Dielectric Relaxation in Binary and Ternary Mixtures of Ethanol, Water, and Benzene or n-Hexane

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The complex permittivity of the partially miscible systems ethanol-water-benzene and ethanol-water-n-hexane has been measured in the frequency range from 20 MHz to 36 GHz at 20 °C. The results are described as superposition of Debye-terms, which are considered as physically significant and are ascribed to (i) higher, ill-defined, fluctuating self- and hetero-associates (main term), (ii) associates of lower order, relaxing by rotational tumbling, (iii) free molecules. The demultimerization by benzene appears to be more effective than by hexane.

Introduction

The dielectric relaxation in liquids which associate via hydrogen bonding, in particular alcohols and water, has widely been investigated during many years. There is little doubt that the dominating low frequency absorption of alcohols is caused by fluctuations within the network of hydrogen bonds rather than by rotational motion of single molecules or quasi rigid complexes [1–3]. There is, however, still some debate on the details of the mechanism [4–6]. To further elucidate it, mixtures of alcohols with other liquids have often been studied [7–13]. Alcohol-water mixtures had been considered less frequently, but growing interest is now taken in those systems [14–19].

The present work was undertaken to obtain some additional information on the dielectric relaxation behaviour of the alcohol-water system by diluting it with a third, nonpolar liquid. We have selected ethanol (E) as a short chained alcohol which is miscible with water as well as with different hydrocarbons, and have chosen benzene (B) and n-hexane (H) as aromatic and aliphatic nonpolar component, respectively. The ternary systems both are only partially miscible, so mostly alcohol rich ternary mixtures will be considered, apart from the binary ethanol-nonpolar and ethanol-water systems. We did not strive for measurements immediately at the miscibility gap, and possible special effects in that region are not within the scope of this work.

Experimental

Measurements of the complex permittivity were made at 9 spot frequencies between 20 MHz and 36 GHz at 20 °C. In the MHz region, a VHF bridge was employed, while above 100 MHz we used the resonator perturbation technique. At 36 GHz, the reflection of a sample cell was measured directly. The measuring system is suited in particular for highly absorptive liquids, which prevented us from studying mixtures rich in the nonpolar component. In the suitable region, the measurements are accurate to a few percent at all frequencies.

Results

We shall consider the results in terms of $\varepsilon''(\omega)$, which means the measured imaginary part of the permittivity corrected for the conductivity contribution. Since in not any case a Debye-type behaviour is obeyed, the data are fitted by a sum of Debye-type spectral components (C_i):

$$\varepsilon''(\omega) = \sum_i S_i \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2}. \tag{1}$$

Instead of the dispersion step S_i it is useful for the ternary systems to consider the normalized intensity parameter $\sigma_i = S_i / v_p$, where v_p is the volume fraction of the polar component(s) of the mixture. Thus the results will be expressed in short form by parameter sets τ_i, σ_i.

All absorption data show a predominant maximum well within the range of measuring frequencies (Figure 1). Asymmetries point to the need of a
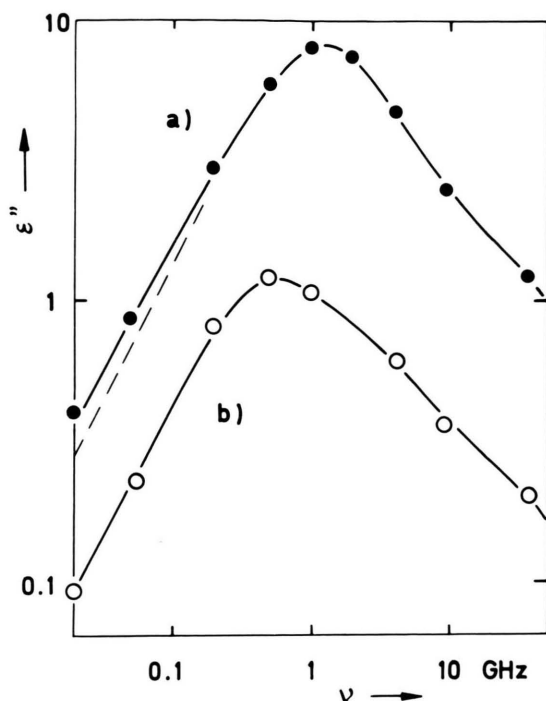
Fig. 1. Log-log plot of the imaginary part ε'' of the permittivity against frequency v for two exemplary systems. a) Ternary EWH system with $x_W = 0.2$, $x_H = 0.1$ (the dashed line indicates, for comparison, the $\varepsilon'' \sim v$ slope). b) Binary system EH with $x_H = 0.6$.

