. (It is instructive to note that even the example cited above on the effect of solute on the compressibility was presented(5) as "a most impressive piece of evidence for the theory of polymerization of water"). In parts I and II of this series an exact mixture-model approach has been developed, which does not require any experimental evidence for its support.

In this paper an attempt is made to accommodate some of the current concepts and ideas prevailing in the literature on aqueous solutions into an exact framework. Although we shall be using classical statistical mechanics throughout, we feel that the basic arguments and conclusions will still be valid in a quantum mechanical extension of the theory. The most important feature of the classical treatment is that all internal properties of a single water molecule are assumed to be separable from the total partition function (these may be treated either classically or quantum mechanically) and are presumed not to be affected by the type of environment of the molecule. In particular, we shall assume that a solute adjacent to a water molecule does not affect its internal properties. The latter could have been accounted for only by using quantum mechanical language.

Our starting point will be the general formalism of quasicomponent distribution functions(1,2) (QCDF) which enables us to view a one-component system as a mixture of any number of quasicomponents. The simplest of these is the so-called "two-structure model" (TSM). The term "model" is somewhat misused here in the sense that no modelistic assumptions are invoked in the construction of TSM.

In the next section the main problem is formulated in the TSM. The Kirkwood–Buff(20) theory of solution is employed in Section 3 to examine the molecular origin of the "structural changes" induced by a solute. The main result of this section is the general expression (valid for any TSM) for the "stabilization effect" of the solute on one of the components, denoted by L; it reads

$$\lim_{\rho_S\to 0}\left(\frac{\partial N_L}{\partial N_S}\right)_{P,T,N_W} = x_L x_H[\eta(\bar{V}_L - \bar{V}_H) - \rho_W \Delta_{LH}] \tag{1}$$

where x_L and x_H are the mole fractions of the two components L and H, $\bar{V}_L$ and $\bar{V}_H$ are their partial molar volumes, $\rho_W = \rho_L + \rho_H$ is the total density

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[5] Some specific applications of the mixture-model approach to aqueous solutions of nonelectrolytes are given in Refs. 7 and 9–19.

of the liquid, and η and $\Delta^S_{L,H}$ are quantities to be defined in (18) and (28), respectively. Though $\bar{V}_L$ and $\bar{V}_H$ may also be expressed in terms of molecular quantities, the expression was found more useful for purposes of interpretation. Some exact consequences of this results are discussed in Section 3.

Section 4 is devoted to a more qualitative analysis of relation (1). Some speculations as to the molecular origin of the thermodynamic properties of aqueous solutions are discussed. The central conclusion of this section may be summarized as follows: If we classified the water molecules into two components, one with relatively "low local density" (L) and the other with relatively "high local density" (H), then a solute S is likely to be accommodated near the former species. This species will therefore be stabilized, in the sense that the derivative (1) is positive. The unique response of water is manifested in the coupling of a *negative* heat transfer, $\bar{H}_L - \bar{H}_H$, to the positive "stabilization effect," thus producing a large, negative relaxation term to the partial molar enthalpy of the solute. It turns out that this peculiar coupling is almost exactly the same argument employed to explain the anomalous temperature dependence of the volume of water.(1,2)

Section 5 is devoted to some general aspects of the mixture-model approach. It is demonstrated that the split of any partial molar quantity of the solute into "static" and "relaxation" terms strongly depends on the way we like to view the solvent. Also, the identification of the "structural changes" in the solvent, though a useful concept in some cases, is purely a matter of choice of the particular QCDF.

2. THERMODYNAMIC TREATMENT

In this section we shall formulate some of the thermodynamic quantities pertinent to aqueous solutions in the same theoretical framework that has been applied to pure liquid in Refs. 1 and 2. The system under consideration consists of N_W water molecules and N_S solute molecules (later we shall restrict the discussion to the case $N_S \ll N_W$) at a given pressure P and temperature T (P and T will henceforth be always kept constant and will be omitted from the notations).

All the treatment in this and the following section will apply to any possible TSM. As a concrete example we may think of the one based on the concept of coordination number, namely(1,2)

$$N_L = \sum_{K=0}^{K^*} N_K \tag{2}$$

$$N_H = \sum_{K=K^*+1}^{\infty} N_K \tag{3}$$

and

$$N_W = N_L + N_H \tag{4}$$

Here N_K is the average number of water molecules having coordination number[6] equal to K. The number K^* is selected in order to induce a distinction between a "low local density" component L and a "high local density" component H.

We shall henceforth use the variables N_L and N_H for the average number of molecules of the two species L and H; however, these are not necessarily the ones defined in (2) and (3). We shall thus reserve the freedom of selecting any specific TSM, and in this sense the treatment will be quite general. At a point where interpretation is called on it will be found useful to employ the specific example cited above with a choice of K^* as 4 or 5.

Any extensive thermodynamic quantity may be viewed as either a function of (P, T, N_W, N_S) or of (P, T, N_L, N_H, N_S). Note that a QCDF has been applied only to the water molecules; a more general case will be treated in Section 5. The partial molar enthalpy, entropy, and free energy of the solute S may be written as

$$\begin{aligned}\bar{H}_S &= \left(\frac{\partial H}{\partial N_S}\right)_{N_W} = \left(\frac{\partial H}{\partial N_S}\right)_{N_L,N_H} + (\bar{H}_L - \bar{H}_H)\left(\frac{\partial N_L}{\partial N_S}\right)_{N_W} \\ &= H_S^* + \Delta H_S^r \end{aligned} \tag{5}$$

$$\begin{aligned}\bar{S}_S &= \left(\frac{\partial S}{\partial N_S}\right)_{N_W} = \left(\frac{\partial S}{\partial N_S}\right)_{N_L,N_H} + (\bar{S}_L - \bar{S}_H)\left(\frac{\partial N_L}{\partial N_S}\right)_{N_W} \\ &= S_S^* + \Delta S_S^r \end{aligned} \tag{6}$$

$$\begin{aligned}\mu_S &= \left(\frac{\partial G}{\partial N_S}\right)_{N_W} = \left(\frac{\partial G}{\partial N_S}\right)_{N_L,N_H} + (\mu_L - \mu_H)\left(\frac{\partial N_L}{\partial N_S}\right)_{N_W} \\ &= \mu_S^* + \Delta \mu_S^r \end{aligned} \tag{7}$$

In each case the first term on the r.h.s., with an asterisk, is referred to as the "static" part, and the second as the "relaxation" part, of the corresponding partial molar quantity.

A general and important result follows immediately from the condition of "chemical equilibrium":

$$\mu_L = \mu_H \tag{8}$$

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[6] Note that in counting neighbors in aqueous solutions we may either count *all* molecules which fall in the R_C sphere (see Ref. 1) of a given molecule, or count *only* water molecules. In both cases we get a proper QCDF; the latter point of view seems more useful for the purpose of this article and will be adopted throughout.

Hence from (7) we get

$$\mu_S = \mu_S^* \tag{9}$$

i.e., for any classification into two components the contribution from the relaxation term to the chemical potential μ_S vanishes. This conclusion is also valid for any multicomponent mixture-model approach. Furthermore, it follows from (8) that

$$\bar{H}_L - T\bar{S}_L = \bar{H}_H - T\bar{S}_H \tag{10}$$

or equivalently

$$\Delta H_S^r = T\Delta S_S^r \tag{11}$$

which means that the relaxation part of $\bar{H}_S$ exactly compensates the relaxation part of $T\bar{S}_S$. This may be viewed as a general formulation of the "enthalpy-entropy compensation" phenomenon,(21) which, again, is valid for any mixture-model approach.

The traditional interpretation of the large, negative enthalpy and entropy of solution of a nonelectrolyte in water is the following.(4) One identifies the L form with the hydrogen-bonded water molecules and the H form with the nonbonded molecules; hence it is expected that $\bar{H}_L - \bar{H}_H$ will be negative. If in addition we postulate that the solute S "stabilizes" the L form, i.e., that

$$(\partial N_L/\partial N_S)_{N_W} > 0 \tag{12}$$

then the relaxation part of $\bar{H}_S$ (and hence of $\bar{S}_S$) will be negative. Since the transfer from the H form to the L form is expected to involve formation of hydrogen bonds, these relaxation quantities are expected to be large and negative—hence a reasonably qualitative interpretation for the observable phenomena is attained.

