dielectric constant argues against the presence of solely $(H_2O)_2SnCl_4$, and in favor of a mixture of complexes, perhaps $Sn(H_2O)_6{}^{4+}$ and $SnCl_6{}^{2-}$.

Finally, the results of other studies support the contention that the products of eq 1 dominate in these solutions. Raman measurements of aqueous solutions of $SnBr_4$ containing excess Br^- demonstrated the presence of $SnBr_6{}^{2-}$, and at high anion concentrations this species dominates.[18] Moreover, in aqueous $SnCl_4$ solutions the process of eq 1 has been suggested to explain the appearance of $SnCl_6{}^{2-}$ even in the absence of excess Cl^-.[18] Thus, it is reasonable to assume that in the solutions of Tables I and II, the presence of large amounts of acetone would produce the same result as large anion concentrations, that is the formation of the hexahalo complex. By analogy, similar Raman measurements and an ion-exchange study of concentrated gallium halide solutions demonstrated the presence of $Ga(H_2O)_6{}^{3+}$ and $GaX_4{}^-$ as the dominant species.[20-22] Their presence as the sole species in much more dilute solutions in aqueous acetone mixtures was confirmed by

pmr and ^{69}Ga nmr studies.[12,13] It is apparent that Raman and variable temperature ^{119}Sn and ^{17}O nmr measurements in these aqueous acetone solutions would be decisive in the identification of the species present.

(20) L. A. Woodward and A. A. Nord, *J. Chem. Soc.*, 3721 (1956).

(21) T. F. Young, L. F. Maranville, and H. M. Smith, "The Structure of Electrolytic Solutions," W. J. Hamer, Ed., Wiley, New York, N. Y., 1959, Chapter 4.

(22) K. A. Kraus and F. Nelson, see ref 21, Chapter 23.

Molecular Motion and Structure of Aqueous Mixtures with Nonelectrolytes

As Studied by Nuclear Magnetic Relaxation Methods

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Appropriate sets of reorientational correlation times τ_c—to be derived from nuclear magnetic relaxation times—and self-diffusion coefficients D are introduced. Between these quantities rules are given which must hold if the mixture has certain structural properties as to be described. After a brief discussion of the pure components of the binary mixtures water and acetonitrile, pyridine, methanol, ethanol, *tert*-butyl alcohol, acetone, and tetrahydrofuran, the structural rules are applied to the experimental results reported. These latter data are τ_c and D of both components of the mixture and of different nuclei as a function of the composition and the corresponding activation energies. Among the various nuclei are the heteronuclei ^{14}N and ^{17}O of some of the organic molecules. The most important result of this investigation is the statement that generally a structural reinforcement appears in the water-rich region and that, however, rigid long-lived hydration spheres do not exist for the organic solutes studied. Furthermore, some evidence for the association of the organic molecules which finally develops to a certain degree of microheterogeneity will be reported.

1. Introduction

It is the purpose of the present paper to contribute to our knowledge of the structure of aqueous solutions of nonelectrolytes. The structure of a liquid may be described in a number of different ways. For instance one may say that the liquid contains numbers n_i of clusters with i particles or that in a solution the solute particles are surrounded by hydration cages of n_h solvent mole-

cules. Partly we shall use this structure description on the following pages. To distinguish this type of description from other possible approaches we will call it in the following the "aggregate approach." The limiting case of this aggregate approach is the simple association of two molecules.

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Another more general description which we shall use as well concerns the molecular distribution function approach. In particular, the pair distribution function $f^{(1,1)}(\mathbf{r}_{11}, \Omega_{11}, x_1)$ gives the probability to find a molecule 1 at $\mathbf{r}_{11}$ relative to a given reference molecule 1 and with the orientation Ω_{11} (set of three Eulerian angles). Both $\mathbf{r}_{11}$ and Ω_{11} are taken relative to a coordinate frame fixed in the reference molecule 1. $f^{(1,1)}(\mathbf{r}_{11}, \Omega_{11}, x_1)$ concerns a mixture of molecules 1 and 2 and the argument x_1 indicates that the mole fraction of particle 1 is x_1. Likewise, in the mixture there may be defined pair distribution functions

$$f^{(1,2)}(\mathbf{r}_{12}, \Omega_{12}, x_1), \quad f^{(2,1)}(\mathbf{r}_{21}, \Omega_{21}, x_1), \quad \text{and} \quad f^{(2,2)}(\mathbf{r}_{22}, \Omega_{22}, x_1)$$

where the first number of the index indicates the reference molecule. Then the degree of structure in a mixture has to be defined as the deviation of $f^{(1,1)}$, $f^{(1,2)}$ ... from those functions which describe the distribution of molecules which is completely uniform in space and isotropic regarding relative molecular orientation.[1] The complete description of the structure of the liquid has to be carried out not only by the pair distribution function but also by the higher molecular distribution functions which concern more than two molecules. Thus, the statement that there exists a number of clusters of i particles in the liquid is equivalent to the statement that there is a finite probability to find $i - 1$ molecules as seen from a given reference molecule in a certain relative configuration according to the geometry of the cluster.

It is well known that so far there is no experimental method available from which the structural informations just indicated can be derived in a direct way. X-Ray diffraction methods give only averages of $f(\mathbf{r}, \Omega, x_1)$ over all orientational details; thus one obtains $f(r, x_1)$; however, the complications arising in mixtures of polyatomic molecules are well known. We omit here the enumeration of the many methods or attempts to derive structural information—mostly in the aggregate approach—in a more or less indirect way from thermodynamic, spectroscopic, or other experimental data.

The starting point as concerns solution chemistry is the famous problem as to what an extent nonpolar molecules or nonpolar (here hydrocarbon) groups are hydrated in aqueous solution (iceberg formation, hydration of the second kind, or hydrophobic hydration, see, e.g., ref 1), i.e., of what kind is the structure reinforcement, if it at all exists, in these solutions.

The central principle of the present work is the statement that the above-mentioned structural properties of a liquid should in some way be reflected by the nature of the molecular motions in this liquid.

In section 2 the connection between structural properties and the molecular motions will be outlined. A number of rules for these interrelations will be given. In section 4 experimental data regarding the aqueous

mixtures with acetonitrile, pyridine, methanol, ethanol, tert-butyl alcohol, acetone, and tetrahydrofuran are reported. The experimental data are rotational correlation times as derived from nuclear magnetic relaxation times, self-diffusion coefficients, and the activation energies for both these quantities. To have a better understanding of the mixtures a brief sketch of the motional behavior of the pure components is given. The application of the above-mentioned rules to the experimental results allows the decision whether certain structural aggregates do exist or not or whether the molecular distribution functions assume sharper or flatter maxima in the mixture as compared with the pure liquids forming the components.

One remark should be added here. It is clear that a huge amount of literature exists regarding the possible structural properties of the aqueous mixtures studied here. We consider our work essentially to be the demonstration of the straightforward application of a number of rules within the conceptional framework underlying the method concerned. Thus we shall refrain from a discussion of each result we obtain in the light of the bulk of other knowledge of this topic accumulated in the literature. The room available in this article would not allow this undertaking. We feel, however, that our results are not in striking contrast to the general view accepted in the literature.

2. Structural Properties and Molecular Motions

A. Introduction of Quantities to Be Used. As has already been mentioned above the central principle of the present work is the statement that the structural properties of a liquid should be in some way reflected by the nature of the molecular motions in the liquid. These motions of a liquid in thermodynamic equilibrium may be characterized by the behavior of a number of appropriately chosen time correlation functions. The experimental data to be presented here are the time integrals of three different time correlation functions[2–5]

$$D = \frac{1}{3} \int_0^\infty \overline{\mathbf{v}(0)\mathbf{v}(t)}\,dt \tag{1}$$

$$\tau_c = \int_0^\infty \overline{Y_{2m}{}^*(0)Y_{2m}(t)}\,dt \qquad m = 0, \pm 1, \pm 2 \tag{2}[6]$$

and

$$\mathfrak{z} = \int_0^\infty \overline{\frac{Y_{2m}{}^*(0)}{(r(0))^3}\frac{Y_{2m}(t)}{(r(t))^3}}\,dt \qquad m = 0, \pm 1, \pm 2 \tag{3}$$

(1) H. G. Hertz, *Ber. Bunsenges. Phys. Chem.*, **68**, 907 (1964).

(2) F. Reif, "Fundamentals of Statistical and Thermal Physics," McGraw-Hill, New York, N. Y., 1965.

(3) P. A. Egelstaff, "An Introduction to the Liquid State," Academic Press, London, 1967.

(4) R. Zwanzig, *Ann. Rev. Phys. Chem.*, **16**, 67 (1965).

(5) A. Abragam, "The Principles of Nuclear Magnetism," Clarendon Press, Oxford, 1961.

(6) If $\overline{Y_{2m}{}^*(0)Y_{2m}(t)}$ has the form $e^{-|t|/\tau_c}$, then its Fourier transform is $2\tau_c/1 + \omega^2\tau_c^2$, and for $\omega = 0$ one obtains eq 2.

D is the self-diffusion coefficient of the molecule considered, $\mathbf{v}(0)$ and $\mathbf{v}(t)$ are its velocities at time 0 and t, respectively, $Y_{2m}(0)$ and $Y_{2m}(t)$ are the normalized spherical harmonics of the second order at time 0 and t, respectively, in eq 2 the arguments ϑ, φ of Y_{2m} are the polar and azimuthal angles relative to the laboratory coordinate system of a given vector fixed in the molecule of interest. In eq 3 the angles ϑ and φ define the direction of the vector connecting two molecules. τ_c we call the rotational correlation time. $\tau_r/3 \lesssim \tau_c \leq \tau_r$ where τ_r is the ordinary reorientation time of the vector considered under the rotational diffusive motion.[7] In eq 3 $r(0)$ and $r(t)$ are the distances between two molecules at time 0 and t, respectively. r varies in time because of the translational diffusive motion of one molecule relative to the other.

From the quantities of the kind eq 1, 2, and 3 we shall derive our structural information and proceed as follows. Since generally we are concerned with mixtures of two components, our experiments (see below) yield two self-diffusion coefficients $D^{(1)}$, $D^{(2)}$ and a set of rotational correlation times

$$\tau_{c1}^{(1)}, \ \tau_{c2}^{(1)}, \ \ldots; \quad \tau_{c1}^{(2)}, \ \tau_{c2}^{(2)}, \ \ldots$$

Here the superscript (1), (2) means molecule compound 1 and 2, respectively, and the index 1, 2, 3 regards the 1st, 2nd, 3rd ... vector in the respective molecule. For instance, in CH_3OH one may consider the vector connecting two methyl protons or the vector pointing in the OH direction. Finally, the experiments may yield a set of data

$$\mathfrak{J}_{11}^{(1,1)}, \ \mathfrak{J}_{12}^{(1,1)}, \ \ldots; \quad \mathfrak{J}_{11}^{(1,2)}, \ \mathfrak{J}_{12}^{(1,2)}, \ \ldots$$

where the superscript, e.g. (1,1), indicates that r is the distance between two molecules 1 and the index 11 means that r concerns the distance between the 1st atomic position within molecules 1, and so on. The data reported here will be, however, only $\mathfrak{J}^{(1,1)}$ and $\mathfrak{J}^{(2,2)}$, that is, they represent averages over many atomic positions within the molecule.

In the next step, for the composition ranges $x_1 \approx 1$ and $x_2 \approx 1$ ($x_{1,2}$ = mole fractions of component 1 and 2, respectively), from the experimental quantities $D^{(1)}$, $D^{(2)}$ and $\tau_{ci}^{(1)} \ldots$, $\tau_{ci}^{(2)} \ldots$ ($i = 1, 2$) "localized" quantities

$$D^{(1)\circ}, \ D^{(1)+} \text{ for } x_1 \approx 1$$

$$D^{(2)\circ}, \ D^{(2)+} \text{ for } x_2 \approx 1$$

$$\tau_{ci}^{(1)\circ}, \ \tau_{ci}^{(1)+} \quad i = 1, 2, \ldots \text{ for } x_1 \approx 1$$

$$\tau_{ci}^{(2)\circ}, \ \tau_{ci}^{(2)+} \quad i = 1, 2, \ldots \text{ for } x_2 \approx 1$$

may be derived. Here the indication $+$ means in the immediate neighborhood of the solute particle the mole fraction of which is close to 0, and $\circ$ means elsewhere in the solution. Figure 1 shows a model liquid in order to explain the quantities to be introduced here. The re-
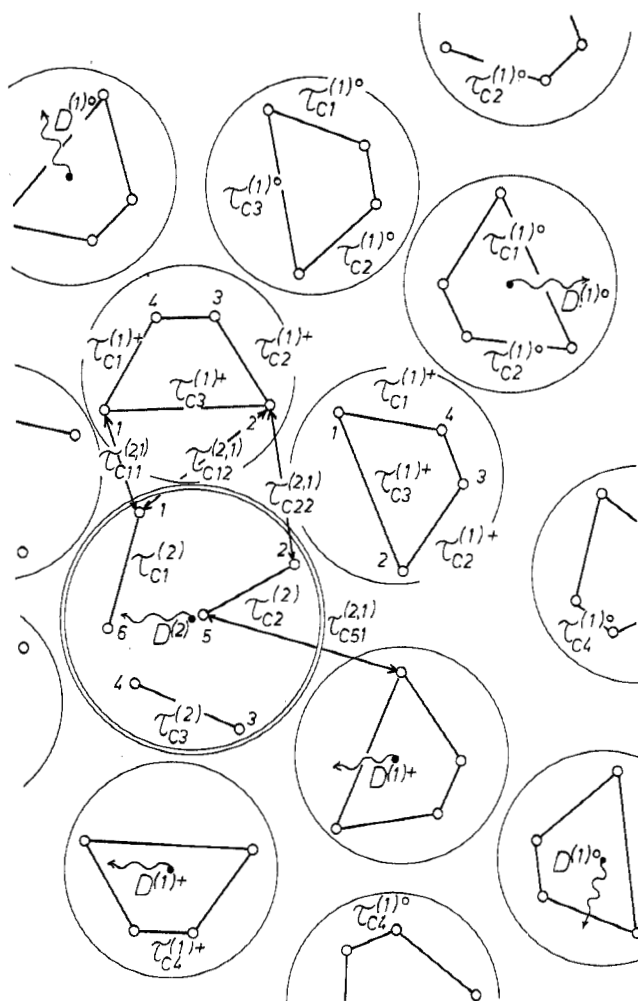
Figure 1. A model of a liquid in order to explain the various microdynamic parameters appearing in the text. The double circle represents a solute molecule 2. Note that, e.g., for water as solvent (molecule 1) the two points 3 and 4 would coincide. To simplify the figure not all possible vectors are drawn.

lation between the measured quantity $D^{(1)}$, $D^{(2)}$ and the localized quantities $D^{(1)\circ}$, $D^{(1)+} \ldots$ is known and is independent of the special system considered; however, the relation between the τ_c and the $\tau_c^{+,\circ}$ depends on the rapidity of the exchange of molecules between the local regions $+$ and $\circ$. Details will be presented below. For a pure liquid (e.g., H_2O) it may be useful to decompose D and τ_c to a further degree. Details will be given as well below.

After the introduction of the localized correlation times τ_{ci}^+ it is meaningful to define further rotational correlation times (see Figure 1) $\tau_{c11}^{(2,1)}$, $\tau_{c12}^{(2,1)}$, $\ldots$; $\tau_{c11}^{(1,2)}$, $\tau_{c12}^{(1,2)}$, $\ldots$. For instance, $\tau_{c12}^{(2,1)}$ describes the reorientational motion of the vector connecting the 1st atomic position of the (solute) molecule 2 at $x_1 \approx 1$ with the 2nd atomic position of (solvent) molecule

(7) See, e.g., H. G. Hertz, *Progr. Nucl. Magnetic Resonance Spectrosc.*, **3**, 159 (1967); or H. G. Hertz, *Ber. Bunsenges. Phys. Chem.*, **71**, 979 (1967).

1 in the next neighborhood—*i.e.*, the first coordination sphere—of molecule 2. $\tau_{c21}^{(1,2)}$ regards the vector connecting atomic position 2 of molecule 1 (now the solute) with atomic position 1 of molecule 2 (now the solvent) in the solvation sphere of 1 at $x_2 \approx 1$. The extension of the other symbols is obvious (see Figure 1).

We confine our consideration to molecules and aggregates which are essentially of spherical symmetry. The more complicated treatment of markedly nonspherical systems is possible, in principle; in the following pages it will occasionally be necessary to treat the cases of anisotropic motions.

B. Structural Rules. Now we are prepared to present some rules which form a bridge between the structural properties of the liquid and the molecular motions. We first use the aggregate approach.

Rule No. 1. If the probability is essentially 1 to find a crystallike geometric arrangement of solvent molecules around a solute molecule, *i.e.*, that there exists a rigid long-lived solvation cage, then

$$
\left.
\begin{aligned}
D^{(1)+} &= D^{(2)} \text{ for } x_1 \approx 1 \\
D^{(2)+} &= D^{(1)} \text{ for } x_2 \approx 1
\end{aligned}
\right\} \tag{4}
$$

must hold as a necessary condition.