second term, normally on the high frequency side with a relaxation time slightly below 10 ps, which, though weak, can relatively unambiguously be identified provided its maximum is still within the limits of experimental frequencies. In some cases, however, this additional term is not sufficient. Two examples for that are given in Figure 1. In Fig. 1 a, the slope of the low frequency side is clearly less than proportional to the frequency, which points to the existence of a term with long relaxation time ($\approx 10^3$ ps). In Fig. 1 b, on the other hand, the gradual decrease of the high frequency side requires two additional terms, the "normal" one with a relaxation time below 10 ps, and an intermediate one in the $30-60$ ps range.

The occurrence of those different terms led us to fit the data generally by making allowance of 4 spectral components: C_1 in the 10^3 ps range, C_2, as the main term, determined by the maximum position fairly reliably, C_3 in the intermediate range, and C_4 below 10 ps. The parameters obtained for the subordinate components have a wider variabil-

ity range, and the results become to a certain degree consequences of the constraints. For example, a component C_3 with, say, $\tau_3 = 30$ ps and a component C_4 with $\tau_4 = 8$ ps may in the presence of the main component C_2 become undistinguishable from one component in the 16 ps region, so that the partition into two components follows merely from the condition that the high frequency contribution should not exceed 10 ps. It must be stressed, however, that this ambiguity depends in particular on the position of the maximum and does not generally occur, e.g. not for situations such as Figure 1 b.

The sum of the dispersion steps obtained, $\sum S_i$, was checked against the difference of static permittivity and squared refractive index, $\Delta = \varepsilon_s - n^2$. For neat ethanol, $\sum S_i$ is ca. 10% less than Δ. The "missing" part is smaller in all other cases and tends to vanish on dilution with the nonpolar component. Consequently, minor contributions at frequencies beyond the experimental maximum are to be expected, which possibly give an additional uncertainty to C_4.

The parameter sets τ_i, σ_i obtained in this way are graphically presented in two manners. Figure 2 shows the results for the three binary mixture series and two exemplary ternary mixtures with constant mole fraction of the nonpolar liquid. Figures 3, 4 represent parameters for the ethanol rich part of the Gibbs triangle ($x_E > 0.5$).

Discussion

The spectral components have so far no more than a formal meaning. One may, however, hope to understand them in terms of the dynamical behaviour of certain polar species, that is "free" molecules and self- as well as hetero-associates. Though we do not intend to consider detailed association models, we need a qualitative description of association, regardless of the physical interactions which are really operative. For that purpose, some simplifying assumptions will be made in the following. They will allow for a qualitative interpretation of the relaxation parameters, especially the relaxation time, within the framework of the model.