We believe that the above reasoning is basically correct. The fact that the quantity $\bar{H}_L - \bar{H}_H$ is negative may be accepted by virtue of the definition of the two components, and does not necessarily involve the concept of the hydrogen bond. The crucial question may be stated as follows: Suppose we have chosen the two components in such a way that $\bar{H}_L - \bar{H}_H < 0$; how do we know that in this case the stabilization effect is positive? Or conversely, we could have chosen the two components in such a way that (12) is valid; then the question may be raised about the sign of $\bar{H}_L - \bar{H}_H$. These questions have been studied by many authors(9–19) by using *ad hoc* model for water.

The central theme of this paper is to examine the exact condition under which a stabilization of, say, the L form occurs. The tactic of the present investigation differs from the traditional one, where a model for water is assumed and then the condition (12) is examined. We shall first derive a general and exact expression for the derivative $(\partial N_L/\partial N_S)_{N_W}$ which is valid for any TSM. Then we shall seek the general requirements under which this derivative is positive.

A convenient starting point for our investigation is the thermodynamic identity[2,4]

$$\left[\frac{\partial N_L}{\partial N_S}\right]_{N_W} = -(\mu_{LL} - 2\mu_{LH} + \mu_{HH})^{-1}\left[\frac{\partial(\mu_L - \mu_H)}{\partial N_S}\right]_{N_L, N_H} \tag{13}$$

where $\mu_{ij} = \partial^2 G/\partial N_i\,\partial N_j$, and the quantity $\mu_{LL} - 2\mu_{LH} + \mu_{HH}$ is always positive.[22]

The advantage of using the identity (13) is twofold. In the first place the problem of finding the sign of $(\partial N_L/\partial N_S)_{N_W}$ in the *equilibrated* system, with respect to the equilibrium L — H, is reformulated, on the r.h.s. of (13), in a system where the equilibrium has been "*frozen in*." Second, all of the derivatives appearing on the r.h.s. of (13) may be expressed in terms of molecular quantities through the Kirkwood-Buff theory of solution, a feature which will be exploited in the next section.

3. APPLICATION OF THE KIRKWOOD-BUFF THEORY OF SOLUTION

The Kirkwood–Buff theory[20] enables us to express the quantity $(\partial N_L/\partial N_S)_{N_W}$ in terms of integrals over the various pair correlation functions. Such an expression can be derived for any mixture model. However, the general case is fairly complicated and does not lend itself to a simple interpretation. Hence we shall develop only the case of the TSM and also specialize for the limiting case of very dilute solutions of S. It is important to note that all quantities appearing on the r.h.s. of Eq. (13) pertain to the "frozen-in" system. Therefore we can view our system as a virtually three-quasicomponent system with compositions N_L, N_H, and N_S.

The basic relations employed here are those connection the composition fluctuations and the thermodynamic quantities.

Let $g_{ij}(R)$ be the angle-averaged pair correlation function, or the radial distribution function, for the pair of species i and j. The following relation follows directly from the definitions of the singlet and pair distribution functions in the grand canonical ensemble[20]:

$$G_{ij} = \int_0^\infty [g_{ij}(R) - 1]4\pi R^2\,dR = V\left(\frac{\langle N_i N_j\rangle - \langle N_i\rangle\langle N_j\rangle}{\langle N_i\rangle\langle N_j\rangle} - \frac{\delta_{ij}}{\langle N_i\rangle}\right) \tag{14}$$

Here V is the volume, δ_{ij} is the Kronecker delta function, and the angular brackets stands for an average in the grand canonical ensemble. The connection with thermodynamics is established through the following relations. Define the matrix elements

$$B_{ij} = \rho_i\rho_j G_{ij} + \rho_i \delta_{ij} \tag{15}$$

where ρ_i is the average number density of the ith species. The various derivatives of the chemical potentials required in relation (13) are given by

$$\mu_{ij} = \left[\frac{\partial\mu_i}{\partial N_j}\right]_{P,T,N_{k,k\neq j}} = \frac{kT}{V}\frac{B^{ij}}{|B|} - \frac{\bar{V}_i\bar{V}_j}{\kappa^* V} \tag{16}$$

Here k is the Boltzmann constant, B^{ij} is the cofactor of the element B_{ij} in the determinant $|B|$, $\bar{V}_i$ is the partial molar volume of the ith species, and κ^* is the isothermal compressibility. The asterisk is added to stress the fact that we are working here in the "frozen-in" system. Note also that μ_{ij} are derivatives at P and T constant as required in relation (13).

We shall now specialize our relation to the limiting case where $\rho_S \to 0$. We write

$$\zeta = 1 + \rho_L G_{LL} + \rho_H G_{HH} + \rho_L\rho_H(G_{LL}G_{HH} - G_{LH}^2) \tag{17}$$

$$\eta = \rho_L + \rho_H + \rho_L\rho_H(G_{LL} + G_{HH} - 2G_{LH}) \tag{18}$$

The Kirkwood–Buff theory provides the relations[20]

$$\kappa^* = (1/kT)(\zeta/\eta) \tag{19}$$

$$\bar{V}_H = [1 + \rho_L(G_{LL} - G_{LH})]/\eta \tag{20}$$

$$\bar{V}_L = [1 + \rho_H(G_{HH} - G_{LH})]/\eta \tag{21}$$

The quantities in (19)–(21) pertain to the limiting case $\rho_S \to 0$, hence they are for pure water.[7]

We shall also need the limiting value of the (static) partial molar volume of the solute S. The general relation is [see Eq. (13) of Ref. 20]

$$\bar{V}_S{}^* = \frac{\rho_S B^{SS} + \rho_L B^{LS} + \rho_H B^{HS}}{\rho_S{}^2 B^{SS} + \rho_L{}^2 B^{LL} + \rho_H{}^2 B^{HH} + 2\rho_S\rho_H B^{HS} + 2\rho_S\rho_L B^{LS} + 2\rho_L\rho_H B^{LH}} \tag{22}$$

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[7] Note that in general a quantity like κ^* is not equal to the experimental isothermal compressibility of pure water. We are here concerned with the static part of κ only [see relation (2.16) of Ref. 2], which depends on the particular choice of the classification into two components. This comment holds for $\bar{V}_L$ and $\bar{V}_H$ as well, though an additional asterisk is not included in the notation since these quantities are definable only in the "frozen-in" system.

where the various cofactors are computed from the determinant

$$|B| = \begin{vmatrix} \rho_S + \rho_S^2 G_{SS} & \rho_S\rho_L G_{SL} & \rho_S\rho_H G_{SH} \\ \rho_L\rho_S G_{LS} & \rho_L + \rho_L^2 G_{LL} & \rho_L\rho_H G_{LH} \\ \rho_H\rho_S G_{HS} & \rho_H\rho_L G_{HL} & \rho_H + \rho_H^2 G_{HH} \end{vmatrix} \tag{23}$$

with $G_{ij} = G_{ji}$.
The limiting form of this determinant is

$$|B| \xrightarrow{\rho_S \to 0} \rho_S\rho_L\rho_H\zeta \tag{24}$$

Retaining only linear terms in ρ_S in the numerator and in the denominator of (22), we get

$$V_S^* \xrightarrow{\rho_S \to 0} \frac{\zeta - \rho_L G_{LS}[1 + \rho_H(G_{HH} - G_{LH})] - \rho_H G_{HS}[1 + \rho_L(G_{LL} - G_{HL})]}{\eta} \tag{25a}$$

$$= kT\kappa^* - \rho_L G_{LS}\overline{V}_L - \rho_H G_{HS}\overline{V}_H \tag{25b}$$

The last two relations for V_S^* are quite general. They may be applied to any real three-component system, in which case the asterisk on V_S^* is redundant. However, in application of TSM, one must add the asterisk to indicate that we are referring only to the "static" part of the partial molar volume. Some checks of consitency are examined in Appendices A and C.