Furthermore, if the solute molecule is incorporated rigidly, *i.e.*, immovably in the solvation cage in a completely fixed position, then, besides eq 4 the equations

$$
\left.
\begin{aligned}
\tau_{c1}^{(1)+} &= \tau_{c2}^{(1)+} = \ldots = \tau_{c1}^{(2)} = \tau_{c2}^{(2)} = \\
&\ldots \tau_{c11}^{(2,1)} = \tau_{c12}^{(2,1)} = \ldots \text{ for } x_1 \approx 1 \\
\tau_{c1}^{(2)+} &= \tau_{c2}^{(2)+} = \ldots = \tau_{c1}^{(1)} = \tau_{c2}^{(1)} = \\
&\ldots \tau_{c11}^{(1,2)} = \tau_{c12}^{(1,2)} = \ldots \text{ for } x_2 \approx 1
\end{aligned}
\right\} \tag{4a}
$$

must hold as a necessary condition.

Long-lived means here that the distances between the centers of masse of the cage molecules and that of the central solute molecule are constant for a time τ longer than the time of molecular reorientation $\tau_r \approx 5 \times 10^{-12}$ sec (for H_2O at 25°); *i.e.*, $\tau \gtrsim 10^{-11}$ sec. Rigid means that the well-structured configuration (all intra- and intermolecular distances given) exists a time τ longer than the rotational correlation time of the aggregate, a typical example will be as well $\tau \gtrsim 10^{-11}$ to 10^{-10} sec.

In this paper we shall primarily use the first line of eq 4 and 4a (1 → H_2O); measurements concerning the second line are still somewhat preliminary and of less interest here. The first line of eq 4a has previously been used by one of the present authors (H. G. H.) for the study of the ions F^-,[8] Li^+,[9] Mg^{2+}, and Al^{3+}.[10] Here, of course, no intramolecular correlation time for the solute exists, and eq 4a only holds for the times $\tau_c^{(1)}$ and $\tau_c^{(2,1)}$. For the ion BF_4^- a full analysis is possible.[8] [We omit here the case that the hydration sphere is longlived and rigid; however, the central (solute) particle performs independent rotational motion. No experimental results are so far available to study such behavior. The extension of eq 4a to this case is obvious.]

Rule No. 2. If the probability is essentially 1 to find a geometrical arrangement of solvent molecules around the solute molecule of such a kind that the distance between the center of mass of any solvent molecule in the coordination sphere and the center of mass of the solute molecule has a given constant value, then

$$
\left.
\begin{aligned}
D^{(1)+} &= D^{(2)} \text{ for } x_1 \approx 1 \\
D^{(2)+} &= D^{(1)} \text{ for } x_2 \approx 1
\end{aligned}
\right\} \tag{4}
$$

must hold as a necessary condition. Now, generally, there does not exist any of the relations eq 4a between the various reorientational correlation times. In this event we have still a long-lived solvation sphere in the sense as defined above, however, only regarding the centers of mass of the molecules. Clearly now the aggregate is no longer rigid.

Rule No. 3. If the probability is essentially 1 to find a long-lived *pair* association between the solute molecule and one solvent molecule, then

$$
\text{or} \quad
\left.
\begin{aligned}
D^{(1)+} &= D^{(2)} \text{ for } x_2 \lesssim 1/2 \\
D^{(2)+} &= D^{(1)} \text{ for } x_1 \lesssim 1/2
\end{aligned}
\right\} \tag{5}
$$

must hold as a necessary condition. Now $D^{(1)+}$, $D^{(2)+}$ concerns the one solvent molecule attached to the solute molecule. Furthermore, we must have

$$
\text{or} \quad
\left.
\begin{aligned}
\tau_c^{(1)+} &= \tau_c^{(2)} \text{ for } x_2 \lesssim 1/2 \\
\tau_c^{(2)+} &= \tau_c^{(1)} \text{ for } x_1 \lesssim 1/2
\end{aligned}
\right\} \tag{5a}
$$

as necessary conditions if the vectors corresponding to the above correlation times have both the direction of the bond between the molecules 1 and 2. If only one of these vectors points in the direction of this bond, then the reorientational correlation time of this latter vector cannot be shorter than that of the other vector not pointing in the direction of the bond, provided both molecules are relatively small. Whereas the reason for the rules 1 and 2 is immediately obvious, the statement of rule 3 concerning the rotational motion arises from the nature of the decay of the respective correlation function under anisotropic or intramolecular rotation.[11–13] Again, here $\tau_c^{(1)+}$ concerns the one solvent molecule attached to the solute molecule.

It is important to note that the fulfillment of eq 4, 4a, 5, 5a is never sufficient to warrant the presence of the corresponding structural situation.

(8) H. G. Hertz, G. Keller, and H. Versmold, *Ber. Bunsenges. Phys. Chem.*, **73**, 549 (1969).

(9) H. G. Hertz and H. Versmold, to be published.

(10) H. G. Hertz and R. Tutsch, to be published.

(11) W. T. Huntress, *J. Chem. Phys.*, **48**, 3524 (1968).

(12) D. W. Woessner, D. S. Snowden, and G. H. Meyer, *ibid.*, **50**, 719 (1969).

(13) H. Versmold, *Z. Naturforsch. A*, **25**, 367 (1970).

Rule No. 4. If $D^{(i)+}$ or $\tau_{cj}^{(i)+}$ characterizes the motion of a molecule which is a member of a (rigid) long-lived cluster or solvation sphere, then these quantities cannot have any value but must lie within a certain range given by the size of the cluster or solvation sphere. Here, *e.g.*, for the reorientational motion, the Debye relation should be mentioned

$$\tau_c = \frac{4\pi a^3}{3kT}\eta^* \qquad (6)$$

where $\eta^* = \eta\zeta$, η = viscosity, ζ = microviscosity factor,[14] and a = radius of the aggregate.

It is well known that this relation is only approximately valid for small molecular aggregates. For translational diffusion the corresponding relation is the Einstein formula

$$D = \frac{kT}{6\pi\eta a\zeta'} \qquad (7)$$

where ζ' = microviscosity factor for translational diffusion.[14] If there are aggregates of fluctuating size, then D may be written

$$D = \frac{kT}{6\pi\eta}\sum\frac{p_{a_i}}{a_i\zeta_{a_i}'} \qquad (8)$$

where p_{a_i} is the probability that an aggregate of size a_i occurs in the liquid. ζ_{a_i}' is the translational microviscosity factor for the aggregate of size a_i. Likewise

$$\frac{1}{\tau_c} = \frac{3kT}{4\pi\eta}\sum\frac{p_{a_i}}{a_i^3\zeta_{a_i}} \qquad (9)$$

where ζ_{a_i} is the rotational microviscosity factor for the aggregate with size a_i. Equation 9 is not the only possible relation between τ_c and the a_i; another relation will be given below.

Rule No. 5. The rule to be given now does not use the aggregate approach but is written in terms of maximum values of the pair distribution functions. Suppose that $f^{(1,1)}(r_{11}, \Omega_{11}, x_1)$ at certain sets of coordinates $(r_{11})_1, (\Omega_{11})_1; (r_{11})_2, (\Omega_{11})_2; \ldots$ assumes relative maximum values $f_1^{(1,1)}, f_2^{(1,1)}, \ldots$. Likewise at certain $(r_{12})_1, (\Omega_{12})_1; (r_{12})_2, (\Omega_{12})_2; \ldots; f^{(1,2)}(r_{12}, \Omega_{12}, x_1)$ has relative maximum values $f_1^{(1,2)}, f_2^{(1,2)}, \ldots$. Then the probabilities p_{a_i} occurring in eq 8 and 9 may be expressed in terms of the $f_1^{(1,1)}, \ldots f_1^{(1,2)} \ldots$, and it may be shown[15] that the relations

$$1/D^{(1)} = \varphi_{D1}^{(1)}(f_1^{(1,1)}, f_2^{(1,1)}, \ldots) +$$
$$\varphi_{D2}^{(1)}(f_1^{(1,2)}, f_2^{(1,2)}, \ldots) \qquad (10)$$

$$\tau_c^{(1)} = \varphi_{\tau1}^{(1)}(f_1^{(1,1)}, f_2^{(1,1)}, \ldots) +$$
$$\varphi_{\tau2}^{(1)}(f_1^{(1,2)}, f_2^{(1,2)}, \ldots) \qquad (11)$$

hold.[16a,b] Here $\varphi_{Di}^{(1)}$ and $\varphi_{\tau i}^{(1)}$, $i = 1, 2$, are certain functions which increase monotonously with increasing values of any of the $f_j^{(1,1)}, f_j^{(1,2)}, j = 1, 2, \ldots$. Since any increase in the degree of structure in the liquid is

manifested by increasing numerical values of $f_j^{(1,1)}$, $f_j^{(1,2)}$, each structural reinforcement causes $D^{(1)}$, the self-diffusion coefficient of component 1, to decrease and $\tau_c^{(1)}$, the rotational correlation time of the component 1, to increase. Note that eq 10 and 11 are direct consequences of eq 8 and 9. In a previous work one of the authors (H. G. H.[1]) had written a more primitive form

$$\tau_c^{(1)} \sim (f_1^{(1,1)} + f_1^{(1,2)})$$

Clearly, for component 2 one may write in the same way

$$1/D^{(2)} = \varphi_{D1}^{(2)}(f_1^{(2,2)}, f_2^{(2,2)}, \ldots) +$$
$$\varphi_{D2}^{(2)}(f_1^{(2,1)}, f_2^{(2,1)}, \ldots) \qquad (12)$$

$$\tau_c^{(2)} = \varphi_{\tau1}^{(2)}(f_1^{(2,2)}, f_2^{(2,2)}, \ldots) +$$
$$\varphi_{\tau2}^{(2)}(f_1^{(2,1)}, f_2^{(2,1)}, \ldots) \qquad (13)$$

Rule No. 6. The following rule concerns the solute-solute particle distribution (component 2, 1 at $x_{1,2} \approx 1$). Let us choose component 2 as the solute here. It may be shown that the relation holds (see eq 3 and see below)

$$\mathfrak{z}^{(2,2)} = \frac{1}{15\mathring{a}_{22}D^{(2)}}\left(1 + \alpha\frac{\langle r^2\rangle}{\mathring{a}_{22}^2}\right) \qquad (14)$$

where $\mathring{a}_{22}$ is the closest distance of approach between two protons on different solute particles, $\langle r^2\rangle$ is the mean-square displacement of particle 2 under a translational jump, and $0 \leqslant \alpha \leqslant 1$ and depends on the particular mechanism of translational diffusion (for a model proposed by Torrey: $\alpha = {}^5/_{12}$[7,17]). Generally the expression added to 1 in the parentheses of eq 14 is small. Equation 14 has been calculated for a uniform distribution in space of the particles 2 relative to the reference particle 2. Now our rule 6 reads that if $\mathfrak{z}^{(2,2)}D^{(2)}$, as a function of the concentration, deviates significantly from a constant value, and in particular, if starting from $x_2 = 0$ $\mathfrak{z}^{(2,2)}D^{(2)}$ decreases with increasing concentration of component 2, then the effective closest distance of approach $\mathring{a}_{22}$ increases with concentration which, however, is equivalent to the statement that the solute distribution around a given solute particle is not uniform but that there is a crowding of solute molecules around the reference molecule at low concentrations.

C. Average Values of D and τ_c. Now we must explain the connection between the local quantities D^+ and τ_c^+ and the measured quantities D and τ_c (section

(14) A. Gierer and K. Wirtz, *Z. Naturforsch. A*, **8**, 532 (1953).

(15) H. G. Hertz, *Ber. Bunsenges. Phys. Chem.*, **74**, 666 (1970).

(16) (a) Both component molecules must be essentially of the same size. (b) To simplify the treatment in eq 10 and 11 the same maximum values of the pair distribution function appear. Of course, this is not strictly correct, often for the translational diffusion only the dependence of $f_1^{(1,1)}, \ldots f_1^{(1,2)}, \ldots$ on the intermolecular distances will be important.

(17) H. C. Torrey, *Phys. Rev.*, **92**, 692 (1953).

2B). Consider a solution of 2 in 1. In this work 1 will always be H_2O. The molality of 2 is C_2; that of 1 is C_1. Assume that every solute molecule (2) is surrounded by a hydration sphere of n_h water molecules. The self-diffusion coefficient of the water not being a member of the hydration sphere is $D^{(1)\circ}$; $D^{(1)+}$ is the self-diffusion coefficient of the water in the hydration sphere. Then it may be shown[18] that the relation

$$D^{(1)} = D^{(1)\circ}(1 - x_2^+) + D^{(1)+}x_2^+ \qquad (15)$$

with $x_2^+ = n_h C_2/55.5$, $0 < x_2 < 1$ holds. This equation connects the measurable quantity $D^{(1)}$ (and $D^{(1)\circ}$) with the "local" quantity $D^{(1)+}$. $D^{(1)+}$ is to be used in rule 1, eq 4. The relation

$$D^{(1)} = D^{(1)\circ}(1 - \sum x_i) + \sum x_i D^{(1)i}$$
$$\equiv D^{(1)\circ}(1 - \sum p_i) + \sum p_i D^{(1)i} \qquad (16)$$

is an obvious generalization of eq 14 for many environments; it has not yet been proved rigorously to the authors' knowledge. It forms the basis for eq 8. p_i is the probability that the particle is in the ith environment or configuration.

Now let $\tau_c^{(1)+}$ and $\tau_c^{(1)\circ}$ be the correlation time in the hydration sphere and free solvent, respectively. Then[18]

$$\frac{1}{\tau_c^{(1)}} = \frac{1}{\tau_c^{(1)\circ}}(1 - x^+) + \frac{1}{\tau_c^{(1)+}}x^+ \qquad (17)$$

holds only for configurational change or particle exchange very fast compared with the respective correlation times $\tau_c^{(1)+}$ and $\tau_c^{(1)\circ}$. Thus, if τ_h is the lifetime or residence time in a given configuration or environment $\tau_h \ll \tau_c^{(1)+}$, $\tau_c^{(1)\circ}$ must be fulfilled. For the reverse situation, $\tau_h \gg \tau_c^{(1)+}$, $\tau_c^{(1)\circ}$ one has[18]

$$\tau_c^{(1)} = \tau_c^{(1)\circ}(1 - x^+) + \tau_c^{(1)+}x^+ \qquad (18)$$

The generalization to many configurations or environments is obvious, its validity has been proved.[19]

The generalization of eq 17

$$\frac{1}{\tau_c^{(1)}} = \sum \frac{p_i}{\tau_c^{(1)i}} \qquad (17a)$$

forms the basis of eq 9. In the most general case the molecule fluctuates fast among a certain number of configurations, say $1 \leq i \leq k$; then after a time τ_{h1} it enters into another environment where again fast fluctuation among other configurations $i < \nu$ occurs. After a time $\tau_{h2} > \tau_{k+1}, \ldots \tau_\nu$, it returns to the first class of configurations. Now eq 18 holds where both $\tau_c^{(1)+}$ and $\tau_c^{(1)\circ}$ are mean correlation times, the mean values formed according to eq 17a with

$$\frac{1}{\tau_c^{(1)\circ}} = \sum_{i=1}^{k} \frac{p_i}{\tau_{ci}^{(1)}}; \quad \frac{1}{\tau_c^{(1)+}} = \sum_{i=k+1}^{\nu} \frac{p_i}{\tau_{ci}^{(1)}}$$

However, it may happen that we do not know whether we have to apply

$$\frac{1}{\tau_c^{(1)}} = (1 - x^+)\frac{1}{\tau_c^{(1)\circ}} + x^+\frac{1}{\tau_c^{(1)+}} \qquad (17)$$

or eq 18. Then, as will be shown in the Appendix, for the systems of interest here the error in $\tau_c^{(1)+}$ as determined from $\tau_c^{(1)}$ will be not greater than a factor ~ 2.

D. *Experimental Determination of D, τ_c, and $\mathfrak{z}$.* The self-diffusion coefficient D is directly measurable by tracer methods[20] or by (nmr) spin-echo techniques.[21] All data reported in this paper are obtained by the latter method.