Some remarks on relaxation time interpretation

In view of the upper experimental frequency limit, the possible contributions from fast intra-
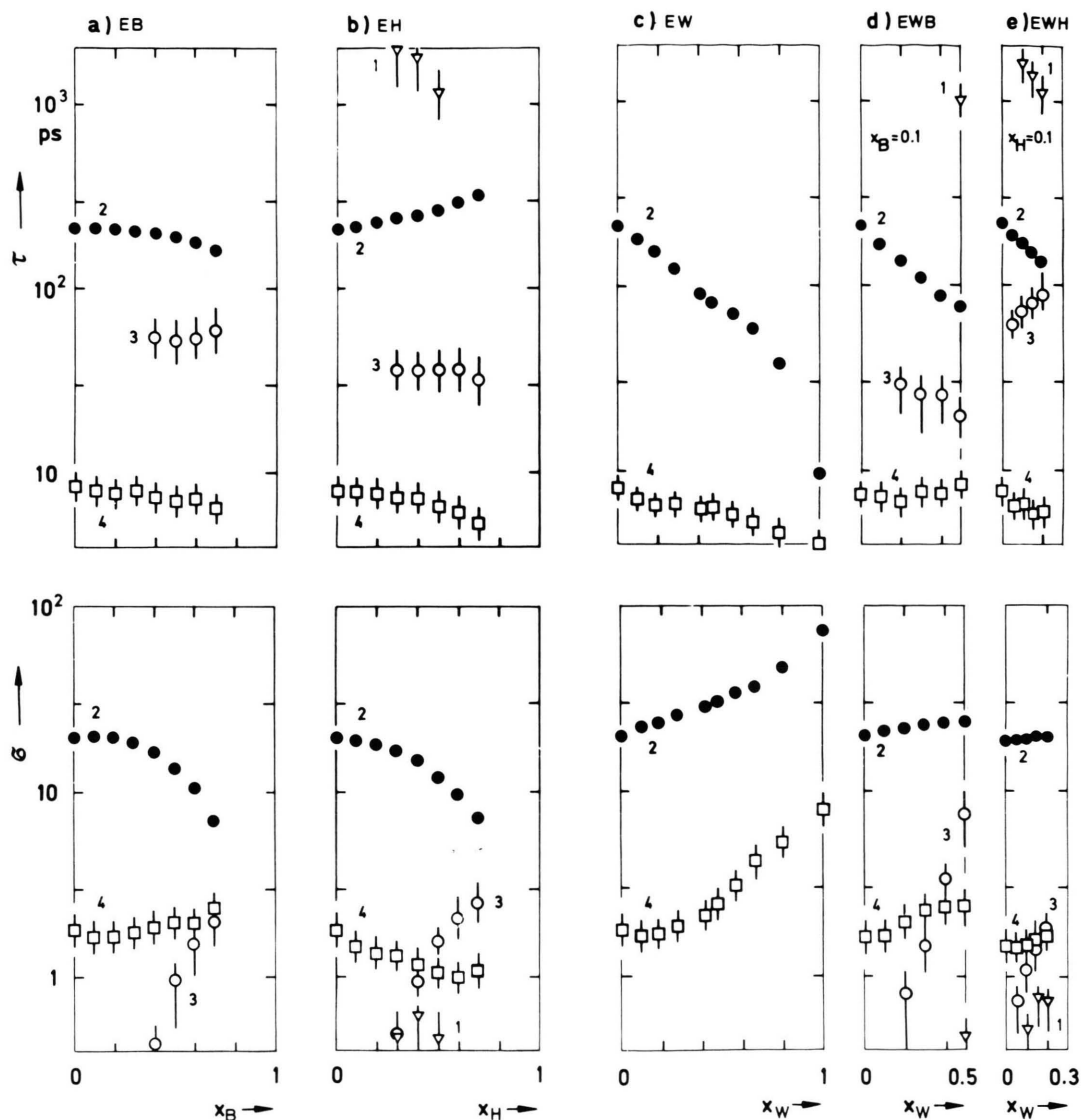
Fig. 2. Plot of log τ_i and log σ_i against mole fraction x of one mixture component. Binary systems: a) ethanol-benzene, b) ethanol-hexane, c) ethanol-water. Ternary systems with constant mole fraction (0.1) of the nonpolar component: d) ethanol-water-benzene, e) ethanol-water-hexane.