We now turn to examine a quantity which tells us in which direction the equilibrium $L \rightleftarrows H$ will be shifted by the addition of S(4):

$$\left[\frac{\partial(\mu_L - \mu_H)}{\partial N_S}\right]_{N_L, N_H} = \frac{kT}{V}\left[\frac{B^{LS} - B^{HS}}{|B|} - \frac{V_S^*(\overline{V}_L - \overline{V}_H)}{kT\kappa^*}\right] \tag{26}$$

For the first term on the r.h.s. of (26) we have

$$(B^{LS} - B^{HS})/|B|$$

$$= \left[-\rho_S\rho_L\rho_H \begin{vmatrix} G_{LS} & \rho_H G_{HS} \\ G_{HL} & 1 + \rho_H G_{HH} \end{vmatrix} - \rho_S\rho_L\rho_H \begin{vmatrix} \rho_L G_{LS} & G_{HS} \\ 1 + \rho_L G_{LL} & G_{LH} \end{vmatrix}\right] \Big/ |B|$$

$$\xrightarrow{\rho_S \to 0} (-1/\zeta)[G_{LS} - G_{HS} + G_{LS}(\rho_H G_{HH} + \rho_L G_{LH}) - G_{HS}(\rho_H G_{LH} + \rho_L G_{LL})] \tag{27}$$

It is now convenient to define the quantity

$$\Delta^S_{LH} = G_{LS} - G_{HS} \tag{28}$$

which measures the asymmetry in the affinity of S toward the two components L and H (see also next section).

Using (19)–(21) and (25), we get the limiting form for (26):

$$\lim_{\rho_S\to 0}\left[\frac{\partial(\mu_L-\mu_H)}{\partial N_S}\right]_{N_L,N_H} = -\frac{kT}{V}\left[(\bar V_L-\bar V_H)+\frac{\rho_W\Delta^S_{LH}}{\zeta}(G_{LH}+\eta\bar V_L\bar V_H)\right] \tag{29}$$

where $\rho_W=\rho_L+\rho_H$. Applying the identity

$$\bar V_L\bar V_H=(\zeta-\eta G_{LH})/\eta^2 \tag{30}$$

we get the final form

$$\lim_{\rho_S\to 0}\left[\frac{\partial(\mu_L-\mu_H)}{\partial N_S}\right]_{N_L,N_H} = -\frac{kT}{V}\left[(\bar V_L-\bar V_H)+\frac{\rho_W\Delta^S_{LH}}{\eta}\right] \tag{31}$$

The sign of this quantity determines which of the components *L* or *H* will be "stabilized" by *S*. It is instructive to note that the first term on the r.h.s. of (31) depends only on the properties of the solvent, whereas the second term depends on the difference in the response of *L* and *H* to the addition of *S*.

In order to determine the amount of stabilization we must turn the whole r.h.s. of Eq. (13). We first note that using the Gibbs–Duhem relations (for pure water)

$$N_L\mu_{LL}+N_H\mu_{LH}=0 \tag{32}$$

$$N_L\mu_{LH}+N_H\mu_{HH}=0 \tag{33}$$

we get

$$\mu_{LL}-2\mu_{LH}+\mu_{HH}=-\mu_{LH}/x_Lx_H \tag{34}$$

where x_L is the mole fraction of the *L* component in pure water. Using relation (16) and the identity (30), we get

$$\mu_{LL}-2\mu_{LH}+\mu_{HH}=kT/x_Lx_HV\eta \tag{35}$$

Combining (35) with (31), we get the final limiting expression for the "stabilization effect" of *S* upon *L*:

$$\lim_{\rho_S\to 0}\left[\frac{\partial N_L}{\partial N_S}\right]_{P,T,N_W}=x_Lx_H[\eta(\bar V_L-\bar V_H)+\rho_W\Delta^S_{LH}] \tag{36}$$

This relation is quite general, and may be applied to any two-component system in chemical equilibrium. In our special application we have preserved a "degree of freedom" which is the choice of a specific TSM. Note also that by combining the "stabilization effect," (36), with say, the heat of conversion $\bar H_L-\bar H_H$, we get the corresponding relaxation term of the partial molar enthalpy [Eq. (5)].

At this juncture it is appropriate to digress to a discussion of some concepts like "structural changes" and structure-"breaking" or -"making" which are so ubiquitous in the literature concerned with aqueous solutions. There is no unique way of defining the concept of the "structure of water" in the first place.(7) One practical way is to choose the L form as the one which we believe to be the more "structured" form. A reasonable choice for water would be the molecules having coordination number equal to four. (A more elaborate one would require molecules with four hydrogen bonds, but this, in turn, requires a definition of the concept of hydrogen bond.) Hence x_L may serve as a measure of the degree of structure of water and (36) will express the structural change caused by S. Indeed in some specific *ad hoc* models for water the L form is identified with the "icelike" form which represents also the more structured form. We shall not need this specific identification in what follows, though we acknowledge the fact that it has been used as a background motivation for our interpretations.

We shall now summarize some general consequences that follow from relation (36).

1. If either x_L or X_H is very small, then clearly the stablization effect will be small, too. This has a direct bearing on the choice of a particular *ad hoc* mixture model. For, suppose we define the L form to be strictly ice like molecules[8]; then it is likely that x_L will be very small; hence the stabilization effect will be small, too.

2. If the two forms are chosen in such a way that they are very "similar" in the sense that

$$\bar{V}_L \approx \bar{V}_H \tag{37}$$

and

$$\Delta^S_{LH} \approx 0 \tag{38}$$

then we shall also have vanishingly small stabilization effect. An assumption of ideality (in the symmetric sense), though it does not necessarily imply extreme similarity of the two components, should be avoided (see also Ref. 2).

3. In a TSM for which $x_L x_H$ is not very small and for which the two components differ markedly the whole term on the r.h.s. of (36) will tend to zero as $\rho_W \to 0$. Note that $\bar{V}_L - \bar{V}_H$ as well as the quantity Δ^S_{LH} becomes constant as $\rho_W \to 0$. [See also relation (C.10) in Appendix C.]

4. For high densities, say when ρ_W approaches the close-packing density, it is expected that either condition 1 or 2 will become effective, i.e., if we choose the component to be different, it is likely that one of them will

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[8] For example, as in the Samoilov model.(23)

have small concentration. On the other hand, if we choose the two components to have comparable concentrations, then it is likely that they will be similar. Hence in this case we shall also have a vanishingly small stabilization effect.

The above considerations are very general and may apply to any fluid. It shows that a large stabilization effect is attainable under very restricted conditions. A reflection on these conditions may suggest a possible molecular reason for such a large effect in water.

To elucidate this point, suppose we construct a TSM by making a cutoff in a continuous QCDF [see, for example, Eq. (2.6) of Ref. 2]. Figure 1 depicts a possible form of the function $x(\nu)$ for a simple fluid and for water. In the first case we expect that the distribution function $x(\nu)$ will be quite narrow. Hence a choice of a cutoff point $\nu_1{}^*$ will produce two dissimilar components but one of them will have very low concentration. On the other hand, a choice of $\nu_2{}^*$ will produce two very similar components with almost equal concentrations. In both cases we shall end up with a small stabilization effect. Liquid water may have, as one of its unique properties, a distribution function which is spread over a relatively large range of values and a cutoff point ν^* may be found in such a way that the two components have different properties and comparable concentrations. This is illustrated schematically in Fig. 1(b). A Monte Carlo calculation of the function $x(\nu)$ has been carried out for Lennard-Jones and for "waterlike" particles in two dimensions.[24]

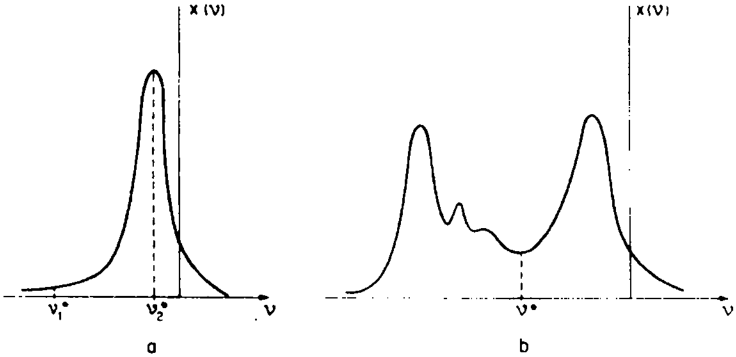

Fig. 1. Schematic possible form of the distribution function $x(\nu)$. (a) A simple fluid is expected to have a narrow distribution. $\nu_1{}^*$ and $\nu_2{}^*$ are two possible cutoff points that may be employed to induce a TSM. If the first choice is made, then the product of the two mole fractions will be small. In the second choice the product of the mole fraction may be large (maximum value $\frac{1}{4}$) but the two components will be very similar. (b) Possible form of the distribution function for liquid water. Here a cutoff point ν^* may be found for which the two components are very different, yet the product of their mole fractions will not be vanishingly small.

