Variation of the Dielectric Relaxation Behaviour of Water by Added Alcohols

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The dielectric relaxation of water rich aqueous solutions of ethanol, ehtylene glycol, glycerol, diethylene glycol, 1,2-butanediol, 1,3-butanediol and 1,4-butanediol has been measured at 20 °C. In all cases the fitting of the data by a sum of Debye type spectral components allows for two description modes which can be interpreted as a collective alteration of the water relaxation or, on the other hand, as formation of a microheterogenous solution where "affected" and "unaffected" water becomes discernible.

Introduction

The alteration of the dielectric relaxation parameters of water under the influence of organic solutes is a well known phenomenon and has been measured with a broad variety of dissolved substances [1–3]. In some cases it has been noticed that within experimental uncertainties the alteration can formally be described in several ways, resulting in limiting descriptions which facilitate qualitatively differing physical interpretations [3]. This is a point of general interest with respect to our understanding of the dynamical dielectric properties of water. The one limiting description is by a main relaxation contribution which on addition of the solute shifts its relaxation time, thus suggesting an interpretation as a collective alteration of the water relaxational behaviour. The other limiting description introduces an additional relaxation contribution which appears on addition of the solute, while all relaxation times stay practically constant, so that the different contributions can be interpreted in terms of a microheterogenous solution picture [4].

It seems worthwhile to gain further comparative material in order to find out to what extent these descriptions may be equivalently applicable. In the present paper we report on the dielectric relaxation behaviour of binary, water rich aqueous solutions of various alcohols.

The alcohols are:

1 Ethanol
2 Ethylene glycol
3 Glycerol
4 Diethylene glycol
5 1,2-Butanediol
6 1,3-Butanediol
7 1,4-Butanediol

Our interest centers on the water properties, viz. on the (limiting) behaviour at low alcohol contents where direct individual contributions of the polar solutes can be expected to be negligibly small.

Experimental

The complex permittivity of the liquids was measured at 20 °C in the frequency range from 30 MHz to 72 GHz at 11 fixed frequencies. The data were fitted by a sum of Debye type components C_i as characterized by parameter sets τ_i (relaxation time) and S_i (relaxation strength).

Results and Discussion

One Debye term was found to be sufficient for a satisfactory description of pure water, while for most of the mixtures three terms are required. Their parameters are variable to a certain degree without impairing the fit quality. Within that variability range, it was tried to obey the following conditions:

Description mode (a): The relaxation strength of the main spectral component which develops from the pure water term was put as high as possible. As a result of that, its relaxation time inevitably increases

