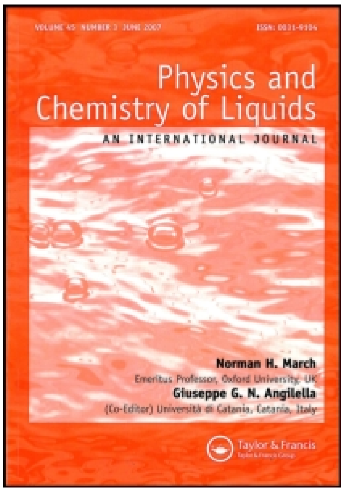

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A DIELECTRIC RELAXATION STUDY OF SOME LIQUID DIHYDRIC ALCOHOLS AND THEIR MIXTURES WITH WATER

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The dielectric relaxation spectrum is measured at 20°C at frequencies up to 72 GHz for the following alcohols and their aqueous mixtures over the whole mixture range: 1,2-ethanediol; 1,2- and 1,3-propanediol; 1,2-, 1,3-, 1,4- and 2,3-butanediol; for comparison moreover: ethanol; diethyleneglycol and 1,2,3-propanediol. It is found possible to analyze the spectra into discrete spectral components according to one and the same scheme in all cases. Three mixture ranges can be distinguished on the volume fraction scale, the parameters of the intermediate and, particularly, the water rich region being rather insensitive to the nature of the alcoholic component.

KEY WORDS: Binary mixtures, dielectrics, hydrogen bonding.

1 INTRODUCTION

Dielectric relaxation is related to the polarization fluctuations of a macroscopic sample. According to the fluctuation-dissipation theorem the frequency dependence of the (negative) imaginary part of permittivity, $\varepsilon''(\omega)$, is determined by the fluctuation spectrum. Consequently the dielectric spectrum reflects the microscopic stochastic motion of those constituents of the sample matter which are polar. Information on structure and microdynamics can thus be gained from measurements of dynamic dielectric properties. This is, for example, the case with protic liquids, where dielectric spectroscopy has thrown insight into the motional conditions of molecules forming hydrogen bonds.

Alcohols, in particular, have been subject of frequency dependent dielectric measurements since the initial stage of relaxation spectroscopy[1]. Their long relaxation times did allow for informative studies already when technical development facilitated measurements only over a limited range of relatively low frequencies (≤ 100 MHz), while nowadays broad band relaxation spectra are accessible covering the whole dielectric absorption range up to FIR. For alcohols it became evident rather early from the properties of the neat substances in comparison to their solutions in non-polar solvents that not the single molecule rotational tumbling process but the correlated motion which is governed by short range intermolecular forces (that is, in quite a broad sense, by self-association), is responsible for the principal relaxation contribution. Remarkably enough, its shape is often found to be close to the Debye type. Concerning a detailed picture of microdynamics which may account for that fact there is still some debate in the literature. In this regard the question of an appropriate formal description of the dielectric spectra (i.e. either by a continuous distribution or by a superposition of discrete components) is closely related to the physical interpretation of the relaxation process.

Binary mixtures of alcohols with water are a special group of liquids which continuously attract attention since some properties of these complex systems, where self and hetero-effects of hydrogen bonding are feasible, are not yet well understood. Dielectric relaxation studies of those mixtures using various alcohols have been reported[2-17] which again touch on the above-mentioned problems. As for the pure mixture partners, the experimental absorption data may be described either by a single spectral component (most applying the Cole-Davidson function[14] for that purpose) or some superimposed components (usually of Debye type[9]). Naturally the former analysis scheme suggests an interpretation in terms of collective motional processes while the latter may preferably be interpreted in terms of distinguishable relaxators. To mention an example for the latter point of view, for the water rich mixture region spectral components have been distinguished as arising from 'unaffected' and, on the other hand, from affected or 'hydration' water[18,19]. Specific effects such as hydrophobic hydration have been taken into consideration, too[13,16].