Some preliminary results indeed show $x(\nu)$ for the "waterlike" particles contains a few peaks compared with essentially one peak for the spherical particles. A detailed account of this work will be published at its completion.

It is important to emphasize that the possiblitity of obtaining a large stabilization effect does not imply a large *negative* relaxation term for say, the enthalpy of solution [see Eq. (2)]. It is the product of the stabilization effect and $\bar{H}_L - \bar{H}_H$ which is of importance. This product involves another unique feature of liquid water, akin to the one discussed in Ref. 2, and will be further examined in the next section.

Finally, we should like to note some advantages of the Kirkwood Buff theory over a previous examination of the stabilization effect.(1) The most important one is that no pairwise-additivity assumption of the potential energy is invoked in any stage. A previous treatment of the same problem had been based on the relation between chemical potential and the radial distribution function, which explicitly depends on the pairwise-additivity assumption. Furthermore, the density dependence of $g_{ij}(R)$ is not required in the present treatment; the Kirkwood–Buff theory provides direct relations between density derivativatives of the chemical potentials and the various $g_{ij}(R)$.

Thus the only assumption introduced in this section involves the application of classical statistical mechanics. We believe that the main result of this section will survive in a quantim mechanical extension of the theory. In such a case new effects may be found, e.g., effects of S on the internal properties of water molecules, which will superimpose on the classical result obtained here.

4. FURTHER CONSIDERATION OF THE TSM FOR AQUEOUS SOLUTIONS

In Section 2 we have seen that the relaxation terms of the entropy and the enthalpy of S are related to each other; hence it is sufficient to discuss only one of these.

The standard enthalpy of solution of S may be written as

$$\Delta\bar{H}_S = \bar{H}_S^{\circ l} - \bar{H}_S^{\circ g} = \Delta H_S^* + (\bar{H}_L - \bar{H}_H)(\partial N_L/\partial N_S)_{N_W}$$
$$= \Delta H_S^* + x_L x_H(\bar{H}_L - \bar{H}_H)[\eta(\bar{V}_L - \bar{V}_H) - \rho_W \Delta_{LH}^S] \tag{39}$$

The first term on the r.h.s. of (39) is the standard enthalpy of solution of S in the "frozen-in" system with respect to the conversion $L \rightleftarrows H$. If we choose a TSM for which either x_L or x_H is very small or the two components are very similar, then $\Delta\bar{H}_S{}^\circ$ will be indistinguishable from $\Delta H_S{}^*$. However, for purposes of interpretation it is more useful to select a TSM in such a way that the relaxation term will be large and negative; hence a qualitative interpretation of the anomalous value of the enthalpy (and entropy) of solution is provided.

The relaxation term is built up of a product of $\bar{H}_L - \bar{H}_H$ and the stabilization effect. We can employ our "degree of freedom" and choose a TSM in which the stabilization effect is positive and then postulate that the corresponding $\bar{H}_L - \bar{H}_H$ is negative. A second route is to choose a TSM in which $\bar{H}_L - \bar{H}_H$ is negative and then show that the stabilization effect is positive.

We shall carry out the former procedure and demonstrate that the molecular origin of the anomalous properties of aqueous solutions are similar to the ones encountered in the discussion of pure water in Ref. 2.

The arguments presented in this section are basically qualitative. Nevertheless, we believe that they are reasonable and in conformity with similar arguments being applied to *ad hoc* mixture-model approaches.[1]

We start by choosing a TSM for which $\bar{V}_L - \bar{V}_H$ is positive. It is presumed that in the case of water the definition of L and H in Eq. (2) with, say $K^* = 4$ or 5 will be satisfactory. The basic idea is that if L is the "low local density" component and H is the "high local density" component, then a fluctuation for which N_L increases at the expense of N_H will result a net increase in volume,[9] i.e. [see also relation (C.10) in Appendix C),

$$dV = \frac{\partial V}{\partial N_L}\, dN_L + \frac{\partial V}{\partial N_H}\, dN_H + \cdots = (\bar{V}_L - \bar{V}_H)\, dN_L + \cdots > 0 \quad (40)$$

which means that

$$\bar{V}_L - \bar{V}_H > 0 \quad (41)$$

Since η is always positive (see Appendix B), we have one positive term in the stabilization effect in Eq. (36). Next we turn to the quantity Δ^S_{LH}, which measures the asymmetry of the effect of S on L relative to H. We claim that within the choice of TSM made above this quantity will be positive.

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[9] The argument is of course not exact. With a choice of, say $K^* = 4$ in Eq. (2) we may think of a process in which an H molecule is converted to an L molecule. If this process was the only one taking place, then a net increase in volume is expected. However, this process may induce a rearrangement within the H or the L group of molecules so that a decrease in volume will follow. For instance, suppose that as a result of the conversion made above, all the molecules with coordination number equal to five were converted to molecules with larger coordination number; then such a process would leave N_H constant yet the net result might be a shrinkage of the volume. The assumption is here made that such processes are unlikely to be the dominant ones.

Recalling the definition of Δ^S_{LH} in (28), we may write

$$\begin{aligned}\Delta^S_{LH} &= \int_0^\infty [g_{LS}(R) - 1]4\pi R^2\,dR - \int_0^\infty [g_{HS}(R) - 1]4\pi R^2\,dR \\ &= \int_0^\infty [g_{LS}(R) - g_{HS}(R)]4\pi R^2\,dR \\ &= \int_{\sigma_{WS}}^\infty [g_{LS}(R) - g_{HS}(R)]4\pi R^2\,dR \qquad (42)\end{aligned}$$

In the last form on the r.h.s. of (42) we have assumed that there exists a hard-core diameter σ_{WS}, which is common to the L-S and H-S pairs, below which the radial distribution function vanishes.[10] For a relatively inert solute S we may use the approximate expansion valid for $R \geq \sigma_{WS}$ and $W_{ij}/kT \ll 1$

$$g_{ij}(R) = \exp[-W^{(2)}_{ij}(R)/kT] \approx 1 - [W^{(2)}_{ij}(R)/kT] \qquad (43)$$

where $W^{(2)}_{ij}(R)$ is the potential of average force for the pair of species i and j at distance R; hence

$$\Delta^S_{LH} \simeq (1/kT)\int_{\sigma_{WS}}^\infty [W^{(2)}_{HS}(R) - W^{(2)}_{LS}(R)]4\pi R^2\,dR \qquad (44)$$

The general expected forms of $W^{(2)}_{HS}(R)$ and $W^{(2)}_{LS}(R)$ are depicted in Fig. 2. Since H must have more neighbors than an L molecule, it is clear that at short distances near σ_{WS}, $W^{(2)}_{HS}(R)$ will show a repulsive behavior relative to $W^{(2)}_{LS}(R)$.

The quantity $W^{(2)}_{HS}(R) - W^{(2)}_{LS}(R)$ is simply the work required to transfer an S molecule at a distance R from L to a distance R from H (see demonstration in Fig. 3).

Because of the peculiar behavior of W_{HS} and W_{LS} near σ_{WS} it is clear that at $R \gtrsim \sigma_{WS}$ this work of transfer will be positive. Moreover since most of the contribution to the integral (44) comes from, say $\sigma_{WS} \lesssim R \lesssim 2\sigma_{WS}$, we conclude that Δ^S_{LH} for our particular choice of the TSM will be a positive quantity.