τ_c is to be derived from nuclear magnetic relaxation time measurements. Here only the spin-lattice relaxation time T_1 is of importance. τ_c is related to T_1 in the following way. If the vector considered connects two protons and relaxation is due to magnetic dipole–dipole interaction[6]

$$\tau_c = \frac{2}{3}\frac{b^6}{\gamma^4\hbar^2}\left(\frac{1}{T_1}\right)_{\text{intra}} \qquad (19)$$

$$\frac{1}{T_1} = \left(\frac{1}{T_1}\right)_{\text{intra}} + \left(\frac{1}{T_1}\right)_{\text{inter}} \qquad (20)$$

$(1/T_1)_{\text{intra}}$ is the intramolecular relaxation rate; it is due to the proton–proton interaction within the molecule. Correspondingly $(1/T_1)_{\text{inter}}$ is the intermolecular contribution to the relaxation rate $1/T_1$ which is caused by interacting protons on different molecules; γ = gyromagnetic ratio, $\hbar$ = Planck's constant/2π, and b = distance between the two protons within the molecule. By special methods it is generally possible to determine $(1/T_1)_{\text{inter}}$. Thus from the measured $1/T_1$, $(1/T_1)_{\text{intra}}$ is known which according to eq 19 yields τ_c. Equation 19 holds for a molecule with two protons like H_2O. If there are more protons in the molecules, an appropriate averaging over all proton–proton vectors has to be made.[22]

Many nuclei have an electric quadrupole moment Q. In this case $1/T_1 = (1/T_1)_{\text{intra}}$ and[6]

$$\tau_c = \frac{40I^2(2I - 1)}{3(2I + 3)}\left(\frac{\hbar}{eQq}\right)^2\left(\frac{1}{T_1}\right) \qquad (21)$$

Now the vector the rotational motion of which is considered is the vector having the direction of the maximum electrical field gradient at the nucleus q, e = elementary charge, I = nuclear spin.

Finally we have[6,7]

$$\mathfrak{z} = \frac{1}{6\pi\gamma^4\hbar^2 N_I}\left(\frac{1}{T_1}\right)_{\text{inter}} \qquad (22)$$

(18) Second paper of ref 7.

(19) J. R. Zimmerman and W. E. Brittin, *J. Phys. Chem.*, **61**, 1328 (1957).

(20) See, *e.g.*, P. A. Johnson and A. L. Babb, *Chem. Rev.*, **56**, 386 (1956).

(21) H. Y. Carr and E. M. Purcell, *Phys. Rev.*, **94**, 630 (1954).

(22) E. v. Goldammer and M. D. Zeidler, *Ber. Bunsenges. Phys. Chem.*, **73**, 4 (1969).

where N_I is the number of spins per cubic centimeter in the liquid. Equation 22 is valid for magnetic dipole–dipole interaction. $(1/T_1)_{inter}$ may generally be determined experimentally (see below).

3. Experimental Section[23]

All proton and deuteron relaxation times have been measured by the pulse method; the 90°–90° pulse sequence has been applied. The spin-echo equipment used has been described previously,[22] and literature cited therein. The resonance frequency was 20 MHz for the protons and 14 MHz for the deuterons. The samples were degassed with the usual freezing–pumping–thawing procedure at the vacuum line. The self-diffusion coefficients were measured by the 90°–180° pulse technique in the usual way.[21,22] In all cases only the echo decay of the protons has been utilized for the self-diffusion measurements. For the proton and deuteron measurements the temperature was stabilized within ±1° by pumping of water or methanol from a Höpler thermostat through the copper probe head.

The proton relaxation times were checked by comparison with our standard value of water at 25°, $T_1 = 3.60$ sec; for the deuteron relaxation the standard comparison value was $T_1 = 0.44$ sec at 25°.[7,22] Our reference value for the self-diffusion coefficient was 2.50×10^{-5} cm²/sec for water at 25°.[24]

The relaxation time measurements for ^{14}N and ^{17}O were line-width measurements. The apparatus used was the Varian DP 60 spectrometer with the variable frequency unit V-4210 A. The frequency for the ^{14}N relaxation was 4.34 MHz, that for the ^{17}O measurements 8.13 MHz. Temperature variation and stabilization for these nuclei was done by the Varian gas-flow device (V-4557-9). The line-width measurements were partly performed by the differential scanning method, partly by the side-band method,[25] depending on the line width in the particular case. The line width of ^{14}N was sufficiently large so that we felt justified to neglect field inhomogeneity broadening. Our ^{14}N data are in satisfactory agreement with results of other authors (see Table I). For the ^{17}O line width we reproduced the result $\Delta H = 82 \pm 2.5$ mG for (nonneutral) water at 25° as reported previously.[26] All activation energies reported have been derived from measurements at 5, 15, 25, and 35°. Satisfactory straight lines appeared in the plot log $1/T_1$ vs. $1/T$; the activation energies are correct to ±20%. The accuracy for the T_1 measurements was ±5%. The self-diffusion measurements caused the greatest trouble; unfortunately we had to be content when our measurements were reproducible within ±10%, the scatter being found sometimes greater than this. The experimental error of the line-width measurements is between 5 and 10%. All materials used were of commercial origin and were used without further purification. The ^{17}O relaxation measurements were performed with 7% ^{17}O-enriched methanol and

Table I: Some Nuclear Magnetic Relaxation Rates for Organic Molecules in the Pure Liquid at 25°

Compound	Nucleus	$1/T_1$, sec^{-1}	$(1/T_1)_{intra}$, sec^{-1}	eQq/h, MHz
Acetonitrile CH₃CN	^{14}N	246[a]	246	3.74[b]
CH₃CN	^1H	6.2×10^{-2}	4.4×10^{-2}	
CD₃CN	^2H	0.15	0.15[c]	
Pyridine C₅H₅N	^{14}N	675[d]	675	4.6[e]
Methanol CH₃OH	^{17}O	440	440	...
Ethanol C₂H₅OH	^{17}O	780	780	...
CH₃CD₂OH	^2H	0.86	0.86	
CD₃CH₂OH	^2H	1.06	1.06	
Acetone (CH₃)₂CO	^{17}O	163	163	12.4[f]

[a] Woessner, Snowden, and Strom: 228 ± 5 sec^{-1}.[36] [b] P. A. Casabella and P. J. Bray, *J. Chem. Phys.*, **29**, 1105 (1958). [c] Woessner, Snowden, and Strom: 0.15 sec^{-1}.[36] [d] Kintzinger and Lehn: 671 sec^{-1} (J. P. Kintzinger and J. M. Lehn, *Mol. Phys.*, **14**, 133 (1968)). [e] E. A. C. Lucken, *Trans. Faraday Soc.*, **57**, 729 (1961). [f] QCC for H₂CO (E. A. C. Lucken, "Nuclear Quadrupole Coupling Constants," Academic Press, New York, N. Y., 1969).

ethanol supplied by Miles-Yeda Ltd., Rehovoth, Israel; the oxygen of acetone exchanges slowly with that of water in nonneutral aqueous solution ($\tau_{1/2} \approx 15$ hr in acidic solution[27]).

4. Experimental Results and Their Evaluation

A. The Pure Liquids. (i) Water. On the following pages we shall present a number of new experimental results. From these together with some older experimental data we shall draw the relevant conclusions regarding the structure of the mixtures. In this procedure the first step will be the discussion of the structural information which can be obtained from molecular reorientational motion in pure water. Thereafter a brief description of the pure organic components used here will follow.

Suppose water is a mixture of clusters, the clusters containing n_i molecules $i = 0, 1, 2, 3 \ldots$; $i = 0$ corresponds to the monomeric water molecule. The reorientational correlation time $\tau_c^{(1)}$ is known for an appreciable temperature range, e.g., at 25° $\tau_c^{(1)} = 2.5 \times 10^{-12}$ sec.[7,22] Let the correlation time of the ith cluster be $\tau_{ci}^{(1)}$. Then we have

(23) We wish to thank Mrs. I. Siepe for her assistance with some measurements.

(24) N. J. Trappeniers, C. J. Gerritsma, and P. H. Oosting, *Phys. Lett.*, **18**, 256 (1965).

(25) See, *e.g.*, O. Haworth and R. E. Richards, *Progr. Nucl. Magnetic Resonance Spectrosc.*, **1**, 1 (1966).

(26) F. Fister and H. G. Hertz, *Ber. Bunsenges. Phys. Chem.*, **71**, 1032 (1967).

(27) M. Cohn and H. C. Urey, *J. Amer. Chem. Soc.*, **60**, 679 (1938).

$$\frac{1}{\tau_c{}^{(1)}} = \sum \frac{p_i}{\tau_{ci}{}^{(1)}} \text{ for } \tau_h \ll \tau_{ci}{}^{(1)} \qquad (23)$$

or

$$\tau_c{}^{(1)} = \sum p_i \tau_{ci}{}^{(1)} \text{ for } \tau_h \gg \tau_{ci}{}^{(1)} \qquad (24)$$

where τ_h is a representative lifetime in a given cluster configuration. We know that for the long-lived octahedral hydration sphere of Mn^{2+} $\tau_c \approx 3 \times 10^{-11}$ sec.[7,28-30] Replacing the central Mn^{2+} ion by a water molecule, we have a cluster of seven molecules. Rounding off the number 7 so as to have 10 in order to take account of the partially bound (short-lived) second hydration sphere we expect $\tau_{c10}{}^{(1)} \approx 3 \times 10^{-11}$ sec. $\tau_{c0}{}^{(1)}$ is as well known from Hindman and co-workers[31] measurements of dilute solutions of H_2O in inert organic solvents: $\tau_{c0}{}^{(1)} \approx 5 \times 10^{-13}$ sec. Inserting these numbers into eq 24 with $p_i = 0$ for $i \neq 0$, 10, we find $p_{10} = 0.068$ which is certainly too small. Thus we conclude if there are larger clusters with $i \geqslant 10$ in water, the lifetime of these clusters must be very much smaller than an average $\tau_{ci}{}^{(1)}$, that is, $\tau_h \approx 10^{-12}$ to 10^{-11} sec. Putting $1/\tau_{ci}{}^{(1)} = 0$ for all clusters present, we obtain from eq 23 $p_0 \approx 0.20$ which is a reasonable figure. If this situation really occurs, then the "free" reorientation is the only contribution to the total molecular reorientation in water. One of the authors (H. G. H.) has derived the following formula for $\tau_c{}^{(1)}$ [7]

$$\frac{1}{\tau_c{}^{(1)}} = \frac{1}{\tau_{cc}{}^{(1)}} + \frac{1 - C_2}{\tau_h}$$

where C_2 is a constant $0 \leqslant C_2 \leqslant 1$. $\tau_{cc}{}^{(1)}$ is the average correlation time for all clusters. In the situation just indicated one has to put $C_2 \rightarrow 0$ (see ref 7); then, with $\tau_{cc}{}^{(1)} \gg \tau_h$ (τ_h = average residence time in a cluster)

$$\tau_c{}^{(1)} = \tau_h \qquad (25)$$

As shown elsewhere[7] the interesting consequence of eq 25 is the additional validity of $\tau_c{}^{(1)} = \tau_r{}^{(1)}$, where $\tau_r{}^{(1)}$ is the reorientation time. For an ordinary slow diffusion process we would have $\tau_r{}^{(1)} = 3\tau_c{}^{(1)}$. Thus, knowledge of $\tau_r{}^{(1)}/\tau_c{}^{(1)}$ would give us the desired information regarding cluster distribution. The dielectric relaxation time τ_d is experimentally well known: 8.2×10^{-12} sec at $25°$.[32] However, the macroscopic dielectric relaxation time τ_d is connected with the microscopic dielectric relaxation time or reorientation time $\tau_r{}^{(1)}$ by a factor δ: $\tau_d = \delta \times \tau_r{}^{(1)}$. δ is not known exactly; $1 < \delta < 2$.[33,34] With $\delta = 2$ we get $\tau_r{}^{(1)} = 4 \times 10^{-12}$ sec, thus $\tau_r{}^{(1)} \neq \tau_c{}^{(1)}$ and the pure free state rotation or rotational jump model seems not to be correct.

(ii) Pure Organic Liquids. As will be seen below the motion of the polar group of the organic molecules is of great interest for our structural investigation in the aqueous mixtures. Therefore, as a starting point, we studied the reorientational motion of the polar group in the pure organic liquids. We utilized the ^{14}N relaxation in acetonitrile and pyridine and the ^{17}O relaxation in acetone, methanol, and ethanol. Our relaxation rates $1/T_1$ are collected in Table I. For comparison, some data obtained by other authors are also given in this table. The quadrupole coupling constant eQq/h may also be found in Table I for those molecules where experimental data are available in the literature. For acetone only the ^{17}O coupling constant of formaldehyde in the gaseous state has been measured;[34] we used this coupling constant for acetone. It will be seen shortly that this approximation is essentially correct. For some of the organic liquids we measured the proton and deuteron relaxation rates, too; the results are included in Table I.

Then, with the data of Table I and with eq 21 we calculated the correlation time of the heteronucleus in the polar group. The results are given in Table II. Furthermore, for methanol and ethanol the correlation time of the hydroxyl group as determined from the deuteron relaxation may be found in Table II. For comparison we added in Table II the correlation times of the hydrocarbon part of the molecules which are of interest in this paper. All these latter data are taken from ref 22.

The correlation time $\tau_c(H-H)$ which is derived from the proton relaxation rate represents an average over the motion of all proton–proton vectors in the molecule.[22] $\tau_c(D-C)$ is derived from the deuteron relaxation rate and is the average of all direct CD bond vectors in the molecule. The OD results regard the OD bond vector.

In Table II for the quadrupole coupling constant of the hydrocarbon deuteron a constant mean value of 170 kHz has been assumed.[35] The individual coupling constants may deviate from this value by $\pm 10\%$, thus $\tau_c(D-C)$ may be longer or shorter by $\pm 20\%$. The same is true for the OD coupling constant, here the coupling constant of OD in DOD has been used.[22] The activation energies for the reorientational motion of the molecules or respective parts of the molecules may also be found in Table II. In all cases the quadrupole coupling constant was assumed to be independent of the temperature which may be only approximately true.

(28) N. Bloembergen and L. O. Morgan, J. Chem. Phys., 34, 842 (1961).

(29) H. Pfeifer, Z. Naturforsch. A, 17, 279 (1962).

(30) R. Hausser and F. Noack, Z. Phys., 182, 93 (1964).

(31) J. C. Hindman, A. Svirmickas, and M. Wood, J. Phys. Chem., 72, 4188 (1968).

(32) See, e.g., R. Pottel and O. Lossen, Ber. Bunsenges. Phys. Chem., 71, 135 (1967).

(33) R. H. Cole, "Magnetic and Dielectric Resonance and Relaxation," J. Smidt, Ed., North-Holland Publishing Company, Amsterdam, 1963, p 96.

(34) E. Fatuzzo and P. R. Mason, Proc. Phys. Soc., 90, 729, 741 (1967).

(35) T. T. Bopp, J. Chem. Phys., 47, 3621 (1967).

Table II: Reorientational Correlation Times and Activation Energies for Some Pure Organic Liquids (25°)

Compound	$\tau_c(^{14}N)$, psec[a]	$\tau_c(^{17}O)$, psec	$\tau_c(DO)$, psec	$\tau_c(H-H)$, psec	$\tau_c(D-C)$, psec	eQq/h for ^2H, kHz[b]	E_a (polar group),[c] kcal/mol	E_a (hydrocarbon part),[c] kcal/mol
CH₃CN	1.2			0.4^d			1.85 (^{14}N)	
CD₃CN					0.35	170		1.3^e
C₅H₅N	2.1			1.65				
C₅D₅N					2.2	170	...	2.4
CH₃OH							2.2 (^{17}O)	
CH₃OD			3.7	0.9		248	2.75 (^{2}H)	
CD₃OH					0.45	170		1.7
C₂H₅OH							2.3 (^{17}O)	
C₂H₅OD			8.0	2.2		248	4.4 (^{2}H)	
C₂D₅OH					2.5	170		3.4
CD₃CH₂OH					2.6	170		3.0
CH₂CD₂OH					2.1	170		3.7
(CH₃)₃COD			47.7	8.0		248		
(CD₃)₃COH					13.5	170		
(CH₃)₂CO	1.1			0.6				
(CD₃)₂CO					0.5	170		1.6
C₄H₈O (THF)				0.6				
C₄D₈O (TDP)					0.8	170		2.5

^{a} psec $= 10^{-12}$ sec. ^{b} Assumed average standard values; ^{2}H $\equiv$ D. ^{c} Definition of E_a: $\tau_c = \tau_c^{\circ} e^{E_a/RT}$. ^{d} After correction for spin rotation interaction.[36] ^{e} Woessner, Snowden, and Strom: $E_a = 1.37$ kcal/mol.[36]

We shall now briefly discuss the data collected in Table II and before doing so we state once more—as a standard of comparison—that the rotational correlation time of water at 25° is 2.5×10^{-12} sec.

Acetonitrile. The molecule performs anisotropic rotational motion, the rotation about the symmetry axis of the molecule being very fast. This is seen from the fact that $\tau_c(H-H)$, $\tau_c(D-C) < \tau_c(^{14}N)$. Woessner and coworkers[36] report that the ratio of the rotational diffusion coefficient about the symmetry axis, D_1, is ca. ten times as great as D_2, the rotational diffusion coefficient about the axis perpendicular to the former axis.