Most of these dielectric studies were carried out with monohydric alcohols. As yet, di- and trihydric alcohols and their aqueous mixtures, which, depending on the molecular geometry, may permit a variety of inter- and even intra-molecular hydrogen bonds, have scarcely been investigated[10,20-29]. The work reported here deals with aqueous mixtures of some short chain dihydric alcohols. We have, over the whole mixture range, measured the dielectric spectra of

1,2-ethanediol (ethyleneglycol, ED),
1,2- and 1,3-propanediol (PD),
1,2-, 1,3-, 1,4- and 2,3-butanediol (BD).

It is a major objective of this study to test whether the dielectric properties of these chemically similar mixture systems can systematically be described in the same way and, if so, whether a correlation of relaxation parameters to steric factors may be revealed. In order to broaden the basis of comparison, we have also looked at corresponding aqueous systems using

ethanol (E),
diethyleneglycol (DEG),
1,2,3-propanetriol (glycerol, PT).

2 EXPERIMENTAL

The total complex permittivity $\varepsilon'(\omega) - i\varepsilon''_{tot}(\omega)$ was measured at 11 to 13 spot frequencies ranging between 5 MHz and 72 GHz with an accuracy of a few percent, using different lumped circuit, coaxial and waveguide apparatus. The dielectric spectrum is primarily considered in terms of dielectric loss, viz. the imaginary part $\varepsilon''(\omega)$, which means the value $\varepsilon''_{\mathrm{tot}} - \varepsilon''_{\mathrm{c}}$ as already corrected for the conductivity contribution $\varepsilon''_{\mathrm{c}} = \kappa/(\varepsilon_0\omega)$, where κ is the conductivity and ε_0 the permittivity of empty space. The static permittivity ε_s was determined by extrapolation of the real part $\varepsilon'(\omega)$ to low frequencies. Viscosity η, density ρ and refractive index n_{D} were measured in addition. All measurements were carried out at 20°C.

Chemicals from Aldrich, Fluka, Merck and Riedel-de Haën were used as obtained. No attempts were made to gain information on the stereoisomeric composition in the case of chiral compounds, since from the dielectric results on other chiral molecules[30] this is expected to induce only negligible effects. (At the most, diastereomers of 2,3-butanediol might be suspected to differ somewhat in their tumbling motion due to conformation dependent moments of inertia).

3 RESULTS AND DISCUSSION

For most of the systems studied the dielectric absorption spectrum $\varepsilon''(\omega)$ appears to be roughly of Debye character with a slight broadening towards the high frequency side, which suggests to fit a Cole-Davidson (CD) function to the data. Closer examination, however, reveals systematic differences in the higher frequency region. There the fit quality can significantly be improved by employing a superposition of Debye type spectral components. These findings lead us to proceed in two stages. First, the Cole-Davidson fitting results shall be regarded since they are best suited to formally describe the principal (lower frequency) relaxation contribution, which is most important for understanding hydrogen bonding effects, by an only small number of parameters which can be determined with small variance. Second, some more detailed analyses will be carried out employing a superposition of discrete spectral components which then will be appropriate for the whole experimental frequency range. The latter fits will be based on certain assumptions which will result from the first stage considerations.

3.1 *CD Analysis for Principal Relaxation Region*

By fitting the imaginary part of the complex CD function

$$\varepsilon - \varepsilon_\infty = \frac{S_{\mathrm{CD}}}{(1 + i\tau_{\mathrm{CD}}\omega)^\beta} \tag{1}$$

to the experimental ε'' data one obtains the CD relaxation time τ_{CD}, the relaxation strength S_{CD} and the CD distribution parameter $\beta < 1$ ($\beta = 1$ for Debye behaviour). The position of the absorption maximum $\varepsilon''_{\max}$ as given by the (circular) frequency $\omega_{\max}$ can equivalently be characterized by an 'effective' relaxation time $\tau_{\mathrm{eff}} = 1/\omega_{\max}$.

Table 1 Relaxation parameters (according to CD fit) and viscosities η of the pure substances, 20°C.