---

[10] Since both L and H molecules are water molecules, it is always possible to find such a common hard-core diameter σ_{WS} which is roughly equal to $(\sigma_W + \sigma_S)/2$. One should remember that g_{LS} is essentially the radial distribution function of S around a *water* molecule with the additional restriction that this water molecule must have at most K^* neighbors in the sense of Ref. 2. Similarly, g_{HS} involves the restriction that the water molecule must have more than K^* neighbors. In both cases an impenetrable radius should exist which is characteristic of the water-solute pair. It is possible that for an H molecule a larger hard-core diameter will be effective. For instance, if H is defined as a molecule with 12 coordination number, an S molecule will be excluded from a sphere of about $\sigma_{WS} + \sigma_W$ around the center of H. (See also Fig. 2.)

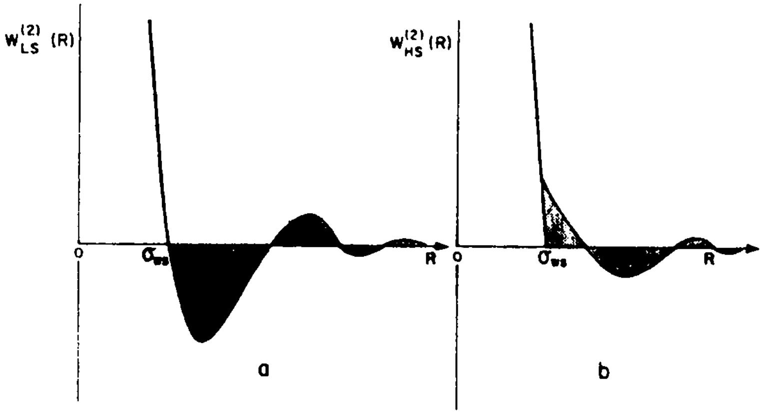

Fig. 2. Schematic form of the functions $W_{LS}^{(2)}(R)$ and $W_{HS}^{(2)}(R)$. The essential differences between the two curves are: (1) $W_{HS}^{(2)}(R)$ may exhibit an additional repulsive range, say, at $\sigma_{WS} \lesssim R \lesssim \sigma_{WS} + \sigma_W$. (2) The first minimum of $W_{HS}^{(2)}(R)$ is expected to be shallower than the corresponding minimum of $W_{LS}^{(2)}(R)$. The quantity Δ_{LH}^{S} in (44) is related to the difference of the two shaded areas under $W_{HS}^{(2)}(R)$ and $W_{LS}^{(2)}(R)$.

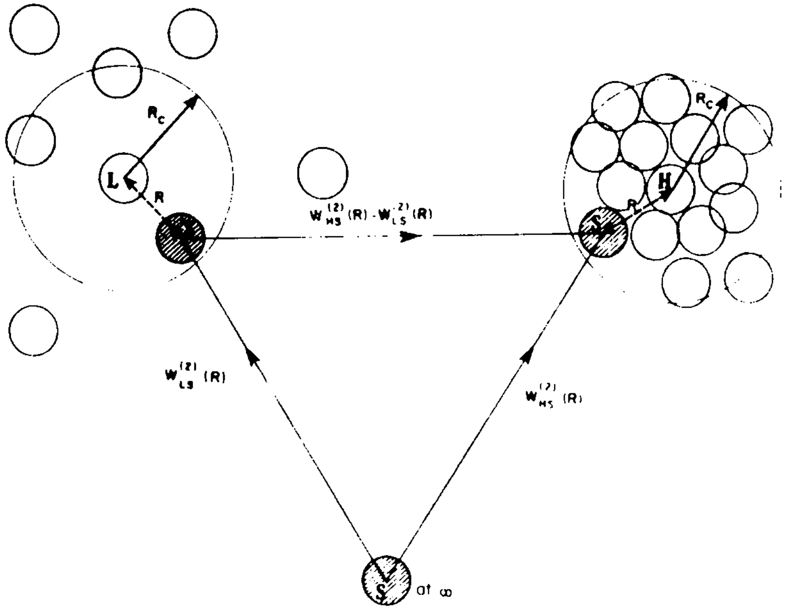

Fig. 3. The process of transferring an S molecule from L to H is depicted in two parts: (1) Transfer of S from infinity to the distance R from L involves the work $W_{LS}^{(2)}(R)$. (2) Transfer of S from infinity to a distance R from H involves the work $W_{HS}^{(2)}(R)$.

The positive sign of Δ^S_{LH} may also be reinterpreted in terms of the excess "affinity" of S to L relative to an H molecule. From the form of Δ^S_{LH} in (42) it is clear that $\rho_S\, \Delta^S_{LH}$ measures the excess of S molecules, beyond the distance of σ_{HS}, around L relative to H. A positive value of Δ^S_{LH} would mean that S "prefers" to be near an L molecule rather than an H molecule. In fact the latter interpretation coincides with some specific models of aqueous solutions in which S is allowed to interact only with one form, hence introducing such an asymmetry in the very definition of the model.$^{(1)}$

So far we have shown that the stabilization effect is positive for this particular choice of a TSM. We may sum up the arguments as follows. If we choose any TSM for which one species has lower local density than the other, then it is likely that this species will have a larger contribution to the volume and simultaneously[11] will provide more space to accommodate S, hence the equilibrium $L \rightleftarrows H$ will be shifted toward the L form.

The unique response of water is manifested in the following properties. In the first place a TSM may be found for which the stabilization effect may be large,[12] i.e., the conditions listed in the end of the previous section are fulfilled. More important, however, is the phenomenon that positive stabilization effect is coupled with a negative "heat of reaction" ($\bar{H}_L - \bar{H}_H < 0$). It is most instructive to recall that the sign of the product $(\bar{H}_L - \bar{H}_H)(\bar{V}_L - \bar{V}_H)$ was found to be decisive in explaining the temperature dependence of the volume,$^{(1,2)}$ which in turn reflects the unique property of water that "low local density" is on the average related to "strong binding energy" (see Appendix B of Ref. 2).

Although we have avoided the explicit introduction of the concept of hydrogen bonds, it is clear that the L form chosen in this section may be identified with the hydrogen-bonded water molecules. We cannot say anything about the exact geometry of the molecules surrounding such a molecule. For our purposes it is sufficient to assume that fully hydrogen-bonded molecules have low local density. If these are stabilized by a solute S, then it is likely that more hydrogen bonds are induced by the addition of such solutes.

Finally, we should like to comment on one interesting feature of the expression (36) for the stabilization effect. We note that the effect is built up of two parts. The first, $\bar{V}_L - \bar{V}_H$, is purely a property of the solvent,

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[11] We feel that the signs of $\bar{V}_L - \bar{V}_H$ and Δ^{H}_{SL} are somehow related to each other. A species L which is locally more "open" is likely to provide more space to accommodate a solute molecule. We did not succeed in establishing such a relationship, however.

[12] By "large," we may be satisfied if the stabilization effect is of the order of unity. In which case, multiplication by $\bar{H}_L - \bar{H}_H$, which may be of the order of magnitude of hydrogen bond energy, will already produce a large relaxation term to the enthalpy of solution.

whereas Δ_{LH}^{S} reflects the relative preference of S as to the choice of its environment.

The question raised is the following: Is it possible to find either a real solute S or a TSM in such a way that $\Delta_{LH}^{S} = 0$ but at the same time $\bar{V}_L - \bar{V}_H > 0$? If that is possible, we shall have a somewhat queer situation: that the stabilization effect, though induced by the presence of S, is independent of any property of S, and is purely a property of the solvent.[13] One interesting example could be a point particle which does not interact *at all* with the water molecules. (Note that if the solvent molecules have an effective hard core of radius r, then a suitable "hard" point particle must have a radius of $-r$.) In this case $\Delta_{LH}^{S} = 0$ since $g_{LS}(R) = g_{HS}(R) = 1$. The reason for the "stabilization" effect in this case is quite clear, for the point particle still contributes to the pressure. Under constant pressure, the system should expand upon the addition of these point particles, hence the L form is expected to be more favorable than before. (The author is very grateful to the referee of this article for pointing out this example.)

5. APPLICATION OF A CONTINUOUS MIXTURE-MODEL APPROACH

In this section some general consequences of the application of the mixture-model approach to solutions will be discussed. It will be shown that the general concept of the "structural changes" in the solvent is totally dependent on our choice of the classification into components. Nevertheless, for some particular QCDF a distinction between a static and a relaxation term may be useful.