Pyridine. Our hydrogen and nitrogen reorientation times are rather alike. Thus anisotropic tumbling is not discernible from our measurements although anisotropic motion has been observed for pyridine in a more detailed investigation selecting particular CD vectors in the ring.[37]

Methanol. The correlation time of both the vectors H–H (methyl) and CD (methyl) is much shorter than that of the vector OD. The relatively long correlation time $\tau_c(DO) = 3.7 \times 10^{-12}$ sec (longer than τ_c for H_2O) has been confirmed independently as will be described elsewhere.[38] The difference between these correlation times is due to the internal rotation of the methyl group.[22,38]

The ^{17}O-quadrupole coupling constant in methanol is not known. Use of $eQq/h \approx 8$ MHz which is the coupling constant in $H_2^{17}O$ gives $\tau_c(^{17}O) \approx 8 \times 10^{-12}$ sec which, as compared with the $\tau_c(DO)$ values, is too long. We were unable to see any spin–spin coupling

effects of the ^{17}O resonance; the line shape was Lorentzian. The activation energy of the ^{17}O relaxation is smaller than the one for $\tau_c(DO)$ (see Table II). Tentatively, we interpret the low activation energy of ^{17}O as caused by the anisotropic motion of the atomic array C–O–H due to hydrogen bonding and by the modulation of the quadrupole coupling constant due to the internal rotation of the CH_3 group.

Ethanol. Again the correlation time of the alkyl part of the molecule is faster than the OH group. The slow motion of the latter group has been confirmed independently.[38] Thus here internal motion in the molecule is present, too. The quadrupole coupling constant of ^{17}O is again not known $(eQq/h = 8$ MHz would give $\tau_c(^{17}O) = 14 \times 10^{-12}$ sec which is too long), and as for methanol the activation energy of the ^{17}O relaxation is remarkably low as compared with E_a of the OD group as found from the deuteron relaxation (Table II). Obviously here as well the ^{17}O relaxation reflects some internal motion of the nonhydroxylic part of the molecule. Details are unknown as yet.

tert-Butyl Alcohol. Internal rotation about the O–C axis and rotation of the methyl group about the C–C axis causes the difference between the OD and methyl reorientation rate.

Acetone. The result $\tau_c(OC)$ as derived from the ^{17}O relaxation with the quadrupole coupling constant of

(36) D. E. Woessner, B. S. Snowden, Jr., and E. T. Strom, *Mol. Phys.*, **14**, 265 (1968).

(37) J. P. Kintzinger and J. M. Lehn, private communication.

(38) M. Grüner and H. G. Hertz, to be published.

formaldehyde is confirmed by the dielectric relaxation time at 25° (interpolated): $\tau_d = 2.9 \times 10^{-12}$ sec[39] (note $\tau_c \approx {}^1/_3\tau_r$ for microstep rotational diffusion). Since τ_c for the methyl group is much shorter we find internal rotation, according to Woessner's formula[40] describing the effect of internal rotation on the correlation time, the time constant for the rotation of the methyl groups about the C–C axis is $\tau_i = 0.8 \times 10^{-12}$ sec.

Tetrahydrofuran (THF). The heteronucleus has not been measured as yet. Most likely the molecule performs isotropic reorientational motion, slight anisotropy being possible.

B. The Aqueous Mixtures. (i) *Structural Information from Rule 1, First Part.* Figure 2 shows the self-diffusion coefficients of H_2O in its mixtures with acetone and ethanol as a function of the concentration (moles of solute/55.5 mol of water, aquamolality) over a limited composition range at 25°. The self-diffusion coefficients of the solute molecules in D_2O are also shown in Figure 2. All diffusion coefficients are given as relative quantities, relative to the self-diffusion coefficient of pure ordinary water = 2.5×10^{-5} cm²/ sec.[24]

Since the D's of the solute particles have been measured in D_2O for the comparison with the H_2O diffusion coefficients, the experimental values have to be corrected in order to take account of the greater mobility in H_2O as compared with D_2O. Thus the data given in Figure 2 for the solute molecules in the range $x_2 \to 0$ are multiplied by a factor 1.23 which corresponds to the mobility (and inverse viscosity) ratio in H_2O and D_2O. These corrected diffusion coefficients in the low C_2 range are given as dashed curves in Figure 2. The correction which is necessary for the H_2O diffusion in the ethanol–water mixture because of the exchange of the OH proton has been neglected. Furthermore, one finds vertical dashed lines at $C_2 = C_2{}^* = 2.4$ and $2.8\ \bar{m}$ for acetone and ethanol, respectively, $C_2{}^* = 55.5/n_h$. The hydration numbers n_h (23 and 20) have been estimated from molar volume considerations. Then, $0 < C_2 < C_2{}^*$ is the concentration range in which it is meaningful to divide the total solvent water in hydration water and free water where $D^{(1)+}$ and $D^{(1)\circ}$ (see Figure 1) are the respective diffusion coefficients. For $0 < C_2 < C_2{}^*$ eq 15 holds, whereas for $C_2 > C_2{}^*$ we directly observe the water of the hydration spheres: $D^{(1)} = D^{(1)+}$, now the word hydration number is no longer meaningful. We call the whole amount of water for $C_2 > C_2{}^*$ "hydration water." Note that in general $D^{(1)+}$ and $D^{(1)\circ}$ are as well functions of the concentration for $0 < C_2 < C_2{}^*$.

Now consider rule 1, first part (section 2B). One sees immediately that $D^{(1)+} = D^{(2)}$ (eq 4, $D^{(2)}$ = self-diffusion coefficient of acetone or ethanol) cannot hold for the whole concentration range $0 < C_2 \leqslant C_2{}^*$, since at $C_2 = C_2{}^*$, $D^{(1)} = D^{(1)+} \neq D^{(2)}$. In Table III $D^{(1)}/D^{(2)}$ at $C_2 = C_2{}^*$ is given. We conclude that long-lived
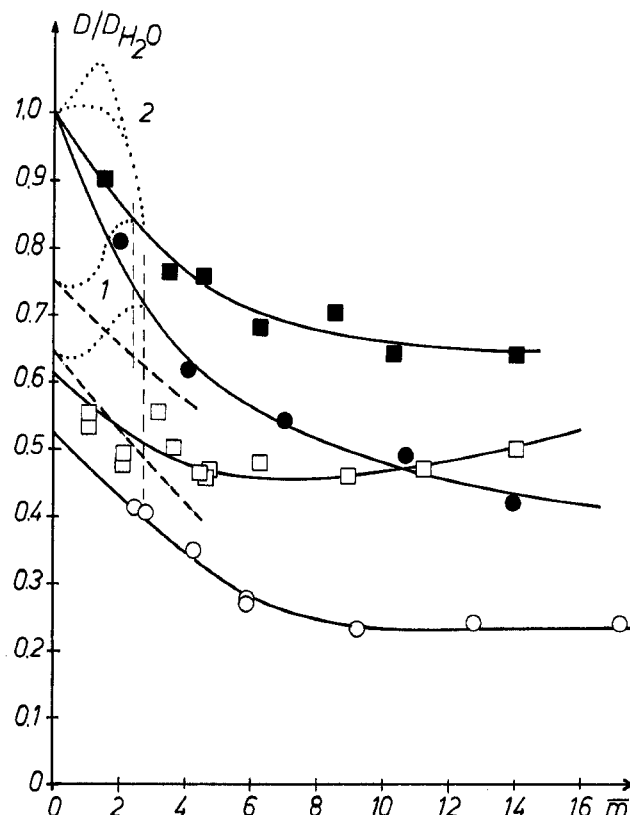

Figure 2. Self-diffusion coefficient of acetone $(CH_3)_2CO$ ($\square$) and ethanol C_2H_5OD (O) in D_2O as a function of the concentration at 25°. ■ and ● give the self-diffusion coefficient of H_2O in the presence of acetone $(CD_3)_2CO$ and ethanol (C_2D_5OH), respectively. All quantities are given relative to $D_{H_2O} = 2.5 \times 10^{-5}$ cm²/sec. The concentration scale is moles of solute/55.5 mol of water. For further details see text.

hydration cages do not exist for acetone and ethanol for the whole concentration range $0 < C_2 \leqslant C_2{}^*$. However, $D^{(1)+} = D^{(2)}$ may be valid for a certain concentration range around $C_2 = 0$. Then the two dotted lines 1 give a possible behavior of $D^{(1)+}$ with $D^{(1)+} = D^{(2)}$ at $C_2 \to 0$ and $D^{(1)+} = D^{(1)}$ at $C_2 = C_2{}^*$. But eq 15 holds over the total concentration range $0 < C_2 \leqslant C_2{}^*$; thus, from eq 15 we have

$$D^{(1)\circ} = \frac{D^{(1)} - \dfrac{n_h C_2}{55.5} D^{(1)+}}{1 - \dfrac{n_h C_2}{55.5}} \qquad (26)$$

The dotted curves 1 for $D^{(1)+}$ of Figure 2 inserted into eq 26 give the dotted lines 2 for $D^{(1)\circ}$. We see that $D^{(1)\circ} > D^{(1)}(0)$ in a certain concentration range where $D^{(1)}(0)$ is the self-diffusion coefficient of pure water. We do not consider $D^{(1)\circ} > D^{(1)}(0)$ to be a physically realistic situation for these solutions. Without struc-

(39) M. I. Shakparonov and Ya. Yu. Akhadov, *J. Struct. Chem. (USSR)*, **6**, 15 (1965).

(40) D. E. Woessner, *J. Chem. Phys.*, **36**, 1 (1962).

Table III: Hydration Numbers n_h (Estimated from Molar Volume Considerations), Ratio $D^{(1)}/D^{(2)}$
at $C_2^* = 55.5/n_h$, and Hydration Numbers for Possible Long-Lived Hydration Spheres

Solute	n_h	$C_2^*, \bar{m}$	$\left(\dfrac{D^{(1)}}{D^{(2)}}\right)_{C_2=C_2^*}$	$n_{h1}(0)$	$n_{h1}(0,1)$	$n_{h1}(0,5)$
Acetone	23	2.4	1.3	16.5		
Ethanol	20	2.8	1.5	19	18	15
Methanol	17	3.3	...	...	...	...
tert-Butyl alcohol 25°[a]	25	2.2	2.4	19	...	...
tert-Butyl alcohol 0°	25	2.2	2.8	23	22	18.5
Acetonitrile	19	2.9	≈1	19.5	18.5	
Pyridine[b]	24	2.3	1.9	12		
THF[b]	24	2.3	1.75	11		
Dioxane[c]	24	2.3	1.75	12		

[a] From ref 22 and $D^{(1)}/D^{(1)}(0) = 0.82, 0.65, 0.53, 0.46, 0.42$ for $C_2 = 1, 2, 3, 4, 5$ mol/kg of water, respectively.   [b] From ref 22
[c] From C. J. Clemett, *J. Chem. Soc. A,* 458 (1969).

ture-breaking effects the self-diffusion coefficient in these solutions cannot increase somewhere while the average $D^{(1)}$ decreases. There is no experimental evidence whatsoever as yet for such a possibility (see also ref 41). At best we can have $D^{(1)°} \leqslant D^{(1)}(0)$ or $dD^{(1)°}/dC_2 \leqslant 0$ at small C_2; that is, if we introduce $D^{(1)+} = D_2$ for small C_2, we deduce from eq 26

$$0 \geqslant \frac{dD^{(1)°}}{dC_2} = \left(\frac{dD^{(1)}}{dC_2}\right)_{C_2\to0} + \frac{n_h}{55.5} \times$$

$$\left\{(D^{(1)})_{C_2\to0} - (D^{(2)})_{C_2\to0} - 2\left(\frac{dD^{(2)}}{dC_2}\right)_{C_2\to0} C_2\right\} \quad (27)$$

as the condition that $D^{(1)+} = D^{(2)}$ as $C_2 \to 0$. Still modifying the argument somewhat we can calculate n_{h1} from eq 27 with $(dD^{(1)°}/dC_2)_{C_2\to0} = 0$

$$n_{h1} = \frac{-55.5\left(\dfrac{dD^{(1)}}{dC_2}\right)_{C_2\to0}}{(D^{(1)})_{C_2\to0} - (D^{(2)})_{C_2\to0} - 2\left(\dfrac{dD^{(2)}}{dC_2}\right)_{C_2\to0} C_2} \quad (28)$$

and formulate rule 1, first part, in the following way. If for a given small C_2, n_{h1} as calculated from eq 28 is sufficiently large so that a complete hydration sphere surrounding the solute particle can be formed from n_{h1} water molecules, then a long-lived rigid hydration cage may exist up to this small concentration. The corresponding results are given in Table III where the number in parentheses in the headings of columns 5, 6, and 7 indicates the concentration C_2 ($\bar{m}$) used in eq 28. Figure 3 shows the corresponding data as in Figure 2 for the system *tert*-butyl alcohol–water at 0°. This system is of particular interest since it has been claimed by Glew and coworkers[42] that *tert*-butyl alcohol is surrounded by a clathrate cage in liquid aqueous solution (at 0°). Our results for *tert*-butyl alcohol–water are also presented in Table III. Furthermore results for some other aqueous systems are included in Table III.
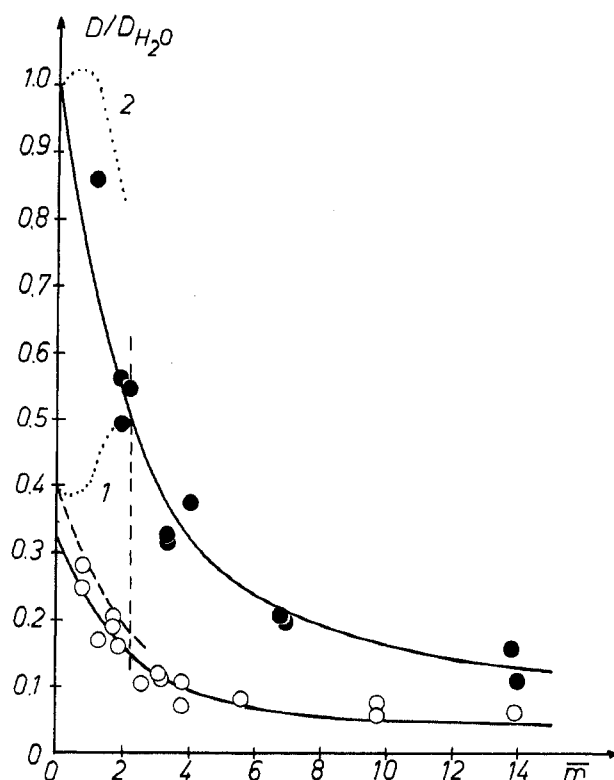
Figure 3. The self-diffusion coefficient of H_2O (●) in the presence of *tert*-butyl alcohol $(CD_3)_3COH$ and the self-diffusion coefficient of $(CH_3)_3COH$ (○) in D_2O as a function of the concentration at 0°. The data are given relative to $D_{H_2O} = 1.1 \times 10^{-5}$ cm²/sec. The concentration scale is moles of solute/55.5 mol of water. For further details see text.

In all cases the hydration numbers n_h are estimated from molar volume considerations. We see from Table III that, except for acetonitrile, in no case a long-

(41) H. G. Hertz, B. Lindman, and V. Siepe, *Ber. Bunsenges. Phys. Chem.,* **73,** 542 (1969).

(42) D. N. Glew, H. D. Mak, and N. S. Rath, "Hydrogen-Bonded Solvent Systems," A. K. Covington and P. Jones, Ed., Taylor & Francis Ltd., London, 1968, p 195.

Table IV: Rotational Correlation Times in Aqueous Solution in the Limit of Infinite Dilution of the Organic Component (25°)

Compound	n_h	$\dfrac{\tau_c^{(1)+}}{\tau_c^{(1)}(0)}$	$10^{12}\tau_c^{(1)+}$, sec	$\dfrac{\{\tau_c^{(2)}(\text{hydrocarbon})\}_{C_2\to 0}}{\{\tau_c^{(2)}(\text{hydrocarbon})\}_{\text{pure 2}}}$	$10^{12}\{\tau_c^{(2)}(\text{hydro-carbon})\}_{C_2=0}$, sec	$\dfrac{\{\tau_c^{(2)}(\text{polar})\}_{C_2\to 0}}{\{\tau_c^{(2)}(\text{polar})\}_{\text{pure 2}}}$	$10^{12}\{\tau_c^{(2)}(\text{polar})\}_{C_2\to 0}$, sec
CH_3CN	19	1.1	2.7	1.05	0.37[a]	1.6	1.9
C_5H_5N	24	1.3	3.2	2.8	5.6[b]	3.0	6.4
CH_3OH	17	1.35	3.4	1.15	$\begin{cases}1.0 \text{ proton}\\0.5 \text{ deuteron}\end{cases}$	(1.15)	(4.2)
C_2H_5OH	20	1.5	3.8	0.68	1.5[c]	(0.68)	(5.5)
$(CH_3)_3COH$	25	1.65	4.3	0.53	4.3[c]	(0.53)	(25)
$(CH_3)_2CO$	23	1.3	3.2	1.3	0.8[c]	2.2	2.4
THF	24	1.4	3.5	2.4	1.5[c]	...	...