	τ_{CD} ps	S_{CD}	β	τ_{eff} ps	$\hat{S}$	η mPa s
ED	205	37.5	0.69	141	39.4	19.9
1,2-PD	675	25.7	0.64	432	27.9	58.4
1,3-PD	562	31.2	0.71	399	33.5	52.1
1,2-BD	1073	19.7	0.63	676	22.0	73.3
1,3-BD	1940	25.9	0.66	1280	27.5	129
1,4-BD	1282	28.0	0.69	885	29.7	91.1
2,3-BD	2050	21.1	0.54	1107	20.8	110
E	233	21.5	0.76	177	23.7	1.19
DEG	470	27.6	0.63	296	29.1	35.1
PT	2604	40.7	0.66	1719	41.4	1490
H_2O	9.5	76.5	1.0	9.5	78.5	1.00

In the present case of a CD function, this is obtained as

$$\tau_{eff} \approx \beta \tau_{CD}. \tag{2}$$

Since the CD fit is not appropriate for higher frequencies, S_{CD} may not accurately represent the total relaxation strength, which alternatively can be approximated by its maximum possible value

$$\hat{S} = \varepsilon_s - n_D^2, \tag{3}$$

where n_D is the refractive index. The quantities τ_{eff}, S_{CD} or $\hat{S}$ and, in addition, the CD parameter β shall now comparatively be regarded for the different alcoholic systems.

Pure Alcohols The relaxation parameters and the viscosities for the pure substances are listed in Table 1.

It is informative to consider in the first instance the relaxation time τ_{eff} in its relation to viscosity η, as displayed in Figure 1. In this figure the data of some additional alcohols are given, too, in order to show that mono-, di- and trihydric alcohols appear as clearly separated 'families'. Ethyleneglycols seem to belong to the diol 'family', which indicates that the polar ether groups of these substances play an only minor role in comparison to the hydroxy groups. Water takes a place close to an extrapolation of the diol line, tending somewhat towards monohydric alcohols. This may be a hint at its '4/3-ol' character, according to the number of hydrogen bond donor and acceptor sites in relation to an isolated OH group. Note that roughly a $\tau_{eff} \sim \eta$ proportionality is observed within each 'family'. From Figure 1 one may draw the preliminary conclusion that the formation of 'families' is due to a discontinuous alteration of viscosity η rather than relaxation time τ_{eff} on changing between mono-, di- and trihydric alcohols, which implies that probably different motional processes are involved in dielectric relaxation and viscous flow.

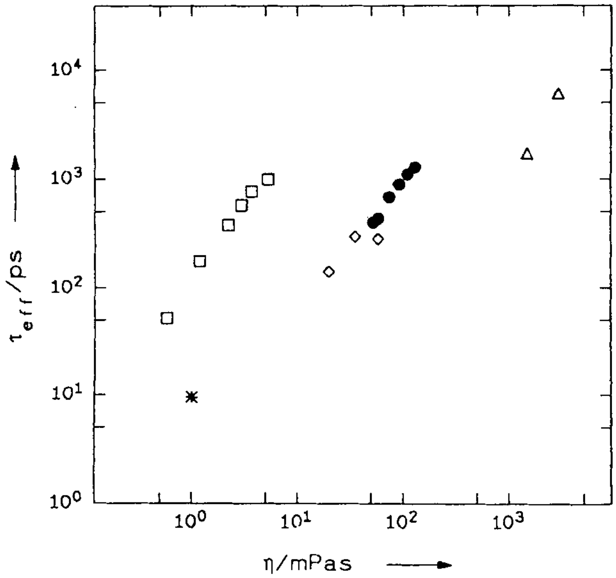

Figure 1 Effective relaxation time τ_{eff} against viscosity η of pure alcohols (log-log plot). Symbols: □ mono-, ● di-, △ trihydric alcohols, ◇ ethyleneglycols, * water. Values for the following substances have been additionally included: Methanol and 1-propanol to 1-hexanol[31], tri- and tetraethyleneglycol[32] and 1,2,6-hexanetriol[33].