Let $N_W(\alpha)\,d\alpha$ be the average number (in the T, P, N_W, N_S ensemble) of water molecules which are distinguished by some local property having a numerical value between α and $\alpha + d\alpha$ [for concreteness we refer to the examples given in Ref. 2]. Similarly $N_S(\beta)\,d\beta$ is the average number of S molecules classified according to some other property, having a value between β and $\beta + d\beta$. The total energy of the system may be viewed either as a *function* of N_W and N_S or as a *functional* of $N_W(\alpha)$ and $N_S(\beta)$. Using the latter point of view, we may apply the generalized Euler theorem to obtain[14]

$$E(\mathbf{N}_W, \mathbf{N}_S) = \int \bar{E}_W(\mathbf{N}_W, \mathbf{N}_S, \alpha)\, N_W(\alpha)\, d\alpha + \int \bar{E}_S(\mathbf{N}_W, \mathbf{N}_S, \beta)\, N_S(\beta)\, d\beta \tag{45}$$

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[13] A related case in which the relaxation term is purely dependent on the property of the "solvent" has been demonstrated in a simplified model in Ref. 7.

[14] As in Refs. 1 and 2, we shall denote the *whole* function by $\mathbf{N}_W$ and its α component by $N_W(\alpha)$.

where the partial molar quantities in (45) are defined as the functional derivatives of the energy

$$\bar{E}_W(\mathbf{N}_W, \mathbf{N}_S, \alpha) = \delta E(\mathbf{N}_W, \mathbf{N}_S)/\delta N_W(\alpha) \tag{46}$$

$$\bar{E}_S(\mathbf{N}_W, \mathbf{N}_S, \beta) = \delta E(\mathbf{N}_W, \mathbf{N}_S)/\delta N_S(\beta) \tag{47}$$

and the integrations in (45) extend over the whole range of values of α and β respectively.

The *experimental* partial molar energy of the solute is

$$\begin{aligned}\bar{E}_S &= \left[\frac{\partial E(N_W, N_S)}{\partial N_S}\right]_{N_W}\\ &= \int \frac{\partial \bar{E}_W(\mathbf{N}_W, \mathbf{N}_S, \alpha)}{\partial N_S} N_W(\alpha)\, d\alpha + \int \frac{\partial \bar{E}_S(\mathbf{N}_W, \mathbf{N}_S, \beta)}{\partial N_S} N_S(\beta)\, d\beta\\ &\quad + \int \bar{E}_W(\mathbf{N}_W, \mathbf{N}_S, \alpha)\frac{\partial N_W(\alpha)}{\partial N_S}\, d\alpha + \int \bar{E}_S(\mathbf{N}_W, \mathbf{N}_S, \beta)\frac{\partial N_S(\beta)}{\partial N_S}\, d\beta\end{aligned} \tag{48}$$

This is the most general expression for $\bar{E}_S$ in the mixture-model approach. The first two terms may be referred to as the "static" terms and the last two as the "relaxation" terms for the solute and solvent distributions, respectively. In general the distinction between the two kinds of terms strongly depends on the choice of the QCDF. It is instructive to demonstrate a specific choice for which $\bar{E}_S$ is purely a relaxation term.[15]

From here on we shall specialize for the case of very dilute solutions ($\rho_S \to 0$) and also assume, for simplicity, pairwise additivity of the total potential energy. We now define the following two QCDF's for W and S:

$$N_W(\nu) = N_W \int dV \int d\mathbf{X}^N P(\mathbf{X}^N, V)\,\delta[B_1^{ww}(\mathbf{X}^N) - \nu] \tag{49}$$

$$N_S(\nu) = N_S \int dV \int d\mathbf{X}^N P(\mathbf{X}^N, V)\,\delta[B_1^{sw}(\mathbf{X}^N) - \nu] \tag{50}$$

where $\mathbf{X}^N$ stands for the configuration of the whole system of $N = N_W + N_S$ molecules, and $P(\mathbf{X}^N, V)$ is the probability density, in the P, T, N_W, N_S ensemble, of observing the volume V and configuration $\mathbf{X}^N$. The binding energies are defined as

$$B_1^{ww}(\mathbf{X}^N) = \sum_{j=2}^{N_W} U_{1j}^{ww} \tag{51}$$

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[15] It is a trivial matter to demonstrate the other extreme case for which $\bar{E}_S$ is a pure static quantity. Choose a TSM with, say $\rho_L \approx 0$ and from (36) it follows that the corresponding relaxation term will be vanishingly small, too.

and

$$B_1^{sw}(\mathbf{X}^N) = \sum_{j=1}^{N_W} U_{1j}^{sw} \tag{52}$$

Here U^{ww} is the solvent–solvent pair potential and U^{sw} is the solute–solvent pair potential. Note the difference in the definitions of B_1^{ww} and B_1^{sw}.

The total energy of the system may be written as

$$E = N_W\epsilon_W{}^K + N_S\epsilon_S{}^K + \tfrac{1}{2}\int \nu N_W(\nu)\,d\nu + \int \nu N_S(\nu)\,d\nu \tag{53}$$

Note that since N_S is presumed small, solute–solute interactions have been neglected in (53); $\epsilon_i{}^K$ is the average kinetic energy per molecule of species i (including any internal energies if exist). Using the normalization conditions

$$N_W = \int N_W(\nu)\,d\nu \tag{54}$$

$$N_S = \int N_S(\nu)\,d\nu \tag{55}$$

we may write (53) in the form

$$E = \int (\epsilon_W{}^K + \tfrac{1}{2}\nu)\,N_W(\nu)\,d\nu + \int (\epsilon_S{}^K + \nu)\,N_S(\nu)\,d\nu \tag{56}$$

In this representation we identify the partial molar energies of the quasi-components

$$\bar{E}_W(\mathbf{N}_W, \mathbf{N}_S, \nu') = \delta E/\delta N_W(\nu') = \epsilon_W{}^K + \tfrac{1}{2}\nu' \tag{57}$$

$$\bar{E}_S(\mathbf{N}_W, \mathbf{N}_S, \nu'') = \delta E/\delta N_S(\nu'') = \epsilon_S{}^K + \nu'' \tag{58}$$

The most significant feature of this classification is that the partial molar quantities in (57) and (58) do not depend on the compositions $\mathbf{N}_W$ and $\mathbf{N}_S$. Hence, using the general expression in (48), we get for the partial molar energy of S

$$\bar{E}_S = \int (\epsilon_W{}^K + \tfrac{1}{2}\nu)[\partial N_W(\nu)/\partial N_S]\,d\nu + \int (\epsilon_S{}^K + \nu)[\partial N_S(\nu)/\partial N_S]\,d\nu \tag{59}$$

In this form $\bar{E}_S$ is viewed as a *pure* relaxation quantity. It includes a relaxation among the solute species and a relaxation among the solvent species. In practical application it is more common to consider only the latter structural changes. A different expression for the partial molar energy has been derived by Buff and Brout.(25) This relation employs molecular distribution functions of order two and three, which, though exact, are less suitable for our purposes. The equivalent expression for $\bar{E}_S$ in (59) is more closely related to current ideas on "structural changes" in aqueous solutions. It may also provide a useful approximation to $\bar{E}_S$ when the form of the QCDF is known [see, for example, the case cited in Eq. (71)].

Since all the derivatives in (59) are for N_W constant, we have

$$\int \epsilon_W{}^K[\partial N_W(\nu)/\partial N_S]\, d\nu = 0 \tag{60}$$

$$\int \epsilon_S{}^K[\partial N_S(\nu)/\partial N_S]\, d\nu = \epsilon_S{}^K \tag{61}$$

and

$$\int \nu \frac{\partial N_S(\nu)}{\partial N_S}\, d\nu = \frac{\partial}{\partial N_S}\left[N_S \int \nu x_S(\nu)\, d\nu\right] \xrightarrow{\rho_S \to 0} B_0^{sw} \tag{62}$$

where $x_S(\nu) = N_S(\nu)/N_S$ is the probability density that a selected S molecule will have binding energy between ν and $\nu + d\nu$ and B_0^{sw} is the average binding energy of the solute to the solvent at infinite dilution.

