Dielectric Spectroscopy of Some Multihydroxy Compound Solutions in Water/Tetrahydrofuran Mixtures

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The dielectric spectra up to 72 GHz have been measured at 20 °C for solutions of glucose and sorbitol (max. 1 mol/l) in the mixed solvent water/tetrahydrofuran (THF) as a function of the THF content (max. volume fraction 0.4). There is no significant difference in the relaxation behaviour of corresponding glucose and sorbitol systems. The spectra of binary water/THF as well as hydroxy compound/water systems show that the respective minor components influence the structure and dynamics of water. The ternary systems hydroxy compound/water/THF, however, exhibit merely a superposition of those effects, thus there is no evidence for an interaction between the hydroxy compound and THF in aqueous environment.

Introduction

Dielectric spectroscopy is a suitable tool to study dynamical and structural circumstances in aqueous solutions. The frequency dependent dielectric properties of water itself are characterized by a microwave dielectric loss $\varepsilon''(\omega)$ which is of Debye type to a surprisingly high degree of accuracy. The relaxation originates probably in the dynamics of the association process via hydrogen bonds rather than in the rotational tumbling motion of single molecules, which under reasonable model assumptions leads to a Debye type spectrum like the single molecule motion but with longer relaxation time [1]. The relaxation strength is a measure for the orientational correlation of the water molecules. Thus the alteration of both relaxation time and relaxation strength on addition of solutes can give insight into dynamical and structural consequences concerning the solvent water, in particular if the solute concentration is low and/or the solute is only weakly polar so that the contribution of water to the experimentally observed absorption can unambiguously be described.

From dielectric relaxation results on aqueous solutions of glucose and polysaccharides [2] it has been concluded that glucose plays a special role among those compounds in fitting into the structure of water such that this structure remains nearly unchanged. It seems worthwhile to extend those studies to the situation where the water properties are already influenced by another solute. For that purpose, tetrahydrofuran (THF), which is weakly polar and has a relaxation time shorter than water, appears to be a promising candidate. In the mixture series water/THF the viscosity passes through a maximum (Fig. 1), indicating remarkable interactions and, as a result of that, a disturbance of the water structure by THF. The aim of the present work is to describe the dielectric spectra of solutions of D(+)-glucose in the water/THF mixed solvent as dependent on the THF content. If the above-mentioned conclusion should be tenable, differences in the relaxation behaviour of glucose/water and glucose/water/THF should be found which should relate to the presupposedly undisturbed/disturbed solvent structure, respectively. As a similar multihydroxy solute, differing not very much in overall size but in shape, D-sorbitol has

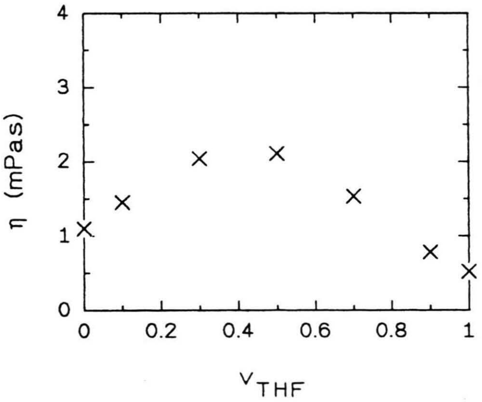

Fig. 1. Viscosity η against composition of water/THF mixtures (volume fraction υ_{THF}), 20 °C.

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been studied, too. Because of the limited solubility of glucose and sorbitol in the water/THF mixture, which decreases with increasing THF content, measurements were restricted to the water rich region. To cover a sufficient water/THF mixture range, the concentration c_M of the multihydroxy compound in the water/THF mixed solvent was kept at $c_M \leq 1$ mol/l.

Experimental

Measurements of the dielectric loss $\varepsilon''(\omega)$ were carried out at 18 spot frequencies between 1 MHz and 72 GHz with different setups specifically designed for high loss liquids [3] (thus less suited for THF rich mixtures). For some THF rich solutions, the static permittivity ε_s (at 2 MHz) and the refractive index n were measured so that the static-optical dispersion step $\varepsilon_s - n^2$ could be obtained. The viscosity was determined with a capillary viscometer. For all measurements the temperature was 20 °C.