The relaxation strengths do not essentially differ between the 'families'. As generally found for alcohols, they indicate a positive orientational moment correlation, which can be described by a Kirkwood g_{OH} factor as customary, referring here to fictitious, independently oriented OH groups. It is derived by comparing the apparent OH moment squared $\mu^2_{OH,app}$ as obtained according to

$$\mu^2_{OH,app} = \frac{27\varepsilon_0 kT}{N_A(\varepsilon_\infty + 2)^2} \frac{S}{c_{OH}} \tag{4}$$

(immersion model[34]) with the partial moment squared of an aliphatic OH group, $\mu^2_{OH} \approx 2.9\text{D}^2$:

$$g_{OH} = \frac{\mu^2_{OH,app}}{\mu^2_{OH}}. \tag{5}$$

With $S = \hat{S}$ after Table 1 and $\varepsilon_\infty = 3$ for all cases (this value is consistent with $\varepsilon_s - \sum S_i$ as obtained from the analyses regarded subsequently in Section 3.2), we get the g_{OH} factors of Table 2.

Table 2 Kirkwood g_{OH} factors for pure alcohols.

	g_{OH}		g_{OH}
ED	3.3	M[a]	4.6
1,2-PD	3.1	E	4.6
1,3-PD	3.6	P[b]	4.9
1,2-BD	3.0	B[c]	4.9
1,3-BD	3.7		
1,4-BD	3.9	PT	2.9
2,3-BD	2.8	HT[d]	2.9

[a] Methanol[31]; [b] 1-propanol[31]; [c] 1-butanol[31]; [d] 1,2,6-hexanetriol[33].

It is particularly noteworthy that within the series of isomers, namely propanediols and butanediols, there is a parallelism between the g_{OH} factors and the CD parameters β:

$$g_{OH} \text{ and } \beta \text{ increasing} \rightarrow$$

$$\text{1,2-PD} \rightarrow \text{1,3-PD}$$

$$\text{2,3-BD} \rightarrow \text{1,2-BD} \rightarrow \text{1,3-BD} \rightarrow \text{1,4-BD}$$

The $g_{OH} - \beta$ parallelism shows that the intensity of the absorption band is enhanced (i.e. g_{OH} increased) as its width is reduced (β increased), corresponding to a decreased weight of higher frequency relaxation contributions. The order within each series of isomers seems to relate to molecular geometry. At least in a qualitative manner, the shielding of OH functions by other parts of the alcohol molecule decreases and, consequently, the ability to form hydrogen bonds increases in the same direction as g_{OH} and β. It should be mentioned that comparatively broad absorption bands have been found for alcohols where intramolecular hydrogen bonds are known to occur[35], so that one might further infer that the tendency towards intramolecular bonds should also decrease in the above order of isomers, provided it be significant at all.

Alcohol-Water Mixtures Relaxation times τ_{eff} and relaxation strengths S_{CD} of all mixture systems considered here vary monotonously with the water content. It is only β which in most cases is found to exhibit a non-monotonous concentration dependence. Since in the subsequent Section 3.2 relaxation parameters as obtained by a modified analysis will be displayed in full, it may suffice here to regard the CD parameters of a few but typical mixture examples.

Let us first look at the relation of relaxation time τ_{eff} to viscosity η which is represented in Figure 2 for some mixture series. This figure corresponds to Figure 1 which shows data for pure liquids. Among the examples given, the ethanol-water system is peculiar in exhibiting a noticeable curvature due to the fact that its viscosity passes through a maximum while the relaxation time changes monotonously. Aqueous mixtures of other mono-alcohols behave in a similar manner inasmuch as swinging in to the $\tau_{eff} \sim \eta$ proportionality which, on the other hand, is nearly perfectly