molecular motions (OH group of ethanol), which presumably contribute to the "missing" components, can be disregarded. Thus both kinds of polar molecules may be considered as quasi rigid ones with permanent dipole moments, by this neglecting also the small moment alterations occurring on formation of hydrogen bonds, as possible relaxation process [5]. The frequency dependence of $\varepsilon''(\omega)$ results from the fluctuation of one component of the

moment vector of these molecules. Now, for simplicity, only two dynamical states of any individual molecule will be distinguished [13, 20]: The "free" state, where the single molecule performs rotational tumbling, characterized by a correlation time τ_f^*, and the associated state, where the molecule is linked to one or more other molecules and experiences a common rotational correlation time τ_a. The latter will depend on composition and asso-
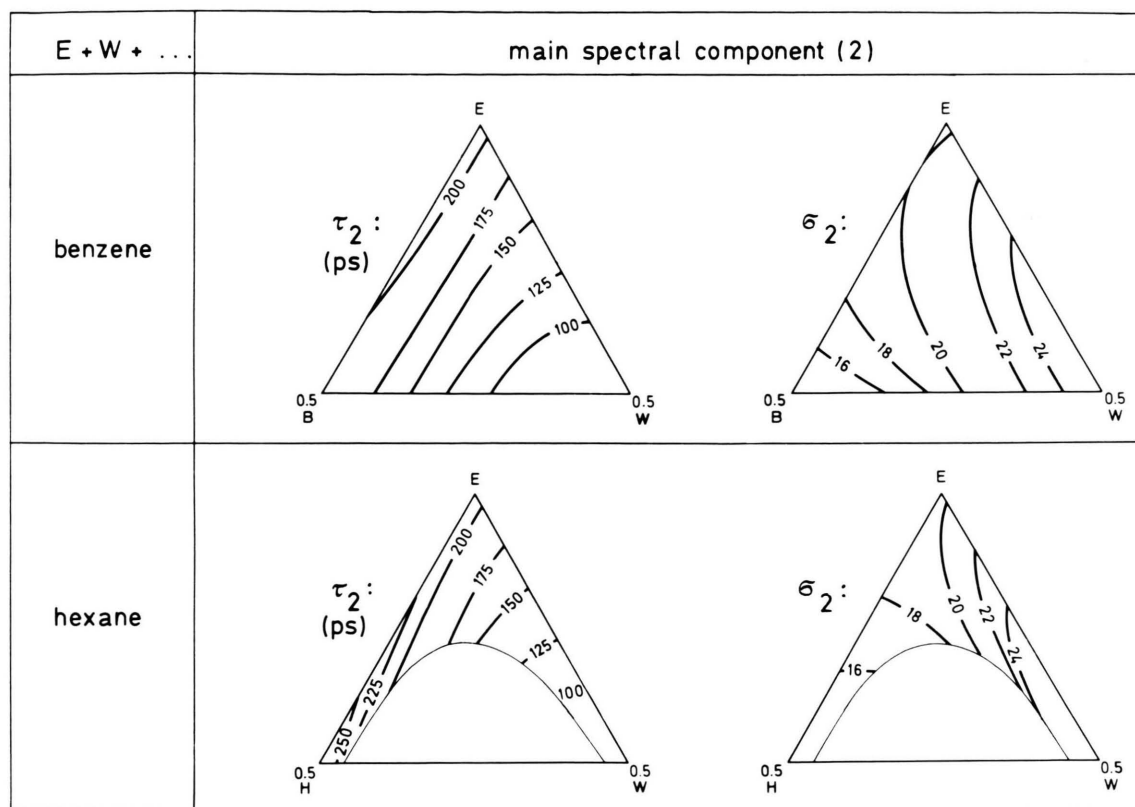
Fig. 3. The main component C_2 in ethanol rich ternary mixtures ($x_E > 0.5$): Relaxation time τ_2 and intensity parameter σ_2.

ciation number of the special aggregation, $\tau_a \to \infty$ being the simplest assumption for large, thus practically motionless associates. The contribution of an associated molecule to the fluctuation spectrum depends further on its mean lifetime T_a in the associated state, and the fraction of time, γ_f or $\gamma_a = 1 - \gamma_f$, spent in its "free" and associated state, respectively.