Chemicals from Fluka and Merck (purity >99%) were used as obtained.

Results

As representative examples, two absorption spectra $\varepsilon''(\omega)$ of ternary systems are shown in Fig. 2 in normalized form. The following features are worth noting.

(i) The shape of the spectra corresponds closely to the Debye function. Deviations on the low and high frequency side suggest a description by the superposition of two additional, minor spectral components. All experimental data have therefore been fitted by

$$\varepsilon''(\omega) = \sum_{i=1}^{3} S_i \frac{\tau_i \omega}{1 + \tau_i^2 \omega^2} . \qquad (1)$$

The spectral components C_i are indexed in the order of increasing frequency; C_2 is the main component. This is the only one appearing for pure water. Binary water/THF mixtures exhibit a weak higher frequency component C_3. On the other hand, with glucose or sorbitol in water (without THF), the lower frequency component C_1 is the only additional one found.

(ii) The spectra of comparable glucose and sorbitol systems, as in Fig. 2, appear to be undistinguishable within the limits of experimental error not only in normalized form but also with respect to absolute values of relaxation times τ_i and relaxation strengths S_i. For clarity, however, the results for both systems will be shown separately in the following.

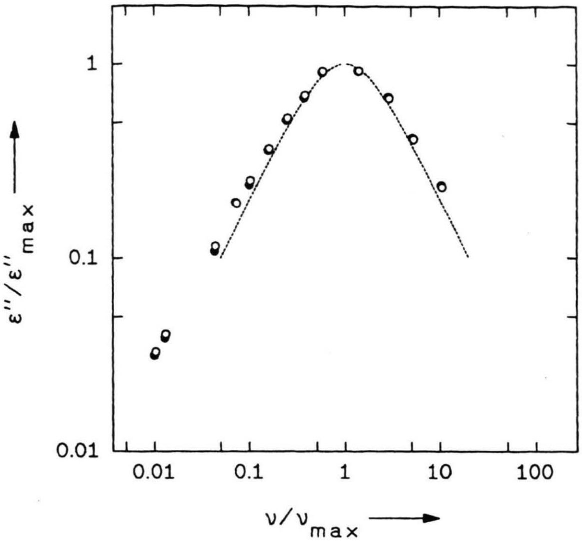

Fig. 2. Normalized relaxation spectra (dielectric loss ε'' against frequency ν) at 20 °C for glucose/water/THF (full symbols) and sorbitol/water/THF (open symbols). Mixture composition (in both cases): $c_M = 0.8$ mol/l, $\upsilon_{THF} = 0.35$. The normalized Debye function is shown for comparison.

The relaxation parameters for the glucose and sorbitol systems are represented in Figs. 3 and 4, respectively.

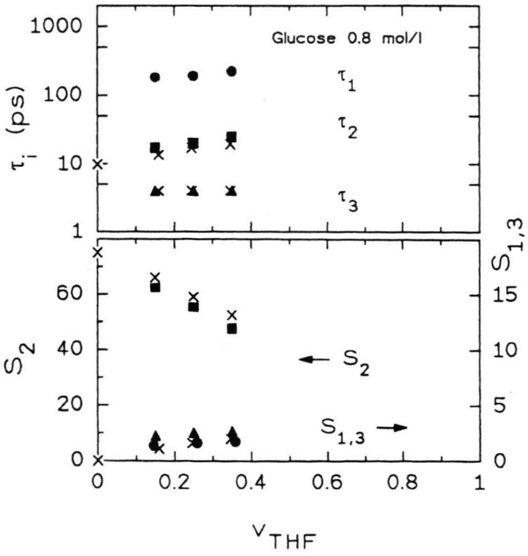

Fig. 3. Relaxation parameters τ_i and S_i against solvent composition (volume fraction υ_{THF}) for water/THF (cross symbols) and glucose/water/THF, $c_M = 0.8$ mol/l (full symbols).