Using (60)–(62) we may rewrite (59) as

$$\bar{E}_S = \epsilon_S{}^K + B_0^{sw} + \tfrac{1}{2} \int \nu[\partial N_W(\nu)/\partial N_S]\, d\nu \tag{63}$$

Here the partial molar energy is expressed as an average kinetic energy, average binding energy to the solvent, and a "structural change" of the solvent induced by the addition of the solute. The standard energy of solution (at infinite dilution) from the gaseous phase is

$$\Delta\bar{E}_S{}^0 = B_0^{sw} + \tfrac{1}{2} \int \nu[\partial N_W(\nu)/\partial N_S]\, d\nu \tag{64}$$

Note that for a hard-sphere solute $B_0^{sw} = 0$ and all of the energy of solution is interpreted through (64) as "structural changes" in the solvent.

We shall now briefly mention a second QCDF which is particularly useful to express the partial molar volume. The appropriate QCDF is the one based on the volume of the Voronoi polyhedra discussed in Ref. 2. Let $N_\alpha(\phi)\, d\phi$ be the average number of α molecules ($\alpha = W, S$) having Voronoi polyhedra of volume between ϕ and $\phi + d\phi$. The total volume of the system may be expressed as[1,2]

$$V(P, T, \mathrm{N}_W, \mathrm{N}_S) = \int \phi N_W(\phi)\, d\phi + \int \phi N_S(\phi)\, d\phi \tag{65}$$

Note that in the construction of the Voronoi polyhedron of each molecule *all* centers of the molecules, solute and solvent, should be considered. The partial molar volume of S is

$$\bar{V}_S = \left[\frac{\partial V(N_W, N_S)}{\partial N_S}\right]_{N_W} = \int \phi \frac{\partial N_W(\phi)}{\partial N_S}\, d\phi + \int \phi \frac{\partial N_S(\phi)}{\partial N_S}\, d\phi \tag{66}$$

As in (59), we have, in this representation, expressed $\bar{V}_S$ as a *pure* relaxation quantity.

At infinite dilution

$$\lim_{\rho_S \to 0} \frac{\partial}{\partial N_S} \left[N_S \int \phi x_S(\phi)\, d\phi \right] = \bar{\phi}_S{}^{\circ} \tag{67}$$

Hence

$$\bar{V}_S{}^{\circ} = \bar{\phi}_S{}^{\circ} + \int \phi [\partial N_W(\phi)/\partial N_S]\, d\phi \tag{68}$$

where $\bar{\phi}_S{}^{\circ}$ is the average volume of the Voronoi polyhedra of the solute at infinite dilution and the second term is the "structural change" of the solvent.

At this stage it is appropriate to reflect on the usefulness of the mixture-model approach.[16] For concreteness we refer to (64). The average binding energy of, say, argon to water and to other liquids such as alcohols is expected to be of similar order of magnitude (this statement becomes exact for hard-sphere solutes). Hence any difference in the energy of solution of argon in two liquids may legitimately be assigned to structural changes. Now, for a simple fluid we expect that the distribution function $x(\nu)$ will consist of a single sharp peak. A limiting case is a solvent of hard spheres, for which $x(\nu) = \delta(\nu)$ and hence

$$(\partial/\partial N_S) \left[\tfrac{1}{2} \int \nu N(\nu)\, d\nu \right] = 0 \tag{69}$$

In a simple solvent with a very narrow distribution function $x(\nu)$ we expect that any structural changes within its ν components will not give rise to a large relaxation term. Next suppose that water has a very widely spread distribution function such as the one depicted in Fig. 1(b). As an extreme example the "idealized" TSM (see Ref. 2) proposes that

$$N_W(\nu) = N_1\, \delta(\nu - \nu_1) + N_2\, \delta(\nu - \nu_2) \tag{70}$$

Hence

$$\Delta \bar{E}_S{}^{\circ} = B_0{}^{sw} + \tfrac{1}{2}(\nu_1 - \nu_2)(\partial N_1/\partial N_S)_{N_W} \tag{71}$$

We have already seen in Section 3 that if the two values ν_1 and ν_2 are well separated and if $x_1 x_2$ is not too small, then a large relaxation in (71) is expected, which, in principle, may have a different order of magnitude than B_0^{sw}.

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[16] A detailed discussion of the question, "In what sense is the mixture model useful?," is presented in Ref. 7, using a very simplified model.

If the real curve of $x_W(\nu)$ looks somewhat like the one in Fig. 1(b), then using a cutoff point ν^*, we construct a TSM by defining

$$N_1 = \int_{-\infty}^{\nu^*} N_W(\nu)\,d\nu \tag{72}$$

$$N_2 = N_W - N_1 \tag{73}$$

and then we rewrite (64) as

$$\begin{aligned}\Delta \bar{E}_S{}^{\circ} &= B_0^{sw} + \frac{1}{2}\frac{\partial}{\partial N_S}\left\{\left[\int_{-\infty}^{\nu^*} \nu N_W(\nu)\,d\nu + \int_{\nu^*}^{\infty} \nu N_W(\nu)\,d\nu\right]\right\}_{N_W} \\ &= B_0^{sw} + \frac{1}{2}\left\{\frac{\partial}{\partial N_S}(\bar{\nu}_1 N_1 + \bar{\nu}_2 N_2)\right\}_{N_W} \\ &= B_0^{sw} + \frac{1}{2} N_1 \left[\frac{\partial \bar{\nu}_1}{\partial N_S}\right]_{N_1, N_2} + \frac{1}{2} N_2 \left[\frac{\partial \bar{\nu}_2}{\partial N_S}\right]_{N_1, N_2} \\ &\quad + \frac{1}{2}(\bar{\nu}_1 - \bar{\nu}_2)\left[\frac{\partial N_1}{\partial N_S}\right]_{N_W}\end{aligned} \tag{74}$$

where $\bar{\nu}_1$ and $\bar{\nu}_2$ are defined as the average binding energies of the two components, respectively. The last form on the r.h.s. of (74) makes a distinction between three kinds of structural rearrangements. The first include rearrangements within the ν components for which $\nu < \nu^*$, the second consists of rearrangements within the ν components for which $\nu > \nu^*$, and the last term reflects the rearrangements in which ν components are transferred from one group to the second.

We can now make a general statement on the conditions required for a useful TSM. If the real curve $x_W(\nu)\,d\nu$ is well concentrated at about two values, say $\bar{\nu}_1$ and $\bar{\nu}_2$, then the structural changes within each group of ν components are likely to produce negligible contribution to the partial molar energy. Therefore the second and third terms in (74) may be absorbed in the average binding energy to construct a new static term

$$\Delta E_S{}^* = B_0^{sw} + \frac{1}{2} N_1 \left[\frac{\partial \bar{\nu}_1}{\partial N_S}\right]_{N_1, N_2} + \frac{1}{2} N_2 \left(\frac{\partial \bar{\nu}_2}{\partial N_S}\right)_{N_1, N_2} \tag{75}$$

The only important structural changes will be the ones associated with the transfer from one group to another. Such a transfer carries a relatively large value of $\bar{\nu}_1 - \bar{\nu}_2$, but more important, the stabilization effect is expected to be large for reasons given in Section 3.

Similar arguments may be employed to construct a useful, say, three-structure model, if it turns out that the function $x_W(\nu)$ exhibits three well-separated peaks.

6. DISCUSSION AND CONCLUSIONS

The most important conclucion of this paper may be stated as follows: Various notions like "structure-making" or "structure-breaking" effects totally depend on how we *choose* to view the solvent. More specifically, they depend on our basic definition of the structure of water. There is no unique way of defining the structure of water, but once we have adopted a reasonable definition, then it becomes meaningful to speak of structural changes in various directions.

One way to invoke the concept of the structure of water is through the mixture-model approach. Here one simply identifies the concentration of one component, presumed to represent the structure, as an index measuring the degree of structure of the system. For any such a definition one may ask how the structure changes by the addition of a solute. Section 3 gives the general answer to this question in terms of molecular distribution functions [see also relation (C.11) in Appendix C].

Of course, it would have been desirable to start with the one-component point of view (for the solvent) and proceed to carry out all the computations and get all answers to our questions. This goal does not seem to be attainable in the foreseeable future.