We presuppose that free molecules give rise to a Debye-type spectral component with relaxation time

$$\tau = \tau_f^*. \qquad (2)$$

Molecules with very short-lived associated phases ($T_a \ll \tau_f^*/\gamma_f$; rapid exchange) will cause one spectral component with a relaxation time τ according to

$$\tau^{-1} \approx \gamma_f \tau_f^{*-1} + \gamma_a \tau_a^{-1}. \qquad (3)$$

In the case of long-lived associated phases ($T_a \gg \tau_f^*/\gamma_f$; slow exchange), two spectral components will appear, whose relaxation times τ_I and τ_{II} are to be

obtained from

$$\tau_I^{-1} \approx T_a^{-1} + \tau_a^{-1}, \qquad (4a)$$

$$\tau_{II} \approx \tau_f^*. \qquad (4b)$$

In both cases, (3), (4a), the associated rotational correlation time τ_a is the upper limit for the relaxation time τ.

For associates obeying (4), there are the following extreme situations. A molecule may be a long-lived member of a small associate, then $\tau \approx \tau_a$. Or it may be a (relative to τ_a) short-lived member of a large associate, then $\tau \approx T_a$. Thus the relaxation time can be controlled as well by the rotational correlation time τ_a as by the associated lifetime T_a.

The binary mixtures ethanol-benzene and ethanol-hexane

These mixtures, where only self-associated must be taken into account, offer a possible explanation of the different spectral components as originating
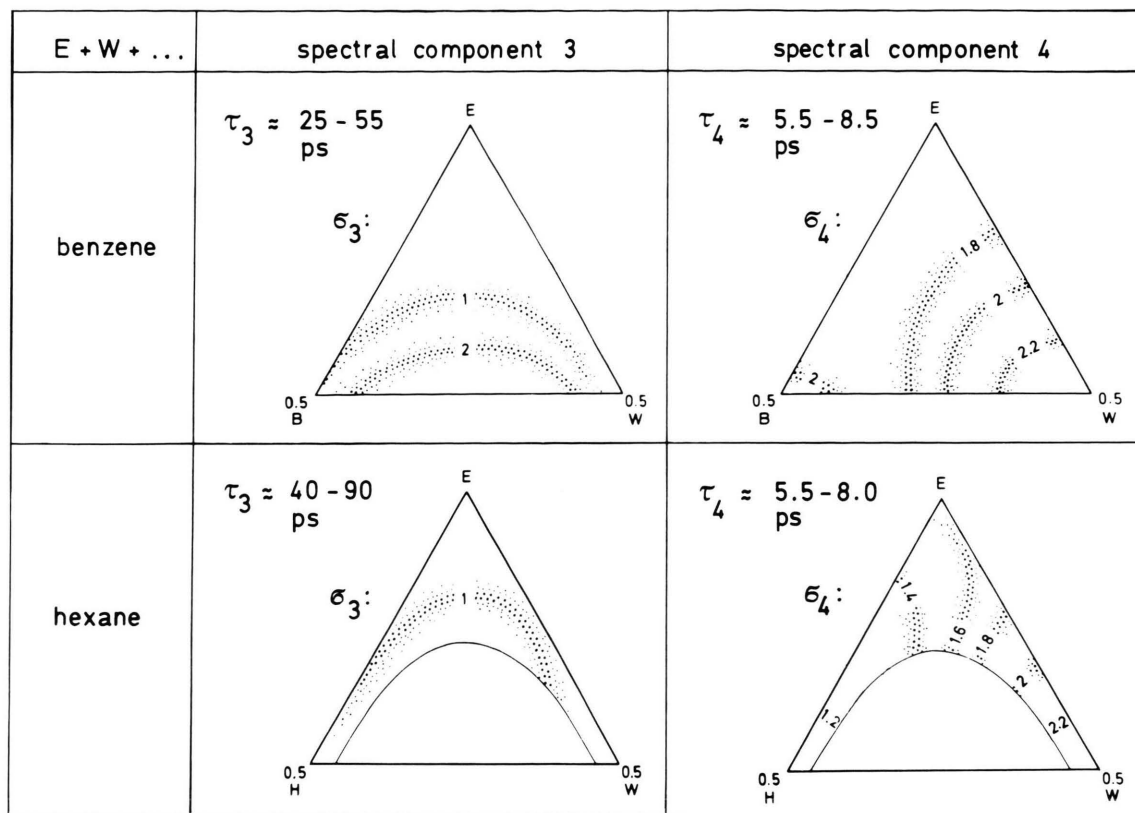
E + W + ...	spectral component 3	spectral component 4
benzene	$\tau_3 \approx 25 - 55$ ps	$\tau_4 \approx 5.5 - 8.5$ ps
hexane	$\tau_3 \approx 40 - 90$ ps	$\tau_4 \approx 5.5 - 8.0$ ps

Fig. 4. Sketch of relaxation time τ_i and intensity parameter σ_i of the weaker components C_3 and C_4 in ethanol rich ternary systems.

from several distinguishable ethanol associates, in addition to free molecules.