[a] Derived from τ_c(D–C) of Table II. [b] Derived from $\tau_c^{(2)}$(hydrocarbon) $= 2 \times 10^{-12}$ sec as rounded off average value of τ_c(H–H) and τ_c(D–C) of Table II. [c] Derived from τ_c(H–H) of Table II.

lived hydration cage can exist at $C_2 \approx C_2^*$ since $D^{(1)}/D^{(2)} \neq 1$, that however, due to the limited experimental accuracy (uncertainty of $\pm 20\%$ for n_{h1}) for ethanol and *tert*-butyl alcohol at 0° a long-lived hydration cage cannot be excluded at $C_2 \leq {}^1/_{10}\ \bar{m}$. For acetonitrile the "positive" result is due to the fact that $D^{(1)} \approx D^{(2)}$ for $0 < C_2 < C_2^*$ as may be seen from Figure 11, where, however, $D^{(2)}$ is not yet corrected for the higher mobility in H_2O. Clearly, as already mentioned above, rule 1 is never a sufficient condition and thus at this stage really a positive statement concerning a hydration cage for CH_3CN cannot be made. Further information will follow below.

(ii) Structural Information from Rule 1, Second Part. We saw in the previous section that from the point of view of rule 1, first part, for certain solutes a long-lived hydration cage cannot be strictly excluded at low concentrations. We ask now whether correlated rotational motion is possible as well at low concentration; that is, we turn to the second part of rule 1.

To examine whether the condition eq 4a is fulfilled we have collected some values for $\tau_c^{(1)+}$, the correlation time of the water molecule in the hydration sphere, in Table IV (25°). The necessary experimental data are partly taken from the literature.[22] New results for $\tau_c^{(1)}$ at 25° as a function of the composition may be found in Figures 4, 6, and 7 (see also ref 43). Furthermore, for H_2O–*tert*-butyl alcohol at 25° we measured $B' \equiv \{T_1 d(1/T_1)/dC_2\}_{C_2=0} = 0.30\ m^{-1}$ for the water protons. The relation between B' and $\tau_c^{(1)+}/\tau_c^{(1)}(0)$ is eq A5 in the Appendix. $\tau_c^{(1)}(0)$ is the rotational correlation time in pure water. The determination of $\tau_c^{(1)+}/\tau_c^{(1)}(0)$ is based on the slow exchange formula, eq 18. The ratio $\tau_c^{(1)+}/\tau_c^{(1)}(0)$ is so close to unity that the error cannot be great if the exchange is not sufficiently slow (see Appendix).

Furthermore, one finds the relative reorientation times of the solute molecule in the limit $C_2 \to 0$ in Table IV. The data are understood as relative to the corresponding reorientation times in the pure organic liquids. They are given for the hydrocarbon and the polar part of the organic molecule. The respective
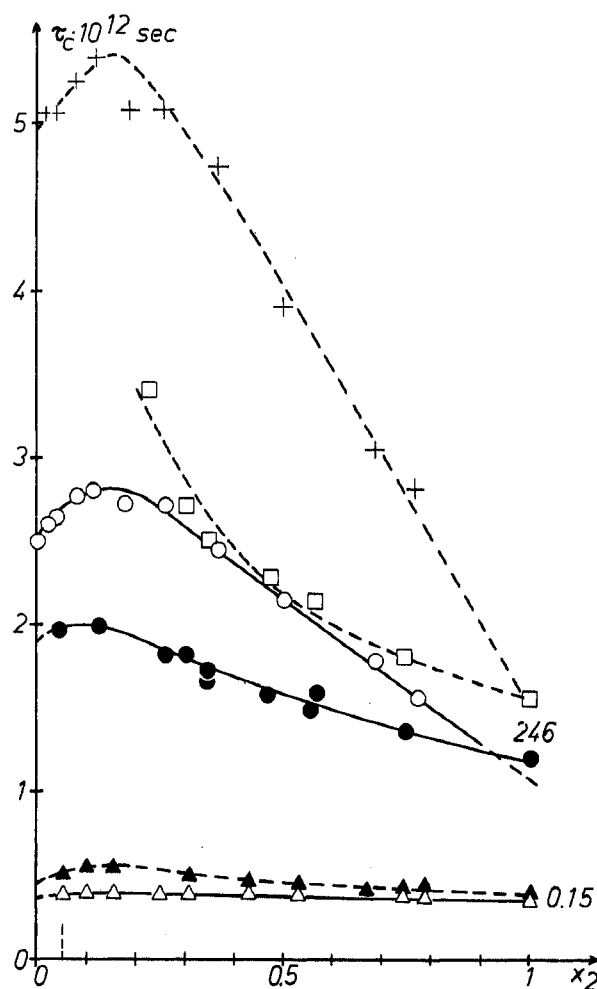

Figure 4. Correlation time $\tau^{(2)}(CD_3)$ ($\triangle$), $\tau_c^{(2)}(^{14}N)$ ($\bullet$), and ($\circ$) $\tau_c^{(1)}(D_2O)$ as a function of the mole fraction $x_2 = x(CH_3CN)$ in the mixture water–acetonitrile at 25°. The dashed curves give the corresponding data $\tau_c^{(2)}(CD_3)$ ($\blacktriangle$), $\tau_c^{(2)}(^{14}N)$ ($\square$), $\tau_c(1)(D_2O)$ ($+$) at 5°. The dashed vertical line corresponds to $C_2^* = 55.5/n_h$; for further details see text.

value at $x_2 = 1$ (x_2 = mole fraction of the organic component) is the time given in Table II; the limiting ab-

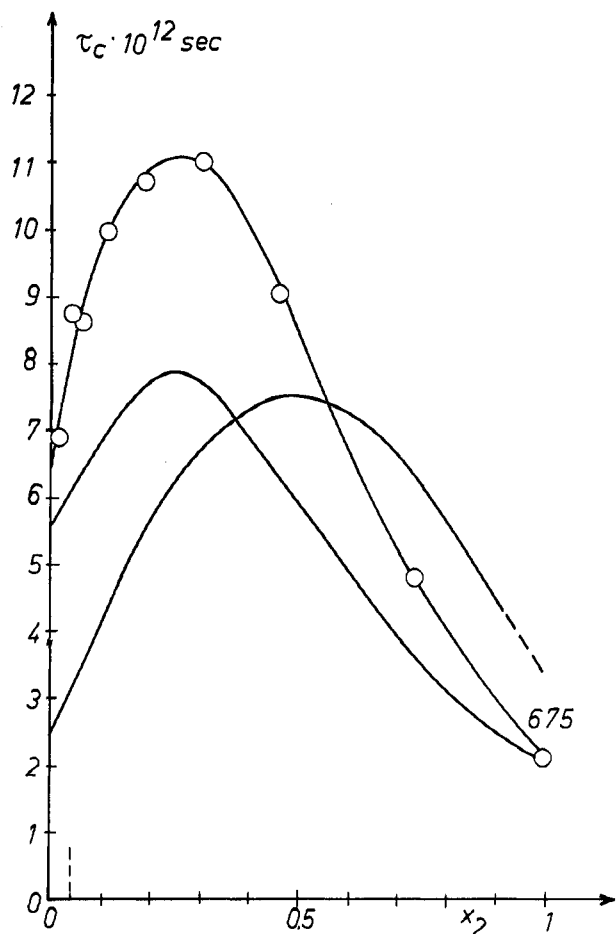(43) H. G. Hertz and M. D. Zeidler, *Ber. Bunsenges. Phys. Chem.*, **68**, 821 (1964).

Figure 5. Correlation time $\tau_c^{(2)}(^{14}N)$ (O), $\tau_c^{(2)}(CD)$, and $\tau_c^{(1)}(H_2O)$ (curve with maximum at $x_2 = 0.5$) as a function of the composition for the mixture water–pyridine at 25°; $x_2 = x(C_5H_5N)$. Vertical dashed line corresponds to $C_2^* = 55.5/n_h$.
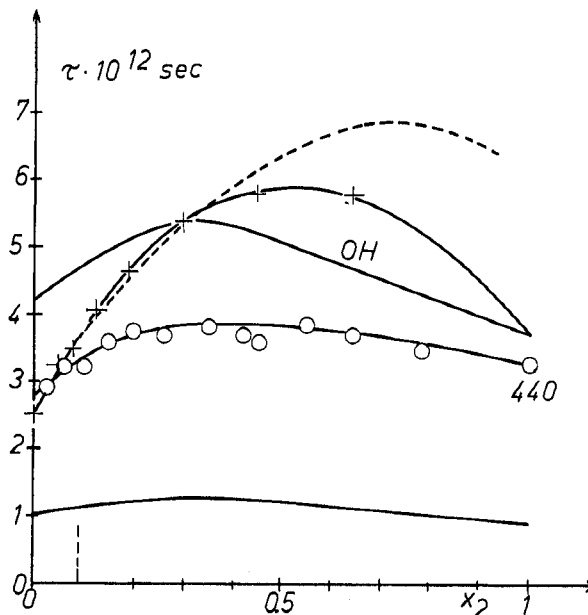

Figure 6. Correlation time $\tau_c^{(2)}(CH_3)$ (lowest curve), $\tau_c^{(2)}(^{17}O)$ (O), and $\tau_c(H_2O–HOR)$ (+) as a function of the composition for the mixture water–methanol at 25°. The absolute value of $\tau_c^{(2)}(^{17}O)$ has been arbitrarily chosen; $x_2 = x(CH_3OH)$. Vertical dashed line corresponds to $C_2^* = 55.5/n_h$; for further details see text.

solute correlation times for $x_2 \rightarrow 0$ are also introduced in Table IV. The necessary data are partly taken from the literature.[22] The new experimental results together with those of ref 22 are presented in Figures 4, 5, 6, 7, and 8. The results of ref 22 are drawn only as solid lines in these figures—if not indicated otherwise—whereas the new experimental results are marked by symbols showing the individual experimental points (and for 25° are connected by other solid curves). The numbers on the right-hand ordinates give the corresponding relaxation rates (in sec^{-1}) for the pure organic liquids; they are identical with the rates quoted in Table I. In all cases the quadrupole coupling constant is assumed to be concentration (and temperature) independent. Thus, since there is always strict proportionality between $(1/T_1)_{intra}$ and τ_c (see eq 19 and 21), from Figures 4–8 the concentration dependence of the relaxation rates may as well be read off.

Actually, the concentration dependence of the reorientational motion of the alcoholic hydroxyl group is not known for two reasons. (1) The hydroxyl hydrogen exchanges with that of water. (2) The hydroxyl ^{17}O relaxation cannot reflect the motion of the

OH vector since the activation energy in the pure alcohol is too small. Thus, the only thing we can do for the alcohols is to assume that the OH reorientation time is longer than the alkyl reorientation time by a factor which is independent of the concentration. In Figures 6 and 7 the solid lines marked with OH are obtained in this way. As a consequence, the entries in columns 7 and 8 of Table IV for the alcohols are put in parentheses. The end points at $x_2 = 1$ for the ^{17}O reorientation in Figures 6 and 7 are arbitrarily chosen. The quadrupole coupling constant is not known, and the form of the motion is not clear. Since the activation energy for ^{17}O is smaller than that for ^2H in the OD group, the end points cannot be the same as those of the ^2H reorientation. Likewise the precise vertical position of the two curves for CD_3CH_2OH and CH_3CD_2OH in Figure 7 is not known; contrary to the curves shown one would expect that CD_3 moves faster than CD_2. The order given in Figure 7 is caused by the constant assumed standard value of the quadrupole coupling constant.

Now we examine the validity of rule 1, second part, and consider first the molecules which have no ring structure. We find the following results. For $tert$-butyl alcohol $\tau_c^{(1)+} = \tau_c^{(2)}(CH_3)$ cannot be excluded; however, in spite of our poor knowledge of $\tau_c^{(2)}(OH)$ we may safely state $\tau_c^{(1)+} \neq \tau_c^{(2)}(OH)$. For all other molecules of this class the correlation times of the alkyl group and of the polar group which are different at $x_2 = 1$ never converge to the same value as $x_2 \rightarrow 0$; in some cases they even diverge. Also, the hydrocarbon
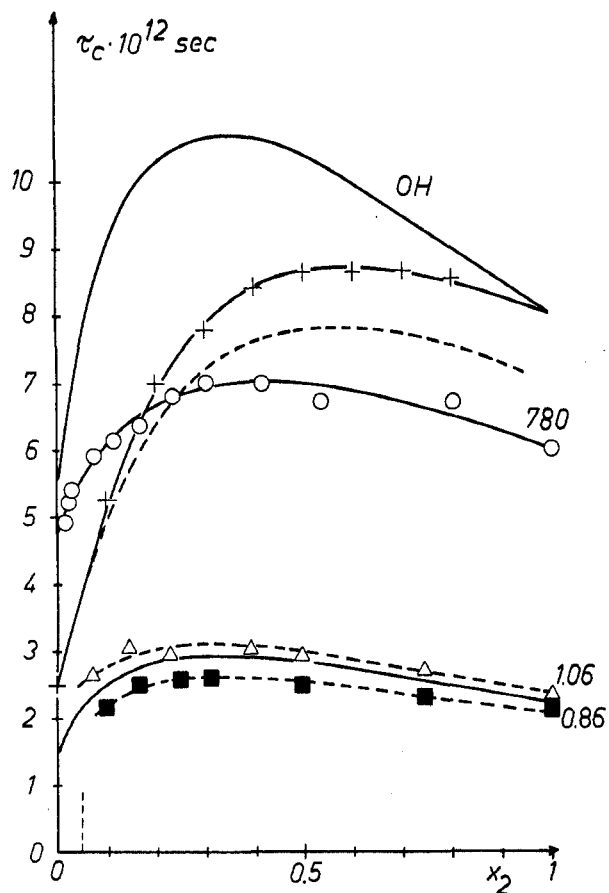
Figure 7. Correlation time $\tau_c^{(2)}(-CH_2-)$ (■), $\tau_c^{(2)}(C_2H_5)$ (lowest solid curve), $\tau_c^{(2)}(CH_3-)$ (■), $\tau_c^{(2)}(^{17}O)$ (△), and $\tau_c^{(1)}(H_2O-HOR)$ (+) as a function of the composition for the mixture water–ethanol at 25°. Absolute values of $\tau_c^{(2)}(-CH_2-)$ and $\tau_c^{(2)}(CH_3-)$ are only approximately correct; absolute value of $\tau_c(^{17}O)$ is arbitrarily chosen; $x_2 = x(C_2H_5OH)$. Vertical dashed line corresponds to $C_2^* = 55.5/n_h$; for further details see text.

Figure 8. Correlation time $\tau_c^{(2)}(CH_3)$ (lowest solid line), $\tau_c^{(2)}$ (^{17}O) (O), and $\tau_c^{(1)}(H_2O)$ (upper solid line) as a function of the composition for the mixture water–acetone at 25°. Further $\tau_c^{(2)}(CH_3)$ (△) and $\tau_c^{(1)}(H_2O)$ (+) at 5°; $x_2 = x((CH_3)_2CO)$. Vertical dashed line corresponds to $C_2^* = 55.5/n_h$.

correlation times are always shorter than the hydration water correlation time $\tau_c^{(1)+}$ (and even shorter than $\tau_c^{(1)}(0)$). Thus, the nonfulfillment of rule 1, second part (eq 4a), tells us that an overall rigid long-lived complex solute molecule + hydration sphere does not exist for any of the systems of this class.

For THF no information of the ^{17}O relaxation is available; the hydrocarbon vectors move faster than the hydration water (and even faster than pure water). For pyridine there is a slight divergence of the hydrocarbon and ^{14}N relaxation (Figure 5); however $\tau_c^{(1)+} \neq \tau_c^{(2)}$. Consequently, according to rule 1, second part, for the ring molecules as well a long-lived overall rigid complex solute + hydration cage must be excluded.

(*iii*) *Application of Rule No. 2.* Since we saw in the previous section that the solute–hydration aggregates do not possess overall rigidity, the situation described under rule no. 2 may be appropriate for the two alcohols ethanol and *tert*-butyl alcohol. We arrived at this result as a consequence of our limited experimental
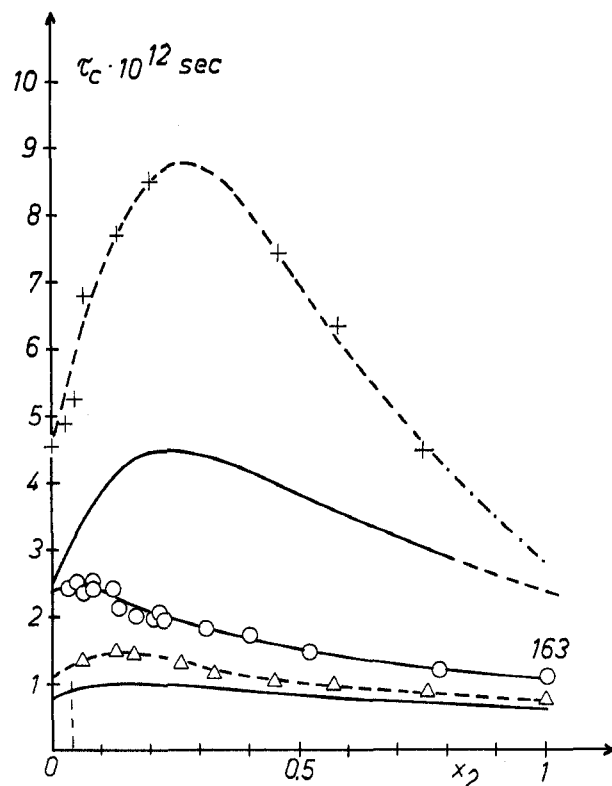
accuracy, that is, the number n_{h1} (eq 28) might be $\approx 20\%$ larger than given in Table III. We recall, however, that the fulfillment of eq 4 is not a sufficient condition for the existence of long-lived aggregates, and we shall indeed find below that as judged from other rules the existence of long-lived hydration spheres is extremely unlikely for all solutes studied here.