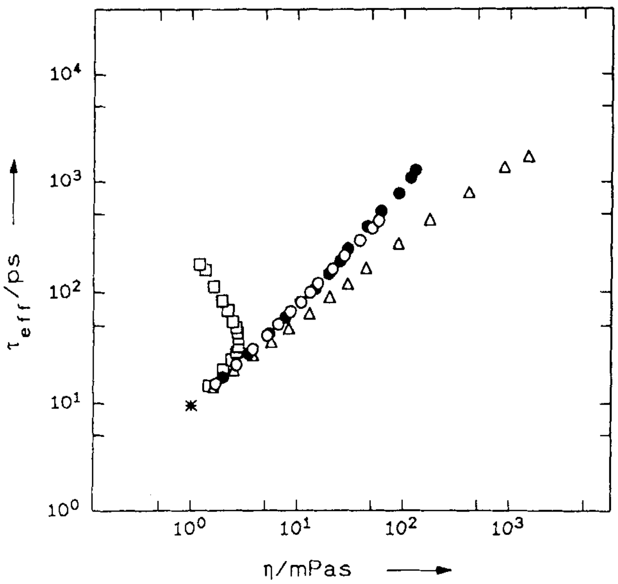

Figure 2 Effective relaxation time τ_{eff} against viscosity η for the whole composition range of some typical aqueous mixture series. Symbols: □ ethanol-water, ○ 1,2-propanediol-water, ● 1,3-butanediol-water, △ propanetriol-water, * pure water.

followed over the whole composition range by the mixture systems of diols. Note that this is the line roughly observed within the 'family' of pure diols (Figure 1). The triol mixture systems approach that line from the higher viscosity side.

On a c_w/c_w^* scale for the water content (the asterisk denotes the pure water concentration, so this ratio is approximately the volume fraction of water) one finds that initially τ_{eff} decreases the steeper the longer τ_{eff} of the pure alcohol but tends towards a common decrease in the water rich region. This may be seen from the logarithmic decrements $\theta_{a,w}$ given in Table 3 for the alcohol rich and the water rich

Table 3 Alcohol-water mixtures: Alteration of τ_{eff} according to CD analysis with water content c_w/c_w^*, expressed as logarithmic decrements $\theta_{a,w}$ for the alcohol rich and the water rich limiting case, respectively (for $\theta_{a,w}$ see Eq. (6)).

	θ_a	θ_w		θ_a	θ_w
ED	1.4_5	1.1	E	2.2	1.6
1,2-PD	2.4	1.4_5			
1,3-PD	1.7	1.4	DEG	1.4_5	1.3
1,2-BD	3.6	1.5			
1,3-BD	3.6	1.6	PT	4.6	1.3
1,4-BD	2.4	1.5			
2,3-BD	3.6	1.6_5			

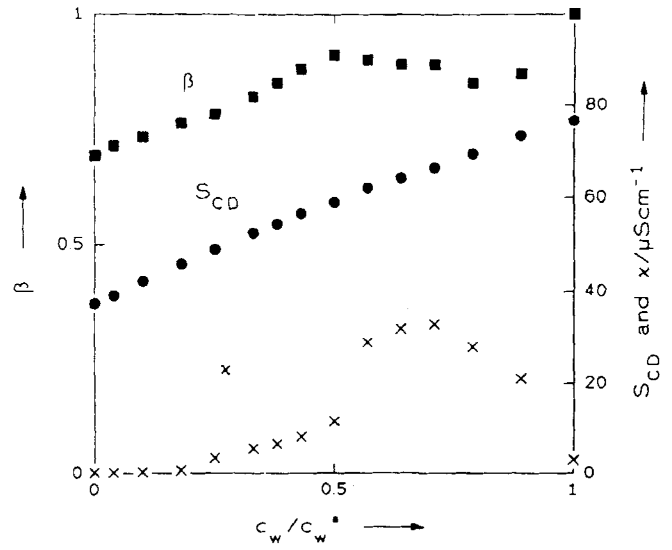

Figure 3 CD parameters S_{CD} and β against relative water concentration c_w/c_w^* (where c_w^* refers to pure water) for the aqueous mixture series of ethanediol. The (accidental) conductivity κ is also represented.

mixtures, respectively. The decrements are defined as

$$\theta_{a,w} = \frac{\Delta_{10} \log(\tau_{eff}/\mathrm{ps})}{\Delta c_w/c_w^*}, \tag{6}$$

where a, w stands for $c_w/c_w^* \to 0, 1$, respectively.