Particularly informative is the EH system, since here all four components are observed. Figure 2b shows that the intensity parameter σ_1 of the weakest component C_1 passes through a maximum on dilution (increasing hexane content). Additional (less accurate) measurements at hexane contents higher than those represented in Fig. 2b, indicate that σ_3 behaves in a similar manner, while σ_4 increases ultimately. This order of maximum appearance of the four components, $2-1-3-4$, resembles a four species association equilibrium, where C_2 originates from aggregations with the highest association number, while C_4 is due to monomeric molecules.

Adopting tentatively this assessment, the question may be raised as to whether it is in accordance with the observed relaxation times. This is the case for τ_4, which is roughly in the order to be expected for

single ethanol molecules in a surrounding of the given viscosity. Concerning the other spectral components, let us assume for the moment that they are due to relatively long-lived species, which may be imagined as quasi rigid associates (dimers, higher multimers), whose relaxation is governed by rotational tumbling. By comparison with other relaxation data (mainly those obtained from dilute solutions of rigid molecules) one gets a rough estimation of the effective radius of the tumbling entities. E.g. with $\tau_3 \approx 30$ ps (mean value for EH) and the viscosity of these mixtures one estimates an effective radius of ca. $0.45-0.5$ nm. This can plausibly be ascribed to an open ethanol dimer. (Note that cyclic dimers, if symmetric, cannot be observed. For comparison it may be mentioned that in the similar case of methanol open dimers are calculated to be more stable than cyclic ones [21]. Also with solutions, NMR results indicate that the former type prevails [22].) In the same way it follows that C_1

(where $\tau_1 \approx 10^3$ ps) could be related to further rigid aggregations of still fairly low association number, say up to tetramers.

So far, long-lived and quasi rigid aggregations could reasonably be assumed. The rotational correlation time of higher order associates, however, will become so long that they should be regarded as motionless, with the consequence that now the associated lifetime T_a must be considered as governing the relaxation process. It might be that T_a is considerably shorter than the tumbling time, so that the order of relaxation times need not correspond to the order of association stages.

Since the observed relaxation times are consistent with the above assessment, we shall generally (also in the case of the ternary mixtures) interpret the spectral components accordingly. Thus the main component C_2 will always be ascribed to higher associates, and its relaxation time τ_2 will be regarded as a measure for the associated lifetime. The subordinate, only in some cases observable components C_1 and C_3 will be attributed to relatively long-lived associates of low order (possibly down to dimers). Finally, component C_4 will be ascribed to free molecules and may comprise unresolved contributions from ethanol as well as water.

There are some remarkable differences between the EB and EH series of mixtures (Figure 2a, b). With hexane as nonpolar component, we have an increase of τ_2 on dilution, resembling cyclohexane mixtures [8], while benzene gives a decrease. The intensity parameter σ_4 in hexane is smaller than in benzene, while the opposite holds for σ_3. According to the above interpretation scheme, this indicates that the tendency towards association of ethanol is more pronounced in hexane rather than in benzene mixtures, in other words, the demultimerization of ethanol by benzene is more effective than by hexane. Since this behaviour is well known from studies by a number of other methods, it corroborates the adopted interpretation additionally.

Ternary and binary mixtures containing ethanol and water

We turn now to the mixtures with two polar components. It is appropriate to consider the ternary systems by keeping the mole fraction of the nonpolar component constant (sections parallel to the EW edge in Figures 3, 4). Two exemplary sets of

relaxation parameters are represented in Fig. 2d, e, which may be compared with the binary EW system, Figure 2c.