(*iv*) *Structural Information from Rule No. 3.* At the beginning we must make one assumption. For the one or two water molecules per solute molecule which interact with the polar group of the solute molecule $\tau_c^{(1)+} \geq \tau_c^{(1)}(0)$ certainly holds. This means that we exclude the very unrealistic possibility that the reorientation time of the H_2O molecule attached to the polar group of the solute molecule is shorter than that of ordinary water. Since according to rule no. 3 (second part) for a long-lived pair of two molecules the correlation time of the vector pointing in the direction of the bond must be longer than (or equal to) that of any other vector of the molecular pair, we conclude from Table IV that for pyridine, ethanol, and methanol long-lived solvent–solute pair association *via* the polar group may occur with a probability close to 1. However, for acetonitrile, acetone, and tetrahydrofuran such pair association occurs with lower probability.

For THF no information concerning the $\diagdown O\diagup$ part of the molecule is available. We assumed that $\tau_c^{(2)}$ for $\diagdown O\diagup$ is essentially equal to the $\tau_c^{(2)}$ of the hydrocarbon vectors, since no internal *rotation* does occur; however, the $\diagdown O\diagup$ correlation time may be slightly longer than 1.5×10^{-12} sec. For $(CH_3)_3COH$ polar group–H_2O pair association is possible. It should be mentioned that according to Table IV for methanol and ethanol the ratio of the alkyl (and polar group) reorientation time in the infinitely diluted aqueous solution and that in the pure alcohol is ~ 1 and ~ 0.7, respectively, whereas the corresponding ratios for the highly diluted alcohols in CCl_4 and pure alcohol are 0.8 and 0.4 for methanol and ethanol, respectively.[38] The former change corresponds to a replacement of the alcoholic surroundings by the water surroundings, the hydrogen bonds being kept connected, whereas the latter change corresponds to the switching off of the hydrogen bonds and replacing the alcoholic surroundings by the relatively large CCl_4 molecules.

When we write

$$\frac{1}{\tau_c^{(2)}} = (1 - p_{2a}) \frac{1}{\tau_{co}^{(2)}} + p_{2a} \frac{1}{\tau_{ca}^{(2)}} \qquad (29)$$

$$1 - p_{2a} = p_{20}$$

(see eq 17a), we can estimate from eq 29 p_{20}, the fraction of acetone, acetonitrile, or tetrahydrofuran molecules which at $C_2 \rightarrow 0$ are bound to the water molecules. $\tau_{ca}^{(2)}$ is the correlation time in the bound state, $\tau_{ca}^{(2)} \gtrsim \tau_c^{(1)+}$ ($\tau_c^{(1)+}$ see column 4 of Table IV), $\tau_{co}^{(2)}$ is the correlation time in the unbound state, $\tau_{co}^{(2)} \lesssim \tau_c^{(2)}$ (pure) ($\tau_c^{(2)}$(pure) see column 2 or 3 of Table II). With the results of Table IV, column 8, we find $p_{2a} \approx 0.65$ and $p_{2a} \approx 0.8$ for acetonitrile and acetone, respectively; for THF about the same figure should be expected.[44]

Finally we note that for all solutes investigated here the self-diffusion coefficient is smaller than that of water. Thus the behavior of the translational diffusion is different from that of the rotational motion. Whereas the rotational diffusion of the solute particle in the water cage at $C_2 \rightarrow 0$ may be faster than that of water, the translational motion is always slower as is to be expected from the larger masses of the solute molecule (see *e.g.*, Figure 11). However, it may occur that the self-diffusion of the solute molecule in the water cage is faster than in the pure liquid formed by the solute. This is the case for ethanol and *tert*-butyl alcohol.[22]

It is easily seen from Table III that regarding the distance between the solute and the water molecule—not the orientation—long-lived pairs H_2O–solute may be present at $C_2 \rightarrow 0$ in all cases studied here. The first part of rule 3 is always fulfilled.

(v) Microheterogeneity and Activation Energies. We now apply the second part of rule 3 (eq 5) to the composition range $x_1 \approx x_2$. As an example consider the

mixture H_2O–acetone at $x_1 = x_2$, *i.e.*, $n_1^\circ = n_2^\circ$ (n_i°, $i = 1, 2$, total number of water and acetone molecules, respectively, in the mixture). Assume for the moment that there are three different molecular species in the liquid: unbound water molecules with correlation time $\tau_{co}^{(1)}$, unbound acetone molecules with $\tau_{co}^{(2)}$ being the correlation time of the vector considered, and bound H_2O–acetone pairs with $\tau_{ca} \equiv \tau_c^{(2,1)}$ for the reorientation of the intermolecular bond vector. The numbers of the three species present are n_1, n_2, and n_a, respectively, $p_1^\circ = n_1/n_1^\circ$, $p_2^\circ = n_2/n_2^\circ$, $p_{1a} = n_a/n_1^\circ$, $p_{2a} = n_a/n_2^\circ$. The mean correlation time of water is $\tau_c^{(1)}$

$$\frac{1}{\tau_c^{(1)}} = \frac{p_1^\circ}{\tau_{co}^{(1)}} + \frac{p_{1a}}{\tau_{ca}^{(1)}} = \frac{p_1^\circ}{\tau_{co}^{(1)}} + \frac{p_{1a}}{\tau_{co}^{(1)}} \xi_1 \qquad (30a)$$

the mean correlation time of acetone is

$$\frac{1}{\tau_c^{(2)}} = \frac{p_2^\circ}{\tau_{co}^{(2)}} + \frac{p_{2a}}{\tau_{ca}^{(2)}} = \frac{p_2^\circ}{\tau_{co}^{(2)}} + \frac{p_{2a}}{\tau_{co}^{(2)}} \xi_2 \qquad (30b)$$

Here $\tau_{ca}^{(1)} = \tau_{co}^{(1)}/\xi_1$; $\tau_{ca}^{(2)} = \tau_{co}^{(2)}/\xi_2$; $k \leqslant \xi_1 \leqslant 1$; $k \leqslant \xi_2 \leqslant 1$. $\xi_{1,2}$ depends on the angle which the vector considered forms with the intermolecular bond direction and on the rapidity of rotational motion of the vector about the intermolecular bond direction.[11-13] If there is no such rotation: $\xi_{1,2} = k$; $k < 1$ corresponds to the fact that the pair of two molecules is a "larger" particle[15,38] than one single molecule. Now for unbound acetone and water we have $\tau_{co}^{(1)} \approx \tau_{co}^{(2)}$, and since the CO vector (the motion of which we observe by the ^{17}O relaxation) has the direction of the $>CO\ldots H$-O-H bond, $\xi_2 = k$ and we expect from eq 30a and b and rule no. 3 with $p_{1a} = p_{2a}$ ($x_1 = x_2$): $\tau_c^{(1)} \leqslant \tau_c^{(2)}$(CO). However, we observe (Figure 8) the contrary, namely $\tau_c^{(1)} > \tau_c^{(2)}$(CO) at $x_1 = 1/2$. The methyl group of acetone shows internal rotation; thus for these groups $\xi_2 > k$ and $\tau_c^{(2)}$(CO) $> \tau_c^{(2)}$(CH$_3$).

To account for the observed fact $\tau_c^{(1)} > \tau_c^{(2)}$(CO) one can assume that $p_{1a} > p_{2a}$ at $x_1 = 1/2$. This means that more than one H_2O molecule is attached to the CO of acetone. Such an accumulation of water molecules around a selected acetone molecule would already cause a drastic deviation from the random distribution of H_2O and $(CH_3)_2CO$ molecules, and this is a first step toward microheterogeneity.

Let us now consider the temperature dependence of the correlation times. The activation energy, say of $\tau_c^{(2)}$, is partly given by the change of p_{2a} with temperature and partly by the change with temperature of the number of nonhydrogen-bonded acetone–water pairs

(44) It should be mentioned here that Davies and Williams[45] reported a dielectric relaxation time of acetone and THF in solid H_2O-clathrates of $\tau_d = 1.7 \times 10^{-12}$ sec at 213 and 243°K for acetone and THF, respectively. If one compares this with the entries of Table IV he finds that, due to the uncertainty in the factor connecting τ_d and τ_c, the reorientational motion in the solid is not slower than in the liquid.

(45) M. Davies and K. Williams, *Trans. Faraday Soc.*, **64**, 529 (1968).
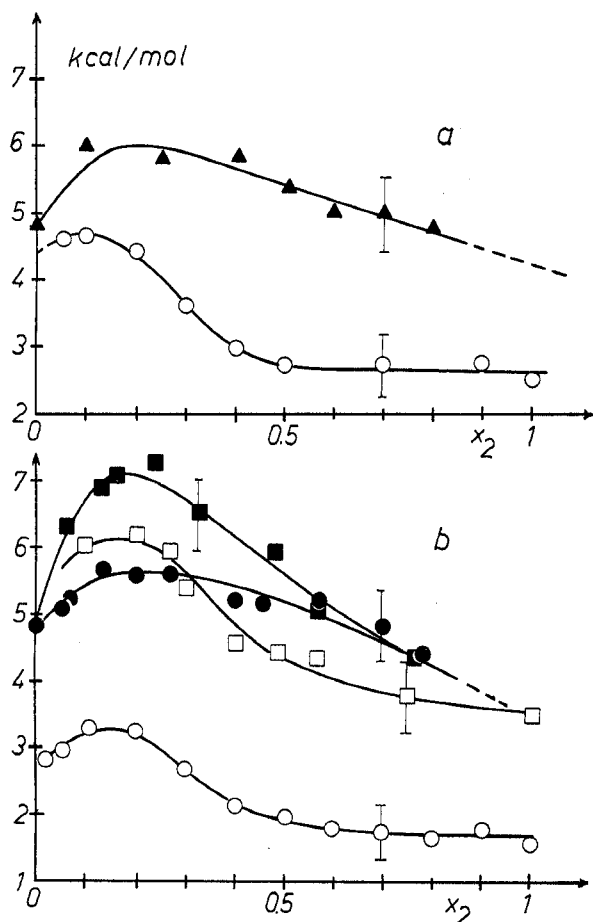
Figure 10. Activation energies for $\tau_c^{(2)}(CD_3)$ (●), $\tau_c^{(2)}(^{14}N)$ (■), $\tau_c^{(1)}(D_2O)$ (▲), $D^{(2)}$ (○), and $D^{(1)}$ (□) as a function of the composition in the mixture water–acetonitrile; $x_2 = x(CH_3CN)$.

Figure 9. (a) Activation energies for $\tau_c^{(2)}(D_2O)$ (▲) and $\tau_c^{(2)}(CD_2)$ (○) as a function of the composition for the mixture water–tetrahydrofuran. (b) Activation energies for $\tau_c^{(1)}(D_2O)$ (●) and $\tau_c^{(2)}(DC_3)$ (○) as a function of the composition in the mixture water–acetone. The activation energies for $D^{(2)}$ (□) and $D^{(1)}$ (■) are as well shown; $x_2 = x(\text{organic molecule})$.

and acetone–acetone pairs. The latter contributions correspond to pure acetone and are small. For H_2O the situation is analogous. Thus from eq 30a and b with $p_{1a} = p_{2a}$ one expects about equal activation energies: $E_a(H_2O) \lesssim E_a(CO)$. If $\varkappa$ water molecules are attached to the CO group the activation energy for the water reorientation is essentially ΔE, ΔE being the energy for the separation of one water molecule from the acetone. For acetone the activation energy should be $\varkappa\Delta E$, because $\varkappa$ water molecules have to be disconnected. On the other hand, $p_{1a} = \varkappa p_{2a}$, thus still we expect $E_a(H_2O) \lesssim E_a(CO)$. These predictions have to be compared with experimental results which are presented in Figure 9b. We see that the activation energy of water is much larger than that of acetone. This is in clear contradiction with the behavior expected so far. The activation energy of acetone only changes slightly in the range $1 > x_2 > 0.4$. Admittedly, the activation energy shown in Figure 9b is that of the CH_3 group, $E_a(CO)$ has not yet been measured, but the difference between $E_a(H_2O)$ and $E_a(CH_3)$ is so great that, con-

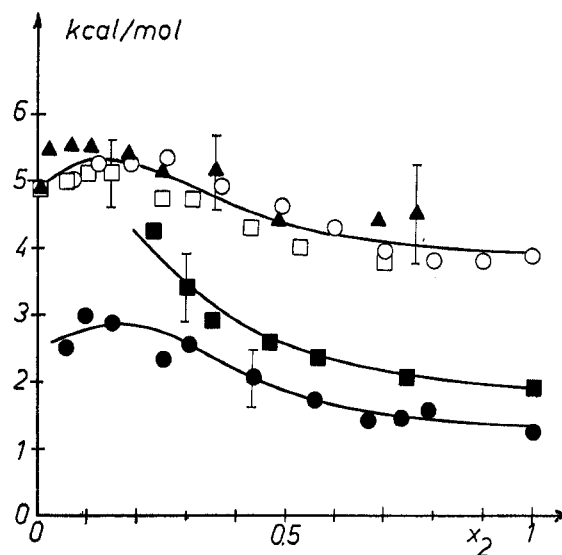sidering also the similar situation for acetonitrile (Figure 10), we may safely state the result $E_a(H_2O) > E_a(CO)$. From this inequality we conclude that the aggregates of $\varkappa$ water molecules are not closely connected with the CO group but that they are more firmly bound among themselves and that the activation energy $E_a(H_2O)$ corresponds to the disconnection of one water molecule from the other members of the water patch in the mixture. Thus we are again lead to the conclusion that there is a certain degree of microheterogeneity in the mixture.

It is now appropriate to write instead of eq 30a

$$\frac{1}{\tau_c^{(1)}} = \frac{p_1^{\circ}}{\tau_{co}^{(1)}} + \frac{p_{1c}}{\tau_{cc}^{(1)}} + \frac{p_{1a}}{\tau_{ca}^{(1)}} \qquad (30c)$$

where again $p_{1a} = p_{2a}$, p_{1c} is the probability for a water molecule to be a member of a water patch or cluster, and $\tau_{cc}^{(1)}$ is the correlation time in this cluster. The activation energy $E_a(H_2O)$ then concerns the temperature dependence of the cluster size $(\tau_{cc}^{(1)})$ and that of p_{1c}. Equation 30c passes steadily into eq 23 where now all terms $\Sigma_{i=1}^{\infty} p_{1i}/\tau_{ci}^{(1)}$ are contracted in the term $p_{1c}/\tau_{cc}^{(1)}$. It might be questionable whether the fast exchange limit eq 17 is still applicable here since from sound absorption measurements it was concluded that the decomposition time of the clusters is relatively long.[46] When we assume that p_1°, $p_{1a} \approx 0$ at $x_2 = 1/2$, then with $\tau_c^{(1)} = 3.8 \times 10^{-12}$ sec and $\tau_{co}^{(1)} \approx 0.5 \times 10^{-12}$ sec by aid of eq 6 we estimate $\varkappa$, the number of water molecules in the patch, to be ~ 6 which seems to be reasonable. As C_2 decreases, the water patches

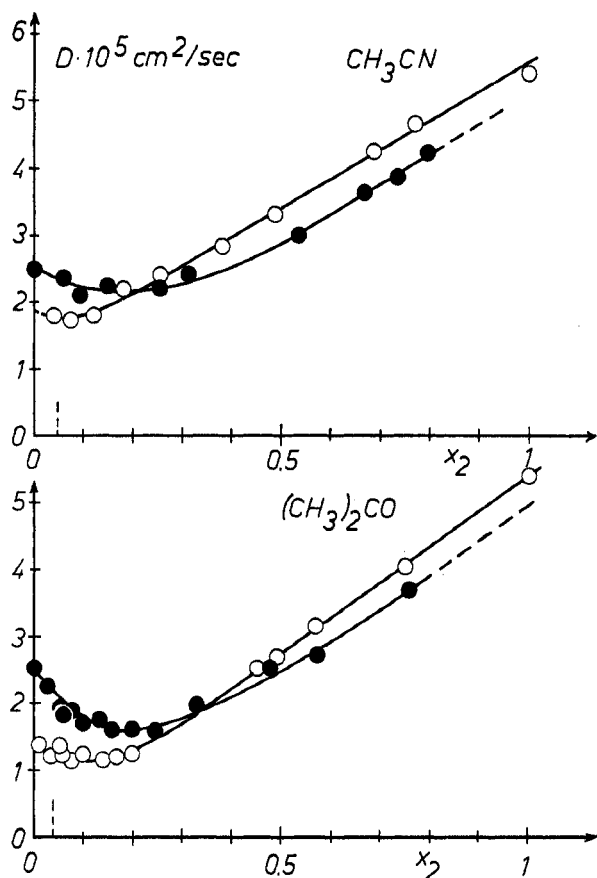(46) J. M. Davenport, J. F. Dill, V. A. Solov'ev, and K. Fritsch, Sov. Phys.-Acoust., 14, 236 (1968).