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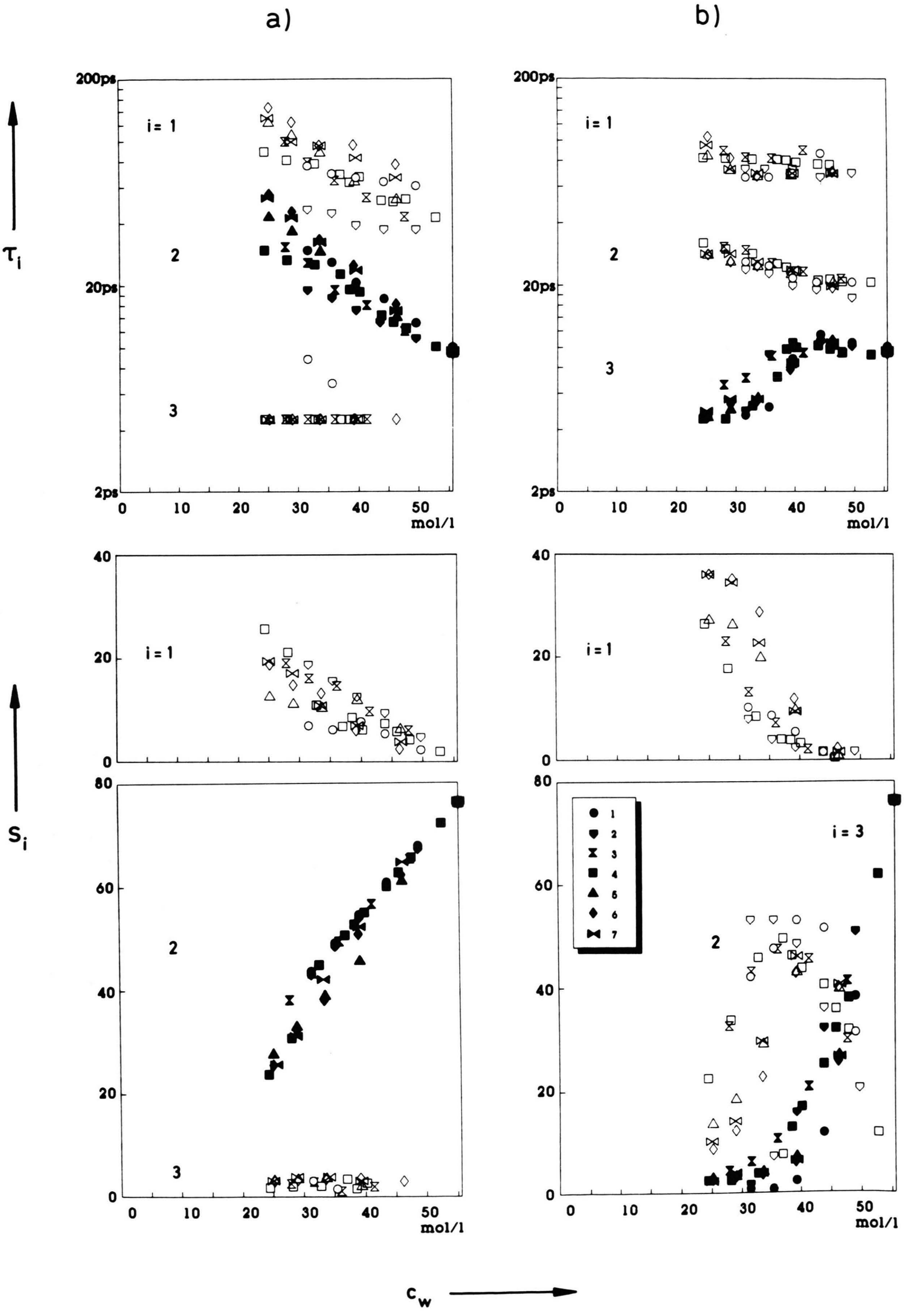
a)
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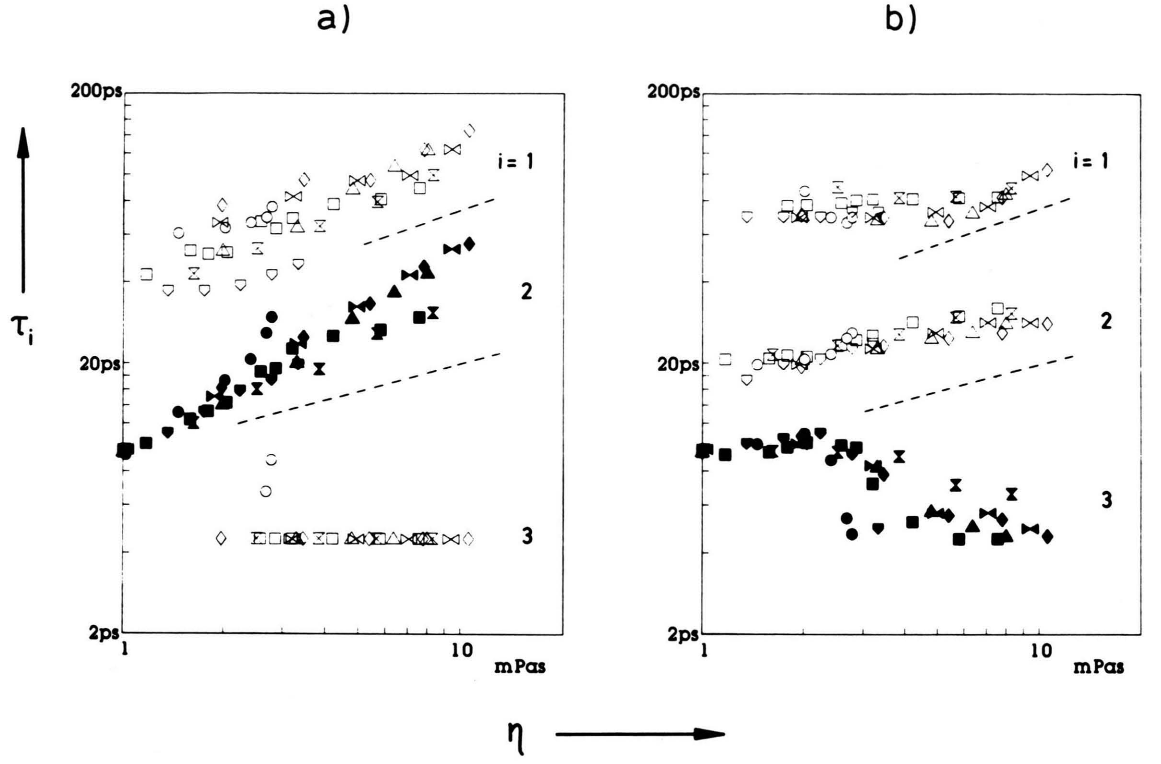

Fig. 2. Relaxation times τ_i from Fig. 1 vs. viscosity η of the solutions (1 mPas = 1 cP). Symbols as in Figure 1. Dashed lines indicate the correlation between τ and η as found for the rotational tumbling motion of single molecules (the two lines correspond to different molecular size which influences also the slope [8]).

with increasing solute content, and two additional spectral components (on both sides of the main component) become necessary to describe the solution relaxation.