The main spectral component C_2 exhibits a striking feature at low and intermediate benzene or hexane contents. Its relaxation time τ_2 depends only on the W/E ratio but is practically unaffected by the presence of the nonpolar mixture component. This is shown in Fig. 5, where the W/E ratio is expressed by $\xi_W = x_W/(x_W + x_E)$. Such a behaviour suggests that the relaxing aggregations should be composed merely from ethanol and water molecules, thus excluding nonpolar ones. The shortening of τ_2 with increasing water fraction is indicative of a decreasing mean lifetime of both ethanol and water molecules in these associated states. The slope in Fig. 5 at $\xi_W \approx 0$ indicates an appreciable shortening effect of only minor water quantities.

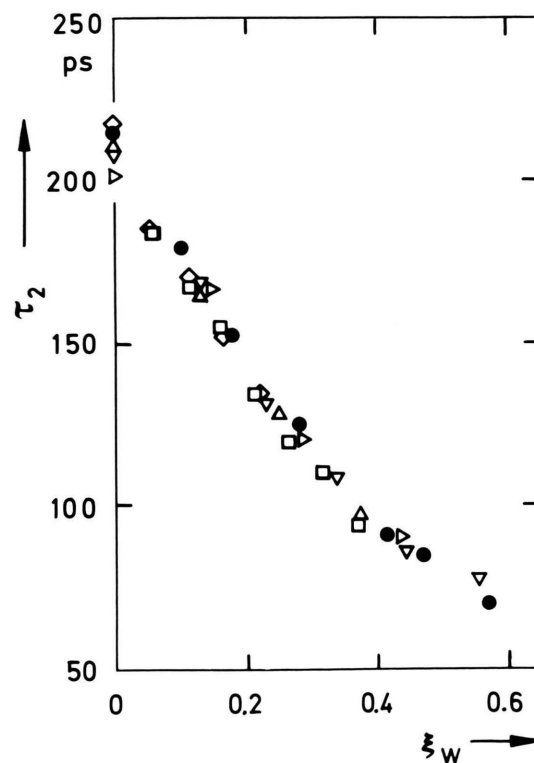We recall that our model describes the "associated" state simply as a certain immobilization. It is

Fig. 5. Relaxation time τ_2 of the main component against water fraction $\xi_W = x_W/(x_W + x_E)$ at constant mole fraction of the nonpolar component. ●: Binary EW; ▽: EWB, $x_B = 0.1$; △: EWB, $x_B = 0.2$; ▷: EWB, $x_B = 0.3$; □: EWH, $x_H = 0.05$; ◇: EWH, $x_H = 0.1$.

reasonable to presume that this is caused by hydrogen bonding. However, it should be stressed that the dielectric results, in isolation, cannot force such a conclusion on the nature of the interaction, and that perhaps further, e.g. hydrophobic effects [11] may likewise play a role.

An interpretation of the main intensity parameter σ_2 will be somewhat dubious, as generally in the case of associates whose stoichiometry is not known or not at all well defined. In principle, it holds always $S_i \sim c_i \langle \mu_i^2 \rangle$, where c_i is the (molar) concentration and μ_i the moment of the *associate* in question, but neither c_i nor μ_i can be specified for ill defined aggregations. There is, however, a peculiarity with the EW system. Here, S_2 changes nearly linearly on the volume fraction scale. A comparison of S_2 values shows that the above mentioned proportionality is met for both neat liquids (and, consequetly, the mixtures too) by taking for c_2 and μ_2 the *single* (monomeric) molecule values, though these are surely inapplicable to that case. This inconsistency is resolved by the assumption that (i) the mean squared moments per molecule of the associates under consideration obey a mixture rule but do not further depend on their composition and size, and that (ii) those associates are by far dominating. Possibly (i) may happen if we have a kind of mixed associates with neither definite composition and association number, nor regularly ordered molecular moment vectors.