Figure 11. Self-diffusion coefficient of water (●), acetonitrile, and acetone, both (O), as a function of the composition in the mixtures water–acetonitrile and water–acetone at 25°. The vertical dashed lines correspond to $C_2^* = 55.5/n_h$; $x_2 = x$(organic component).

Figure 12. Activation energies of $\tau_\sigma^{(2)}(CD)$ (O) and $\tau_\sigma^{(1)}(D_2O)$ (▲) as a function of the composition for the mixture water–pyridine; $x_2 = x(C_5H_5N)$.

coalesce more and more; finally they fully surround the (solute) acetone particle and form the hydration of the second kind.

In Figure 9a one finds the activation energy for the reorientational motion of H_2O and THF; the general behavior is similar to that of acetone. In Figure 10 the activation energies for the reorientation for all three vectors, namely that in D_2O, in CN, and in CD_3, are shown for the mixture D_2O–CD_3CN. Again the concentration dependence corresponds to the general scheme as outlined for acetone + water. The concentration dependence of the self-diffusion coefficients of both components for the systems H_2O–acetone and H_2O–acetonitrile is shown in Figure 11,[47] and the activation energies of these quantities are included in Figures 9b and 10. It is interesting to note that the translational motions of both the component molecules resemble one another much more than the rotational motions do.

In the mixture water–pyridine at $x_1 = {}^1/_2$ the correlation times of ^{14}N and water are almost equal (Figure 5). The activation energies of the water and pyridine deuterons are shown in Figure 12. Here the inter-
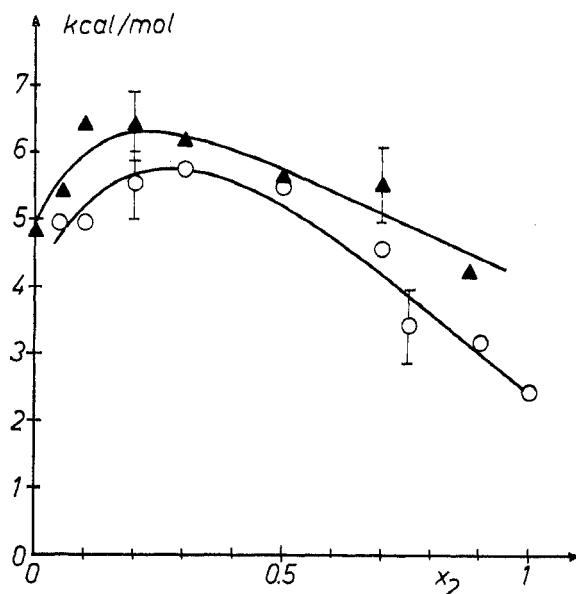
action between the organic molecule and water is much stronger than in the systems described previously and so from the concentration dependences of Figures 5 and 12 we see that the motions of both the component molecules are rather tightly correlated with one another at $x_2 \approx {}^1/_2$. There appears to be a large fraction of water molecules coupled directly to C_5H_5N (approximate equality of τ_σ and E_a), and the clustering term $p_{1c}/\tau_{cc}^{(1)}$ (see eq 30c) seems to be small. Thus microheterogeneity is not so evident here. However, a certain degree of geometrical order beyond simple pair formation cannot be excluded. So one must account for the relatively strong increase with decreasing x_2 of the correlation time of pyridine and the slow water reorientation in the composition range ${}^1/_2 < x_2 < 1$. This effect could come about by the formation of aggregates
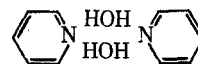
Then, between ${}^1/_4 < x_2 < {}^1/_2$ more water is added to this complex, e.g.
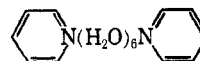
Here the maximum in the correlation time of pyridine occurs. With higher dilution the dissociation of the pyridine pair begins which is observed as a decrease in the pyridine correlation time.

(47) The agreement with the results of McCall and Douglas for acetone–water is satisfactory.[48] Our acetone data are improved as compared with those given in ref 22.

(48) D. W. McCall and D. C. Douglas, J. Phys. Chem., 71, 987 (1967).

Our information is less complete for the alcoholic systems methanol–water and ethanol–water. As already mentioned one of the reasons for this lack of information is the fact that the alcoholic hydroxyl hydrogen exchanges with the water hydrogen. Thus, for the water reorientation we have information only as a part of the measured average behavior (τ_c) of the alcoholic and water OD or OH and *vice versa*. We have already described in what way the curves for $\tau_c^{(2)}(OH)$, indicated with OH in Figures 6 and 7, are obtained. The measured average τ_c is

$$\tau_c = \frac{2x_1}{2x_1 + x_2}\,\tau_c^{(1)}(H_2O) + \frac{x_2}{2x_1 + x_2}\,\tau_c^{(2)}(OH)$$

and thus the water correlation time $\tau_c^{(1)}(H_2O)$ may be determined. The result is seen as the dashed curves in Figures 6 and 7. In particular, in Figure 7 the curve "OH" may be lower; then the dashed H_2O curve would move to higher values.

The activation energies for the systems methanol–water and ethanol–water are shown in Figures 13 and 14, respectively. It is reasonable to assume that over the entire composition range the OH activation energy of methanol and ethanol is larger by roughly a constant factor than that of the methyl and ethyl group. This means that the activation energy of the alcoholic OH and that of the water are very much alike. From Figures 6 and 7 and the accompanying discussion we saw that the correlation times of ROH and H_2O should also not be much different. Thus the motion of the polar ends of both component molecules is similar, and there is no obvious evidence for microheterogeneity. However, with decreasing x_2 at high x_2, $^1/_2 < x_2 < 1$, the correlation time of the hydrocarbon (and polar) part and the activation energy for the reorientation of the hydrocarbon (and polar) part of both molecules increase. In this range the H bond between the alcohol molecules is replaced by the H bond alcohol–water. The water molecule is smaller than the alcohol molecule, and still the two properties indicated increase, which must mean that geometrical arrangements exist which are similar to those proposed for the mixture pyridine–water. With decreasing x_2, $x_2 < ^1/_2$, more and more water neighbors are added, finally surrounding the hydrocarbon part also, and for very small x_2, $x_2 < 0.2$, the water molecules added are no more coupled to other solute molecules and thus the correlation time decreases.

The low activation energy of the ^{17}O relaxation for the alcohols, in particular for ethanol, which extends over an appreciable concentration range, we are unable to explain as yet. At the right-hand ordinate of Figure 12 we have marked the activation energies for the deuteron relaxation of CD_3CH_2OH and CH_3CD_2OH, from which one sees that both these activation energies are larger than that for ^{17}O and that they show the order to be expected, namely $E_a(CD_3) < E_a(CD_2) < E_a(OH)$.

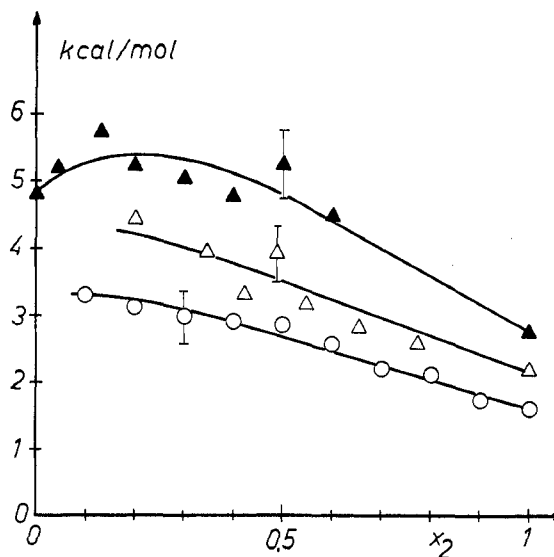Figure 13. Activation energies for $\tau_c^{(2)}(CD_3)$ (O), $\tau_c^{(2)}(^{17}O)$ ($\triangle$), and $\tau_c(D_2O-DOR)$ ($\blacktriangle$) as a function of the composition in the mixture water–methanol; $x_2 = x(CH_3OH)$.
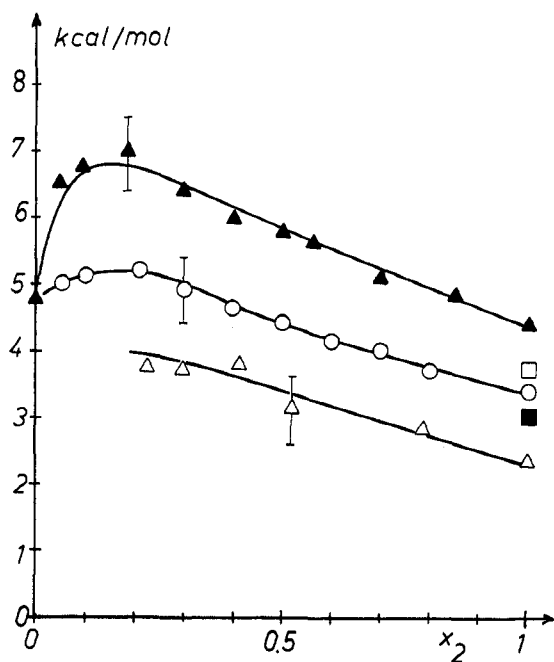
Figure 14. Activation energies for $\tau_c^{(2)}(^{17}O)$ ($\triangle$), $\tau_c^{(2)}(C_2D_5)$ (O), and $\tau_c(D_2O-DOR)$ ($\blacktriangle$) as a function of the composition for the mixture water–ethanol. The activation energies for $\tau_c^{(2)}(CD_3-)$ ($\blacksquare$), and $\tau_c^{(2)}(-CD_2-)$ ($\square$) are only shown for the pure alcohol ($x_2 = 1$).

(vi) Structural Information from Rule No. 4. As already mentioned above the reorientational correlation time of a long-lived rigid aggregate of six water molecules + a central particle + a number of about four short-lived associated water molecules is $\sim3 \times 10^{-11}$ sec. According to Tables III and IV the hydration cages of our solute particles must be much larger aggregates, *i.e.*, we expect $\tau_c^{(1)+} > 3 \times 10^{-11}$ sec. Since,

Table V: Composition of Mixture at Maximum Correlation Time and Minimum Self-Diffusion Coefficient (25°)

Compound	$\left[\dfrac{D^{(2)}}{D^{(1)}}\right]_{C_2\to 0}$	$\left[\dfrac{n_1}{n_2}\right]_{\tau_c^{(1)}max}$	$\left[\dfrac{n_1}{n_2}\right]_{D^{(1)}min}$	$\left[\dfrac{n_1}{n_2}\right]_{\tau_c^{(2)}(CH_3)max}$
CH_3CN	0.9	5.6	4–5	7.5
C_5H_5N	$0.54^{a,b}$	1.0	1–2	3.0^c
CH_3OH	~0.6	(2.2–0.5?)	...	2.2
C_2H_5OH	0.64	(2.3–0.6?)	...	2.3
$(CH_3)_2COH$ 25°	0.4	...		d
$(CH_3)_3COH$ 0°	0.4	...		d
$(CH_3)_2CO$	0.75	3.2	4	6
THF	0.5^a	2.7^a	5–7	10^a
Dioxane			4–5	

^{a} Reference 22. ^{b} B. Brun and J. Salvinien, *J. Chim. Phys.*, **64**, 1319 (1967). ^{c} Here the hydrocarbon part of the ring is concerned. ^{d} No maximum.

however, for all solutes studied here we find $\tau_c^{(1)} \ll 3 \times 10^{-11}$ sec (see Table IV), we conclude that in no case the cage of water molecules surrounding the solute particle can be a long-lived rigid aggregate.

The self-diffusion coefficient of the ion Mg^{2+} at low concentration is 0.7×10^{-5} cm^2/sec, that is $\{D(Mg^{2+})/D_{H_2O}\}_{C_2=0} = 0.28$ at 25°. This figure is taken from conductivity results.[49] Such a value of a self-diffusion coefficient corresponds to a long-lived aggregate of more than 6 but less than 20 water molecules. An aggregate of 20–28 water molecules is expected to have $(D/D_{H_2O})_{C_2\to 0} < 0.28$. As shown in Table V in all cases for the solute particle we have $\{D^{(2)}/D^{(1)}\}_{C_2\to 0} > 0.28$. Further, the results given in Table III may be reformulated so as to demonstrate that with the n_h values of column 2 $\{D^{(1)+}/D^{(2)}\} \geqslant 1$; consequently, $\{D^{(1)+}/D^{(1)}\}_{C_2\to 0} \equiv \{D^{(1)+}/D_{H_2O}\}_{C_2\to 0} > 0.28$. Se we again see that long-lived hydration cages must be excluded for the solutes studied in this work. Also for acetonitrile, ethanol, and *tert*-butyl alcohol where according to rule no. 1, first part, or rule no. 2, some evidence for long-lived aggregates appeared, these must now be ruled out.

Thus in the hydration sphere of the solute particles, geometrically well-ordered closed cage configurations occur at best with probabilities <1, and we have

$$\frac{1}{\tau_c^{(1)+}} = \sum_{i=1}^{\nu} \frac{p_i^+}{\tau_{ci}^{(1)+}}$$
$$D^{(1)+} = \sum_{i=1}^{\nu} p_i^+ D_i^{(1)+}; \quad \sum_{i=1}^{\nu} p_i^+ = 1 \tag{31}$$

where $i = 1, 2, \ldots, \nu - 1$ correspond to truncated cage fragments, and $i = \nu$ correspond to a perfectly closed cage.

(vii) Structural Information from Rule No. 5. It may be seen from Figures 4–8 and ref 22 and 43 that for all aqueous mixtures of the type studied here for small x_2 the reorientational correlation time of the water

molecule, $\tau_c^{(1)}$, increases as x_2 increases. Generally, this increase of $\tau_c^{(1)}$ gets slightly stronger as the temperature decreases (Figures 4, 8–10, 12–14). According to rule no. 5, eq 11, this means that one or more of the maximum values of the pair distribution functions increase, and this is an increase of the degree of structure in the solution.

First the question arises: Is this structural reinforcement due to the first ($H_2O–H_2O$ interaction) or due to the second term (H_2O–solute interaction) in eq 11? For the weakly interacting solutes like acetonitrile, acetone, and THF the structural reinforcement must be ascribed to the first term, that is $f_1^{(1,1)}$, $f_2^{(1,1)}$, ... increase, and the contribution from $f_1^{(1,2)}$, $f_2^{(1,2)}$, ... in the second term on the right-hand side of eq 11 may be neglected. This is a consequence of the fact that for these molecules even the polar end of the molecule (for THF this is to be expected) rotates faster than the water molecules and thus direct solute–water interaction cannot cause the slower motion of the water. For methanol, ethanol, and pyridine the second term containing $f_1^{(1,2)}$, $f_2^{(1,2)}$ ... will probably be more important. Then, in order to give our structural statement a general validity, we must consider the rigid skeleton of rather large molecules—like, *e.g.*, pyridine—also to be a positive contribution to the structure of the liquid, namely an "intramolecular" contribution.[15] However, it can be shown that one or two water molecules bound to the polar group of these solutes with their known reorientation times $\tau_c^{(2)}$(polar) (see Table IV) cannot cause the whole effect of increasing $\tau_c^{(1)}$. So the $H_2O–H_2O$ distribution with the maxima $f_1^{(1,1)}$, $f_2^{(1,1)}$, ... will contribute as well to the lengthening of $\tau_c^{(1)}$ significantly in these mixtures. *tert*-Butyl alcohol presents as yet an open question in this regard.

Clearly, at concentration $C_2 < 2.5\,m$ the statement of

(49) See, *e.g.*, R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London, 1965.

a structure reinforcement of the water does not tell more than given by the aggregate approach, but the view is now more general and the model of localized hydration spheres is abandoned. In particular at concentrations $C_2 > C_2^* = 55.5/n_h$ the model of separated, nonoverlapping hydration spheres becomes meaningless, and still the more general distribution function approach allows the statement that the degree of structure is increased as compared with pure H_2O.

It is just remarkable that this increase of structure extends far over the boundary concentration C_2^* and goes up to rather low values of the ratio of the number of water molecules/number of organic molecules. We shall call this ratio at the maximum of the water correlation time $(n_1/n_2)_{\tau_c^{(1)}max}$. Some results for this quantity are collected in Table V (25°). For the weakly interacting solutes acetonitrile, acetone, and THF beyond the maximum of $\tau_c^{(1)}$ at higher mole fractions of the organic compounds the second term of eq 11 must become more important. Now $f_1^{(1,2)}, f_2^{(1,2)}, \ldots$ increasingly determine the correlation time of the water molecule; obviously, the water–organic molecule distribution is orientationally more isotropic, $f_1^{(1,2)}, f_2^{(1,2)}, \ldots$ have lower values, and the correlation time decreases. In the mixtures with pyridine, ethanol, and methanol the stronger direct water–solute interaction pulls the maximum of $\tau_c^{(1)}$ more in the direction of lower ratios n_1/n_2, that is, to higher mole fractions x_2.