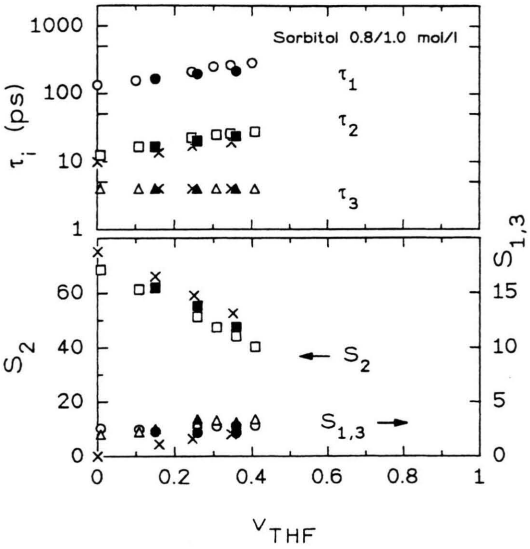

Fig. 4. Relaxation parameters τ_i and S_i against solvent composition (volume fraction υ_{THF}) for water/THF (cross symbols) and sorbitol/water/THF, c_M=0.8 mol/l (full symbols) and c_M=1.0 mol/l (open symbols).

The shortest relaxation time τ_3 corresponds to a spectral component which is not well defined within the experimental frequency range, so it was arbitrarily kept constant.

Figure 5 shows the change of the static-optical dispersion step, given as $\Delta(\varepsilon_s - n^2)$ with respect to pure THF, on the admixture of small amounts of water.

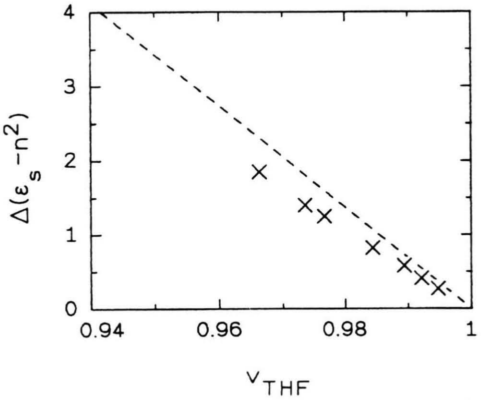

Fig. 5. Static-optical dispersion step $\Delta(\varepsilon_s - n^2)$ of THF rich water/THF mixtures against THF volume fraction υ_{THF}, 20 °C. The difference Δ is taken with respect to pure THF. The straight line indicates a linear extrapolation to pure water.

The composition of the water/THF mixed solvent is expressed in volume fractions υ_{THF} in all cases, since for the hypothetical "ideal" case of two non-interacting mixture components the respective relaxation strengths and dispersion steps would change linearly on the volume fraction scale (provided that volume effects on mixing are negligible). Accordingly, the straight line in Fig. 5 illustrates the 'ideal' case, referring for $\upsilon_{THF} \rightarrow 0$ to the difference of pure water and THF relaxation strengths.

Discussion

In the following an attempt will be made to ascribe the formally obtained spectral components to distinguishable physical processes, though it cannot be excluded that the spectrum as a whole might also be understandable as due to one collective process. Two different interpretation schemes will be taken into consideration, namely relaxation as originating from the tumbling motion of solitary molecules (τ characterizing the rotational correlation time), or from a self or hetero association process (τ characterizing the mean lifetime in the associated state [1]).

Water/THF Binary Mixtures

The relaxation times τ_2 and τ_3 of the two spectral components, required to describe the spectra of water/THF mixtures (Figs. 3, 4, cross symbols) are, as to be expected for pure water and pure THF, respectively (water: 9.5 ps [4]; THF: 5 ps [5]). The relaxation strengths S_2 decreases and S_3 increases nearly linearly with increasing υ_{THF}. Those findings suggest an assignment of the spectral component C_2 to water, and of component C_3 to THF. At first glance, both water and THF seem to behave as quasi independent mixture components. Such a dielectric behaviour is perhaps surprising in view of the interactions indicated by the viscosity, Figure 1. Similar findings, however, have been reported for other aqueous mixtures, e.g. for water/acetonitrile [6], where the viscosity passes through a maximum, too.