Description mode (b): The spectral component corresponding to pure water was given a constant relaxation time as far as possible. In that case its relaxation strength falls off rapidly on increasing the solute content, while again two additional components appear (now both on the low frequency side).

Both description modes are found applicable for all mixtures over the whole concentration range studied (water contents ≥50% vol). They play the role of the limiting descriptions mentioned above.

The results according to conditions (a) and (b) are represented graphically in Figs. 1 a, b, respectively, where the parameters τ_i and S_i for all the systems are compiled in one plot in order to demonstrate that there are some common trends.

For both description modes the spectral components C_2 and C_3 can reasonably be ascribed to water molecules. Component C_1, on the other hand, may be at least partly due to water but is likely to reflect also alcohol relaxation as caused by the interaction with water.

According to description (a), the main spectral component C_2 should result from fluctuations within the network of hydrogen bonded water. In models of fluctuating hydrogen bonds, which were formulated for

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Fig. 1. Relaxation parameters τ_i (log scale) and S_i (lin scale) vs. water concentration c_w for aqueous mixtures with the alcohols **1** to **7** (symbols for the alcoholic component are inserted in the lower right, for numbering see table in the text). Columns (a) and (b) refer to the description modes termed that way

water and alcohols [5–7], the residence time of a molecule in the associated state determines the relaxation time. Under the influence of the alcohols the fluctuations are slowed down. The corresponding increase of τ_2 is relatively steep in comparison to that of the viscosity, as to be seen from Fig. 2a where the τ_i are plotted against the viscosity η. The usually observed η-dependence of rotational tumbling times (obtained from relaxation data on nonassociating liquids [8]) is indicated in that figure for comparison. The relative relaxation strength $S_2\, c_w^*/c_w$ (where c_w denotes the water concentration and the asterisk refers to pure water) stays initially constant on addition of alcohols but decreases below $c_w \simeq 40$ mol/l, approximately where C_3 appears. This spectral component may be assigned to small water aggregations resulting from the decomposition of the water network.

The description according to (b) necessitates the assumption of two kinds of water molecules which, however, are likely to relax in a similar manner. Roughly spoken, there is the 10 ps kind as in pure water (C_3) and an additional 20 ps kind (C_2) caused by the presence of alcohols. Note that the magnitudes of these relaxation times are practically independent of the chemical nature of the alcohol. It is a conspicuous feature that S_3 is followed (on increasing alcohol content) by S_2 as though both were governed by a chemical equilibrium, S_2 passing through a maximum, the position and height of which depends on the alcoholic mixture component. At water concentrations below about $c_w \simeq 40$ mol/l, where τ_3 decreases abruptly, the component C_3 is not any longer ascribable to "unaffected" water but should better be attributed to another kind of relaxing moieties, viz. small aggregations as already considered with description (a). In Fig. 2b the relaxation times from description (b) are again plotted against the viscosity η. Here all τ_i increase weakly as η, but the slope is now less than to be expected for a "normal" rotational tumbling motion.

Attributing C_2 and C_3 from description (b) to "affected" and "unaffected" water, respectively, means in the first instance that they differ in the characteristic times of their dynamical behaviour. Concerning the structural aspect, it should be mentioned that (in both description modes) the total relaxation strength, ΣS_i, is fairly well proportional to the water concentration within the range studied. Thus structural alterations are by no means evident. The decrease of S_3 on addition of alcohols (around $c_w \lesssim 50$ mol/l) may be related to a structural change, as also suggested by IR, neutron and X-ray scattering results [9, 10]. On the other hand one may tentatively assume that the structural conditions of C_2 and C_3 are closely alike. In that case it would be the steep decrease of S_2 at moderate water concentrations ($c_w \lesssim 40$ mol/l) which would definitely indicate the breakdown of the so far maintained water structure. From this an opportunity for water-alcohol interactions may arise, being discernible as C_1, a component which does not become noticeable (at least in description (b)) until C_2 and C_3 vanish.

Comparing both description modes it should be noted that for the ethanol solutions the general trend of the parameters is better described by mode (b) rather than mode (a). This and some further findings (e.g. the only slight η-dependence of the relaxation times, and the reasonable applicability of an equilibrium picture) may be considered cautiously in favour of an interpretation along the description mode (b).

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