Once we have recognized the extreme complexity of persuing our problem along the conventional routes of statistical mechanics, we may either abandon the whole area or try to get partial answers by using nonconventional routes. It is in this respect that the mixture-model approach has been successful, since it provides a qualitative interpretation for an immense body of experimental facts on aqueous solutions.

We should like to end up with two comments regarding attempts to detect structural changes in water.

One way of measuring such an effect is to apply a computer-experiment technique, by the use of which a simulation of the properties of the system of interest may be attained. In particular, all of the quasicomponent distribution functions may be computed and their responses to addition of a solute may be studied. The severe conditions required to achieve a large relaxation effect should be borne in mind, however. One may easily miss such an effect by an improper choice of molecular, as well as thermodynamic, parameters for the system.

A second way of detecting a stabilization effect is through experimental methods. Here there is the ambiguity of interpreting an experimental quantity in terms of structural changes, in the first place. But more important, in most cases one attempts to estimate directly the structural change, say ΔN_L induced by the addition of ΔN_S moles of solute. For very small ΔN_S the corresponding ΔN_L is also small and may be undetectable. For large ΔN_S it is possible that the stabilization effect has already become small or even changed sign, hence again a large value of ΔN_L may be undetectable. These considerations do not apply to the partial molar quantities discussed in this paper. Here the slope itself, $\partial N_L/\partial N_S$, enters, and not dN_L; hence a large contribution from structural changes may be revealed even at infinite dilution, $\rho_S \to 0$.

APPENDIX A. EXAMINATION OF SOME LIMITING CASES

We have seen in section 3 that the stabilization effect tends to zero at one of the following limiting cases: (1) when either x_L or x_H is very small, (2) when the two components are very similar. We shall now show that the static term, say, of the partial molar volume of S has the correct form at these limiting cases.

1. To get a TSM for which, say x_L is very small, we choose any QCDF, say $x(\nu)$, and define

$$x_L = \int_a^{a+\epsilon} x(\nu)\, d\nu, \qquad x_H = 1 - x_L \tag{A.1}$$

Clearly if $\epsilon \to 0$, we get

$$x_L \to 0, \qquad \rho_H \to \rho_W, \qquad G_{HH} \to G_{WW}, \qquad G_{HS} \to G_{WS}, \qquad \bar{V}_H \to \bar{V}_W$$

Hence the static partial molar volume in (25) tends to

$$V_S{}^* \to [1 + \rho_W(G_{WW} - G_{WS})]/\rho_W \tag{A.2}$$

which is the correct form of the limiting partial molar volume of S in water.

2. To get a TSM with very similar components, one makes an appropriate division of the ν axis, $\nu_1, \nu_2, \ldots$, and defines

$$x_L = \sum_{i=\text{odd}} \int_{\nu_i}^{\nu_{i+1}} x(\nu)\, d\nu, \qquad x_H = 1 - x_L \tag{A.3}$$

Clearly if the invervals $\nu_{i+1} - \nu_i$ become very small, then the two species become very similar; hence

$$G_{LS} \sim G_{HS} \sim G_{WS}, \qquad G_{LL} \sim G_{HH} \sim G_{LH} \sim G_{WW}, \qquad \bar{V}_L \sim \bar{V}_H \sim V_W$$

and the static partial molar volume of S in (25) tends to

$$V_S{}^* \to [1 + \rho_W(G_{WW} - G_{WS})]/\rho_W \tag{A.4}$$

which is again the correct form of the limiting partial molar volume of S in water.

APPENDIX B. FORMAL PROOF THAT $\eta \geqslant 0$

For any two-component system with species α and β let

$$\Delta_\alpha = N_\alpha - \langle N_\alpha \rangle \tag{B.1}$$

$$\Delta_\beta = N_\beta - \langle N_\beta \rangle \tag{B.2}$$

be defined in the grand canonical ensemble. Relation (14) may be written as

$$\langle \Delta_\alpha \Delta_\beta \rangle = V(\rho_\alpha \rho_\beta G_{\alpha\beta} + \rho_\alpha \delta_{\alpha\beta}) \tag{B.3}$$

consider the average

$$\begin{aligned} 0 \leqslant \left\langle \left[\frac{\Delta_\alpha}{\rho_\alpha} - \frac{\Delta_\beta}{\rho_\beta}\right]^2 \right\rangle &= \frac{\langle \Delta_\alpha^2 \rangle}{\rho_\alpha^2} + \frac{\langle \Delta_\beta^2 \rangle}{\rho_\beta^2} - 2\,\frac{\langle \Delta_\alpha \Delta_\beta \rangle}{\rho_\alpha \rho_\beta} \\ &= V\left[\frac{\rho_\alpha^2 G_{\alpha\alpha} + \rho_\alpha}{\rho_\alpha^2} + \frac{\rho_\beta^2 G_{\beta\beta} + \rho_\beta}{\rho_\beta^2} - 2G_{\alpha\beta}\right] \\ &= \frac{V}{\rho_\alpha \rho_\beta}\,[\rho_\alpha + \rho_\beta + \rho_\alpha \rho_\beta (G_{\alpha\alpha} + G_{\beta\beta} - 2G_{\alpha\beta})] \end{aligned} \tag{B.4}$$

Hence, from the definition of η in (18) it follows that

$$\eta \geqslant 0$$

This result is also consistent with the implication of the stability condition applied to (35).

APPENDIX C. A CHECK OF CONSISTENCY

In Appendix A we have shown that at two limiting cases $V_S^* \to \bar{V}_S$ (at infinite dilution). Here a stronger test of consistency is examined. The total partial molar volume $\bar{V}_S$ in the TSM representation

$$\bar{V}_S = V_S^* + (\bar{V}_L - \bar{V}_H)(\partial N_L / \partial N_S)_{N_W} \tag{C.1}$$

must be independent of the particular choice of the TSM (though each term depends on the classification procedure).

To show this, we need the following general relations between the various G_{ij}.

For any distance R conservation of the total *water* molecules around S requires that

$$\rho_H g_{HS}(R) + \rho_L g_{LS}(R) = \rho_W g_{WS}(R) \tag{C.2}$$

where $g_{WS}(R)$ is the radial distribution function for a water molecule (any) around S. Similarly we get the following two conservation relations;

$$\rho_L g_{LL}(R) + \rho_H g_{HL}(R) = \rho_W g_{WL}(R) \tag{C.3}$$

$$\rho_H g_{HH}(R) + \rho_L g_{LH}(R) = \rho_W g_{WH}(R) \tag{C.4}$$

Using the definition of G_{ij}, we may integrate these relations to obtain

$$\rho_H G_{HS} + \rho_L G_{LS} = \rho_W G_{WS} \tag{C.5}$$

$$\rho_L G_{LL} + \rho_H G_{HL} = \rho_W G_{WL} \tag{C.6}$$

$$\rho_H G_{HH} + \rho_L G_{HL} = \rho_W G_{WH} \tag{C.7}$$

The last two may be combined to get

$$\rho_L^2 G_{LL} + \rho_H^2 G_{HH} + 2\rho_L\rho_H G_{HL} = \rho_W(\rho_L G_{WL} + \rho_H G_{WH}) = \rho_W^2 G_{WW} \tag{C.8}$$

Relations (C.5) and (C.8) form the link between the TSM and the one-component (for that water) points of view. Applying these relations to (C.1), we get, after some algebra, the expected relation for $\bar{V}_S$:

$$\bar{V}_S = (1/\rho_W)(1 + \rho_W G_{WW} - \rho_W G_{WS}) \tag{C.9}$$

which is independent of the particular classification. Relations (C.6) and (C.7) may also be used to get a simple relation for the difference

$$\bar{V}_L - \bar{V}_H = (\rho_W/\eta)(G_{WH} - G_{WL}) \tag{C.10}$$

The requirement that $\bar{V}_L - \bar{V}_H$ be positive is therefore equivalent to the statement that the average number of excess *water* molecules around H is larger than the average number of excess water molecules around L.

With the help of (C.10) the expression for the stabilization effect may be rewritten in term of molecular properties.

$$\lim_{\rho_S\to 0} (\partial N_L/\partial N_S)_{N_W} = x_L x_H \rho_W[(G_{WH} - G_{WL}) \cdot (G_{LS} - G_{HS})] \tag{C.11}$$

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