Retaining this consideration, the intensity parameters σ_2 of the ternary mixtures may be discussed however. For a given W/E ratio, we find that σ_2 decreases on addition of the nonpolar mixture component, the decrement for hexane being approximately twice that for benzene. This lowering of σ_2 is like to be caused by a decrease of the association number and (or) the concentration of the associates responsible for C_2.

The latter assumption is substantiated by the behaviour of C_3. Its intensity parameter, σ_3, in contrast to σ_2, increases on addition of the nonpolar substance. However, both effects do not compensate, as seen from Fig. 6, where all associate contributions, including C_1, are taken into account. Since we supposed before that the large aggregations exhibit approximately unaltered mean squared moments per molecule, it should be concluded that the lower order associates show a smaller (though not vanishing) value of that quantity.
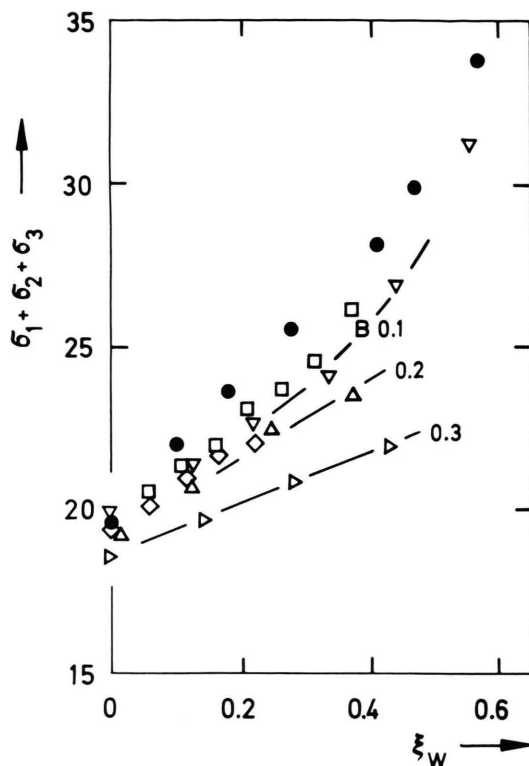

Fig. 6. Sum of associate intensity parameters, $\sigma_1 + \sigma_2 + \sigma_3$, against water fraction ξ_W. See legend to Figure 5.

In a qualitative view, the intensity parameters indicate an increasing amount of lower associates as the concentration of the nonpolar component is increased. It was inferred before that the main aggregations exclude nonpolar molecules. Instead of a participation in these aggregations, the nonpolar component seems to pull off polar molecules from the aggregations, which then appear as lower associates rather than monomeric molecules.

Some additional details to that picture may be contributed from the relaxation time τ_3. As seen from Fig. 2 d, e, τ_3 remains in a region between τ_2 and τ_4 in the case of benzene, but is shifted rapidly towards τ_2 in the case of hexane, so that a discrimination between C_2 and C_3 becomes meaningless. Provided that the relaxation of the smaller associates is governed by rotational tumbling, the latter behaviour may be ascribed to a growing association number, while the former points to a roughly unaltered association number though water is added. In comparison it follows again that the tendency towards association is more pronounced in

the hexane rather than the benzene mixtures, now comprising ethanol as well as water, which probably form both self- and hetero-associates.

The question as to what extent self- or hetero-association may be involved cannot be answered for the weak components C_1 and C_3, because the relaxation parameters are too uncertain. Concerning the main component C_2, on the other hand, the assertion of its Debye-type implies that ethanol and water do not obey specific relaxation mechanisms but exhibit some kind of joint or cooperative behaviour. Their larger associates of the ill defined type, which actually are fluctuating aggregations, may be considered as transient hetero-associates. These obviously are by far dominating in the binary EW system, where only two spectral components are needed at all compositions. Following our relaxation time interpretation, component C_4 will accompany the main component C_2, according to (4a, b), with a certain necessity.

Conclusion

Summing up, the finding of components which can reasonably be ascribed to distinct associates of low order may be considered the principal result of this work. It confirms a hypothesis given recently by Bertolini et al. [15]. The picture of dielectric relaxation in ethanol, water and their mixtures is, from a chemical point of view, somewhat more plausible if it comprises associate types of different order.

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