The composition dependence of relaxation strength S_{CD} and CD parameter β is displayed for one typical example in Figure 3. There is a practically linear variation of S_{CD} with c_w/c_w^* in that case. Also for the other systems S_{CD} behaves fairly 'ideal' in obeying to within ±7 percent a mixture rule

$$S_{CD} \approx \sum_i S_{CD,i}^* \frac{c_i}{c_i^*}, \tag{7}$$

where i = alcohol, water. (The asterisk refers to the respective pure liquid.)

From Figures 2, 3 there are strong indications that the mixture range should conceptually be distinguished into an alcohol rich, an intermediate and a water rich region. This is suggested e.g. by the common approach to the pure water point in Figure 2 and by the composition dependence of β in Figure 3. Also the composition dependence of several parameters measured by other methods points to the reasonableness of such a subdivision[36–41]. As a further instance, we have given in Figure 3 the conductivity of the mixture system under consideration which in that case is an incidental impurity effect but may, however, serve to probe in a rough manner the alteration of structural and microdynamical conditions.

As mentioned above, an analysis employing a superposition of discrete terms is advantageous for describing the dielectric spectrum over the whole experimental frequency range. This is dealt with in the following section, including the just drawn conclusion that mixture regions of differing character should be distinguished.

3.2 *Discrete Term Analysis for Whole Experimental Region*

Starting point of the discrete term analysis is a reconsideration of the pure alcohol spectra. To account for the inconsistencies in the high frequency region mentioned above, two Debye type components for that region (with relaxation times around 10 and 2 ps) are now introduced in addition to the main CD contribution. This leads of course to modified CD parameters in comparison to the former analysis since part of the higher frequency absorption is now accounted for by the additional terms (which, however, still contribute an only minor fraction to the total relaxation strength). Within the variability range of parameters the CD term is chosen to represent the largest possible relaxation strength. The CD terms resulting in this manner have relaxation strengths about 4 percent less than S_{CD} from the former CD analysis (Table 1), while their effective relaxation times τ_{eff} agree with the values of Table 1 to within ± 3 percent.

For the alcohol rich region of mixture systems these alcohol terms are retained, assuming in particular that the CD term stays unchanged in its shape (viz. β = const). The initial slope of log τ_{eff} vs. c_w/c_w^* (viz. θ_a) is chosen as close as possible to the value from the above analysis (Table 3).

The water rich region is treated in a corresponding manner. For pure water, a Debye type component (Table 1) is sufficient. This is presupposed to remain a relaxation contribution in the water rich mixture region, where its relaxation time is allowed to vary with c_w/c_w^*. However, according to comparative studies of water with small amounts of alcohols added[19], we place the constraint on that relaxation time that it should not exceed about 30 ps.

If the spectra should be describable over the whole mixture range by these contributions this would mean a quasi 'ideal' dielectric mixture behaviour where each mixture component retains its individual relaxation characterics more-or-less unaffected by the other component, as sometimes found even with relatively large molecules[42]. However, a satisfactory description of the present spectra at medium mixture ratios is not possible in that way. A complementary absorption must be invoked which in many instances appears to be broader than a Debye component. Since it was not possible to obtain the necessary number of parameters by a free running fit, the intermediate region is arbitrarily supposed to consist of two Debye type components. Assuming moreover, as a further constraint, that their relaxation times stay independent of the mixture composition, these could in any case be chosen such that satisfactory fits were obtained by variation of the relaxation strengths.