The mixture composition corresponding to the viscosity maximum, expressed as water mole fraction, is about $x_W \approx 0.85$. In [2] this water concentration is claimed to be of 'universal' character, indicating that on its water rich side the structure of bulk water is still dominant.

Closer inspection of Figs. 3, and 4 reveals that $\sum S_i$ is somewhat greater than the 'ideal' value in the water rich region, while in the THF rich region (Fig. 5) $\varepsilon_s - n^2$ lies below the 'ideal' line. Both quantities contain essentially the same information, since $\sum S_i \lesssim \varepsilon_s - n^2$. Therefore a point of inflection is to be assumed in the mixture region not studied. These deviations show that the assumption of quasi independent mixture components is not tenable. Rather the admixture of THF leads to an increase in the orientational correlation of water molecules, viz. a structural effect.

It is reasonable to ascribe C_2 to assocation dynamics as in the case of pure water. The increase of τ_2 with υ_{THF} in the water rich region, which parallels that of the viscosity η, is thus a hint at an effect of THF not only on the structure but also on the dynamics of water.

Multihydroxy Component/Water Binary Solutions

The present results on aqueous glucose (and sorbitol) systems agree well with those reported previously for glucose/water solutions [2, 7–9]. Typically, on addition of the multihydroxy component, the main spectral component C_2 is reduced in intensity and slightly shifted towards lower frequencies, while a second lower frequency component C_1 appears.

It seems not unreasonable to ascribe the latter component to the tumbling motion of single solute molecules. Such an interpretation is suggested by a rough estimation of the size of the tumbling entities from τ_1 and η, which can be done on the basis of a significant body of experimental information concerning quasi-rigid polar molecules in the absence of specific interactions [10]. The effective radius estimated that way is about $r_{\mathrm{eff}} \approx 0.53$ to 0.57 nm. This value is in sufficient agreement with the molecular dimensions which, according to space filling molecular models (excluding any hydration), are given by $r_{\mathrm{eff}} \approx 0.50$ and 0.58 nm for glucose and sorbitol, respectively.

On the other hand, it is conceivable that the spectral component C_1 relates to the dynamics of association involving the solute (viz. its hydration) rather than to its rotational motion. In that sense, C_1 is ascribed in [9] 'to modified water of the hydrated glucose complex'. A similar change of dielectric spectra as with the present systems is observed when a dihydric or trihydric alcohol is added to water [11]; the relaxation time corresponding to τ_1 is somewhat shorter in those mixtures but again around 100 ps. Thus, if the spectral component in question should generally by found on addition of small amounts of hydroxy solutes irrespective of their molecular dimensions, its assignment to association dynamics would be preferable.

The shift of C_2, which resembles that in case of water/THF mixtures, is doubtless due to an alteration in the association dynamics of water. It should be mentioned in that context that an alternative description mode can be chosen for C_2, which replaces the one spectral component by two weighted components with fixed relaxation times [12]. In this mode, the term with the longer relaxation time is rapidly intensified on addition of the solute. Both description modes lead to the same conclusion: Obviously the solute exerts an influence on the solvent which appears to be of relatively long range (perhaps collective) character. It remains questionable whether the effective increase of τ_2 could be understood as a stabilization of the water *structure*, as suggested in [2] especially for the case of glucose solutions for reasons of adequate steric requirements. If so, the different shape and size of glucose and sorbitol (not to mention other hydroxy compounds) should result in a more clearly differing dielectric behaviour.

Ternary Mixture Systems

Having considered the binary systems, it is obvious from Figs. 3, 4 that the dielectric relaxation properties of the ternary systems can be described as a superposition of the properties of the binary systems. It is remarkable that there is no evidence for an interference between THF and, on the other hand, multihydroxy compound effects. This means that, in a microscopic picture, solute molecules of both kinds remain well separated by water, in accord with the fact that both glucose and sorbitol are practically insoluble in THF.

Although the water structure appears to be disturbed by the admixture of THF, specific differences in the dielectric behaviour of glucose/water and glucose/water/THF (or the corresponding sorbitol systems) are by no means evident. Thus the present work failed to observe clearcut effects which point to a *special* ability of glucose to fit into the undisturbed water structure.

Acknowledgement

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