Qualitatively the same information may be obtained from eq 10 regarding the self-diffusion coefficient of the water in the aqueous mixtures. The minima of $D^{(1)}$ occur at about the same composition as the maxima of $\tau_c^{(1)}$ do; some numerical results may be found in Table V.

Now we consider the motion of the solute molecule. Let us begin with the behavior of the hydrocarbon part, the methyl group, say. It is useful to consider two groups of maximum values of the pair distribution function referring to the center of the methyl group: (1) the maxima which occur in the direction of the polar group (at $x_2 \rightarrow 0$ they describe the binding of the polar group with the water, and for larger distances the water–water distribution beyond the polar group enters); (2) the maxima which occur in the other direction as seen from the methyl group, that is, the direction pointing straight into the water at $x_2 \rightarrow 0$. These latter maxima correspond to the weak (c.d. Waals) binding between the methyl group and water and then further out they also reflect the water–water configuration in the second coordination sphere as seen from the methyl group. We recall that all these maximum values contribute to the correlation time of the methyl group. In this case the various maximum values of the pair distribution function are the $f_1^{(2,1)}, f_2^{(2,1)}, \ldots$ occurring in the second term of the right-hand side of eq 13. Clearly, at $x_2 \rightarrow 0$ the first term of eq 13 $\rightarrow 0$ since it corresponds to the vanishing 2–2 contribution.

Now we find experimentally (Figures 4, 6–8, and ref 22) that, starting from $x_2 = 0$ in all cases $\tau_c^{(2)}(CH_3)$ increases with increasing x_2 for sufficiently small x_2. As indicated above in our somewhat simplified scheme this has two sources: The direct effect of the aqueous neighbors of the methyl group and the effect of the polar end transmitted by the molecular skeleton, which, however, is partly decoupled by the internal rotation about C–C, C–O, and other bonds. Regarding the direct coupling methyl–water the increase of $\tau_c^{(2)}(CH_3)$ is due to the second coordination water–water distribution since the next neighbor distributions in the hydration cage should not change very much. Thus the increase of the water structure is also reflected by the motion of the inert methyl protons or deuterons via the weak structural bridges extending into the bulk of the aqueous surroundings. In addition, the same "signals" concerning the water structure are also supplied via the polar groups.

However, at a certain composition in many cases a maximum of $\tau_c^{(2)}(CH_3)$ occurs (Figures 4, 6–8). This maximum again is developed slightly stronger when the temperature is lower (Figures 4, 8–10, 12–14). Now, the mixture for which the maximum of $\tau_c^{(2)}(CH_3)$ occurs contains more water than the mixture for which the water correlation time $\tau_c^{(1)}$ has its maximum. Some ratios $(n_1/n_2)_{\tau_c^{(2)}(CH_3)max}$ for which the maximum of $\tau_c^{(2)}(CH_3)$ occurs are also presented in Table V.

Now we saw that the increase of $\tau_c^{(2)}(CH_3)$ at $x_2 \lesssim 0.05$ is determined by the water–water configurations in the second coordination sphere of the solute. The water–water configurations themselves are described by the maxima occurring in the 1–1 distribution, i.e., $f_1^{(1,1)}, f_2^{(1,1)}, \ldots$ which determine $\tau_c^{(1)}$. The fact that the distribution functions which determine the water motion still get steeper, whereas those which determine the motion of the organic molecule already become flatter, indicates that the local surroundings of the two kinds of particles must begin to differ. The correlation times of the methyl group become shorter because more and more organic molecules with their more isotropic orientational distribution (of their hydrocarbon part) approach to the direct neighborhood of a given reference organic molecule. This effect depresses the probability to find a water molecule in the neighborhood of the organic molecule; that is, the second term on the right-hand side of eq 13 decreases rapidly and the first term gains more importance. In this way we are again lead to the conclusion that microheterogeneity exists in these mixtures. The final value of $\tau_c^{(2)}(CH_3)$ as $x_2 \rightarrow 1$ depends on the nature and structure of the pure organic liquid. For instance, in acetone relatively small maximum values $f_1^{(2,2)}, f_2^{(2,2)}, \ldots$ occur in the first and second coordination sphere; the orientational distribution of the molecules relative to one another is almost isotropic, so $\tau_c^{(2)}(CH_3)$ drops to a value lower than in H_2O at $x_2 \rightarrow 0$. In ethanol, however, where

hydrogen bonds exist, the probability to find ordered aggregates is greater and $\tau_c^{(2)}(CH_3)$ for $x_2 \to 1$ does not fall to the value it has in the limit $x_2 \to 0$ in H_2O (see Table IV). It should be noted that in the case of H_2O-tert-butyl alcohol at $25°$ $\tau_c^{(2)}(CH_3)$ never decreases at all with increasing x_2.[22] This means that the intramolecular structuredness of the tert-butyl alcohol and the hydrogen bonds between the tert-butyl alcohol molecules cause such a large first term of eq 13 that the correlation time does not decrease as the water contribution in the second term of eq 13 becomes smaller. Thus one can say that water has less structure than the intra- and intermolecular structure together of tert-butyl alcohol, it has almost as much structure as the intra- and intermolecular structure together of ethanol, and it has more structure in the same sense than the other organic liquids used here.

The correlation time of the polar group of the solute molecule shows essentially the same behavior and thus yields the same structural information as described for the hydrocarbon part. The experimental uncertainties so far do not allow any more definite statements. Just the same is true for the self-diffusion coefficient of the solute particle.

(viii) Structural Information from Rule No. 6. From the Figures 3-9 given in previous work[22] of one of the authors (E. v. G.) one sees that the quantity $(1/T_1)_{inter}$ $D^{(2)}/N_H$ for the organic particle, which is proportional to $\mathfrak{J}^{(2,2)}D^{(2)}$ (see eq 14 and 22), in some cases increases as $C_2 \to 0$. The same is true—and even with greater regularity—for $(1/T_1)_{inter}D^{(1)}/N_H$ regarding the water; i.e., $\mathfrak{J}^{(1,1)}D^{(1)}$ increases as $C_1 \to 0$. Originally, one of the present authors (E. v. G.) together with Zeidler had proposed that the variation of $\mathfrak{J}D$ with composition is due to a change in the mean square displacement $\langle r^2 \rangle$ occurring in eq 14. One can, however, be doubtful whether $\langle r^2 \rangle/d^2$ is large enough so as to account for the entire effect observed. Thus we were led to another explanation which is formulated above as rule no. 6. As a consequence we conclude that for some mixtures the organic components as well as the water associate preferentially among themselves in their respective low concentration ranges, $x_2 \approx 0, 1$; $x_1 \approx 0.1$. This again leads us to the statement that there is evidence for microheterogeneity in these mixtures. However, from the data reported in ref 22 one fact is difficult to understand. In some cases the organic component shows a variation of $\mathfrak{J}^{(2,2)}D^{(2)}$ with composition; in other cases it does not.

Analyzing the situation one finds immediately that the precise measurement of $\mathfrak{J}D$ as a function of the composition is a very difficult task, because low concentration measurements are of crucial importance. As a further example we report the data shown in Figure 15. They concern the system tert-butyl alcohol-water at $0°$. Figure 15a shows the (total) proton relaxation rate as a function of N_H, the number of protons/
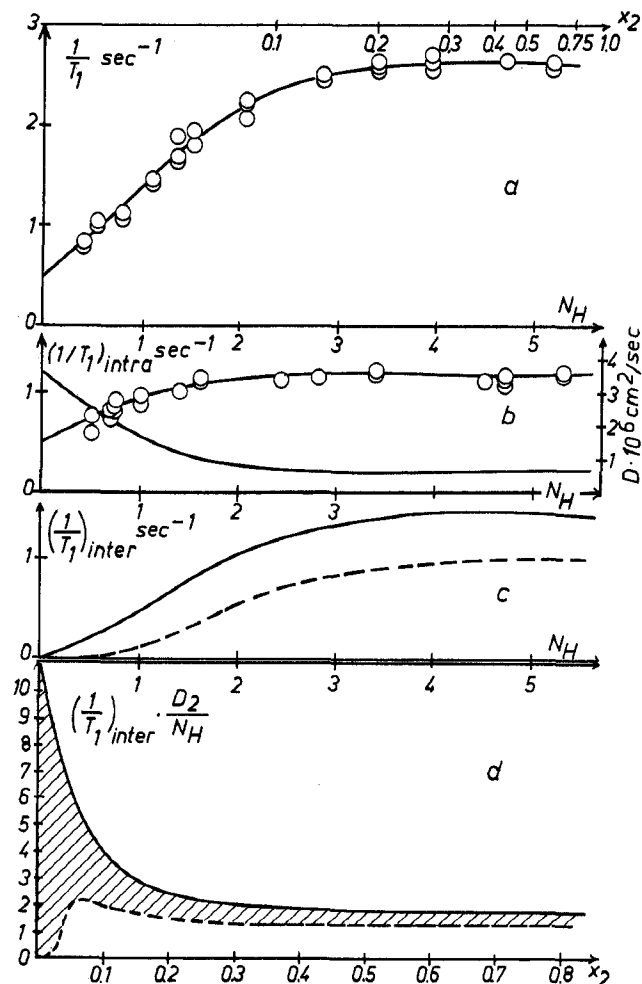

Figure 15. (a) Proton relaxation rate of $(CH_3)_3COD$ in D_2O. (b) $(1/T_1)_{intra}$ for the protons of $(CH_3)_3COD$ in D_2O and self-diffusion coefficient $D^{(2)}$ of $(CH_3)_3COD$ in D_2O. (c) $(1/T_1)_{inter}$ for the protons of $(CH_3)_3COD$ in D_2O. All data are given as a function of N_H, N_H in $10^{22}/cm^3$; temperature $0°$.
(d) $(1/T_1)_{inter}D^{(2)}/N_H$ in 10^{-29} cm^5 sec^{-2}, as a function of the mole fraction x_2.

cm^3, in the system $(CH_3)_3COD + D_2O$. Figure 15b shows the intramolecular relaxation rate of the methyl protons of tert-butyl alcohol. These results are obtained from the deuteron relaxation rate in the mixture $(CD_3)_3COH + H_2O$. By chance $1/T_1$ of the deuteron is by exactly a factor of 10 larger than $(1/T_1)_{intra}$ given in Figure 15b. Furthermore, Figure 15b shows the self-diffusion coefficient of $(CH_3)_3COD$ in D_2O. The solid curve of Figure 15c gives $(1/T_1)_{inter}$, the difference of the two relaxation rates presented in Figures 15a and b. Then $((1/T_1)_{inter}D^{(2)}/N_H) \sim \mathfrak{J}^{(2,2)}D^{(2)}$ is shown in Figure 15d as a function of the mole fraction x_2. The steep increase of $\mathfrak{J}^{(2,2)}D^{(2)}$ as $x_2 \to 0$ yields strong evidence for butyl alcohol-butyl alcohol association. However, considering our experimental error, in particular that arising for the extrapolations to $N_H \to 0$ in Figures 15a and b, the true intermolecular relaxation rate may be as low as shown by the dashed curve in Figure 15d, and the hatched field indicates the uncer-

tainty in $(1/T_1)_{\text{inter}} D^{(2)}/N_H$. One sees that there is evidence for butyl alcohol–butyl alcohol association; however, the definite statement must await better experimental results from improved apparatus for measurements with very weak signals.

5. Summary

We have found essentially three results. (1) Long-lived rigid hydration cages surrounding the solute particles at low concentration are absent. (2) At low concentration of the organic component there is an increase of structure in the solution. (3) There is evidence for solute–solute association in the mixture leading to a certain degree of microheterogeneity.

Appendix

We wish to calculate the error in the correlation time $\tau_c^{(1)+}$ which arises if one erroneously assumes that the exchange of a nucleus between two different environments is slow whereas actually it is fast. For the slow exchange limit we have (see eq 18)

$$\tau_c^{(1)} = \tau_c^{(1)\circ} + \frac{n_h C_2}{55.5} \left(\tau_c^{(1)+} - \tau_c^{(1)\circ} \right) \quad (A1)$$

We divide eq A1 by the correlation time of the pure solvent liquid (here water)

$$\frac{\tau_c^{(1)}}{\tau_c^{(1)}(0)} = \frac{\tau_c^{(1)\circ}}{\tau_c^{(1)}(0)} + \frac{n_h C_2}{55.5} \left(\frac{\tau_c^{(1)+}}{\tau_c^{(1)}(0)} - \frac{\tau_c^{(1)\circ}}{\tau_c^{(1)}(0)} \right) \quad (A2)$$

$\tau_c^{(1)}/\tau_c^{(1)}(0)$ is a function of the concentration; we write the power expansion in C_2

$$\frac{\tau_c^{(1)}}{\tau_c^{(1)}(0)} = 1 + B'C_2 + C'C_2^2 + \ldots \quad (A3)$$

where B', C' are constants. We form $\left\{ d(\tau_c^{(1)}/\tau_c^{(1)}(0)/dC_2 \right\}_{C_2=0}$ and deduce from eq A2 and A3

$$\frac{\tau_c^{(1)+}}{\tau_c^{(1)}(0)} = \frac{55.5}{n_h} \left\{ B' - \frac{1}{\tau_c^{(1)}(0)} \left(\frac{d\tau_c^{(1)\circ}}{dC_2} \right)_{C_2=0} \right\} + 1 \quad (A4)$$

Since according to the same arguments as described

previously before eq 27, we must have $d\tau_c^{(1)\circ}/dC_2 \geqslant 0$, the maximum value of $\tau_c^{(1)+}/\tau_c^{(1)}(0)$ will be

$$\frac{\tau_c^{(1)+}}{\tau_c^{(1)}(0)} = \frac{55.5}{n_h} B' + 1 \quad (A5)$$

This formula has been used for the entries of Table IV, column 3. In the limit of fast exchange we have (see eq 17)

$$\frac{1}{\tau_c^{(1)}} = \frac{1}{\tau_c^{(1)\circ}} + \frac{n_h C_2}{55.5} \left(\frac{1}{\tau_c^{(1)+}} - \frac{1}{\tau_c^{(1)\circ}} \right)$$

or

$$\frac{\tau_c^{(1)}(0)}{\tau_c^{(1)}} = \frac{\tau_c^{(1)}(0)}{\tau_c^{(1)\circ}} + \frac{n_h C_2}{55.5} \left(\frac{\tau_c^{(1)}(0)}{\tau_c^{(1)+}} - \frac{\tau_c^{(1)}(0)}{\tau_c^{(1)\circ}} \right) \quad (A6)$$

Again we substitute eq A3 on the left-hand side of eq A6 and form $\left\{ d(\tau_c^{(1)}(0)/\tau_c^{(1)})/dC_2 \right\}_{C_2=0}$. The result is

$$\frac{\tau_c^{(1)+}}{\tau_c^{(1)}(0)} = \left[1 - \frac{55.5}{n_h} \left\{ B' - \frac{1}{\tau_c^{(1)}(0)} \left(\frac{d\tau_c^{(1)\circ}}{dC_2} \right)_{C_2=0} \right\} \right]^{-1} \quad (A7)$$

Thus, when we divide eq A7 by eq A4 we obtain the final result

$$\frac{\left\{ \tau_c^{(1)+}/\tau_c^{(1)}(0) \right\}_{A7}}{\left\{ \tau_c^{(1)+}/\tau_c^{(1)}(0) \right\}_{A4}} = \left\{ 1 - \left[\frac{55.5}{n_h} \left\{ B' - \frac{1}{\tau_c^{(1)}(0)} \left(\frac{d\tau_c^{(1)\circ}}{dC_2} \right)_{C_2=0} \right\} \right]^2 \right\}^{-1} \quad (A8)$$

We see that with the assumption $\tau_c^{(1)\circ} = \tau_c^{(1)}(0)$, *i.e.*, $d\tau_c^{(1)\circ}/dC_2 = 0$, the error mentioned above is unessential if $55.5B'/n_h \lesssim 0.5$, *i.e.*, $\left\{ \tau_c^{(1)+}/\tau_c^{(1)}(0) \right\}_{A4} \lesssim 1.5$. Indeed, our results in Table IV are of this order. With $55.5B'/n_h \to 1$ and $d\tau_c^{(1)\circ}/dC_2 = 0$

$$\frac{\left\{ \tau_c^{(1)+}/\tau_c^{(1)}(0) \right\}_{A7}}{\left\{ \tau_c^{(1)+}/\tau_c^{(1)}(0) \right\}_{A4}} \to \infty$$

For $55.5B'/n_h > 1$ with $\tau_c^{(1)\circ} = \tau_c^{(1)}(0)$ fast exchange cannot be the correct situation, now for fast exchange in any case $d\tau_c^{(1)\circ}/dC_2 > 0$ must be valid.

Finally, the appropriate formulas for an intermediate rate of exchange between the two limits given here may be found in ref 18 and 19.