Fits were first performed as independent runs for mixture systems falling into the three categories deduced before, that is the alcohol rich, intermediate and water rich region. Making use of the acceptable variability ranges of the fit parameters, these were then adjusted such that a smooth transition between adjoining regions resulted.

Altogether, the analysis comprises six spectral components C_i, which will be indexed in the order of increasing frequency ω_{max}. They are assigned as follows:

C_1 (the CD term), C_5 and $C_6 \rightarrow$ alcohol;
C_2 and $C_3 \rightarrow$ intermediate terms;
$C_4 \rightarrow$ water.

The parameters kept constant for each mixture series are: β^a (for C_1), τ_2, τ_3, τ_5^a and τ_6^a, where the superscript 'a' indicates that the values are taken from the pure alcohol

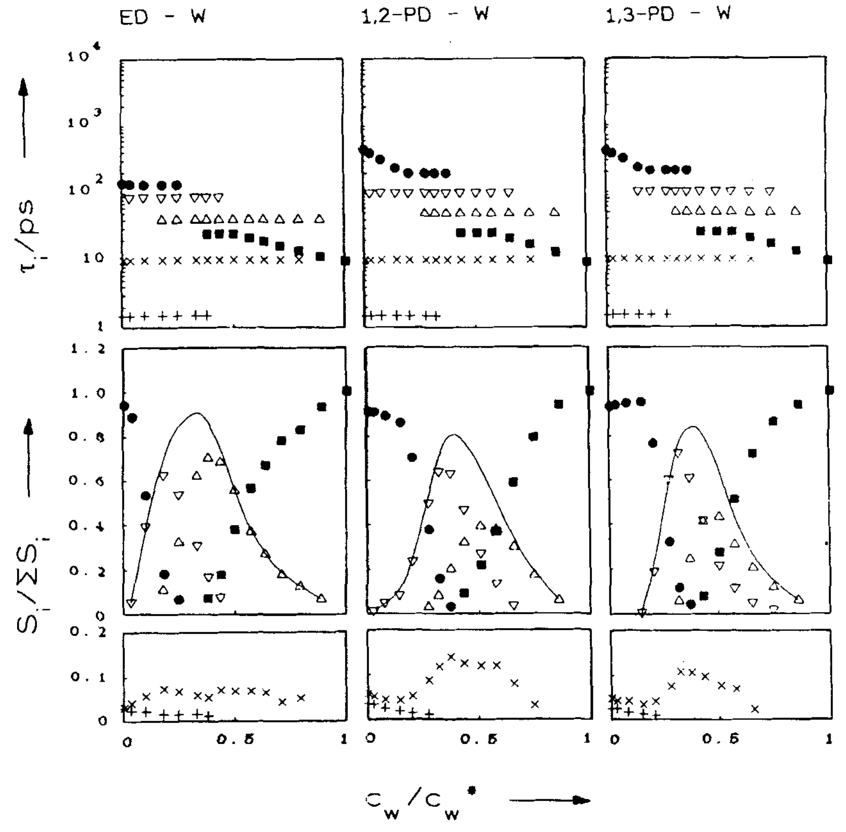

Figure 4 Relaxation times τ_i (above, log scale) and normalized relaxation strengths $S_i/\sum S_i$ (middle) against relative water concentration c_w/c_w^* according to the discrete term analysis, for aqueous mixtures of ethandiol, 1.2-propanediol and 1.3-propanediol. The relaxation strengths of the minor components C_5 and C_6 are shown below. The line represents the sum of 'intermediate' terms, viz. $(S_2 + S_3)/\sum S_i$. Symbols for the spectral components: ● C_1 (CD term; here the τ value shown is $\tau_{1,\mathrm{eff}}$ according to Eq. (2)), ▽ C_2, △ C_3, ■ C_4, × C_5, + C_6. The β values for C_1 are $\beta_{\mathrm{ED}} = 0.86$, $\beta_{1,2\text{-PD}} = 0.78$, $\beta_{1,3\text{-PD}} = 0.82$.

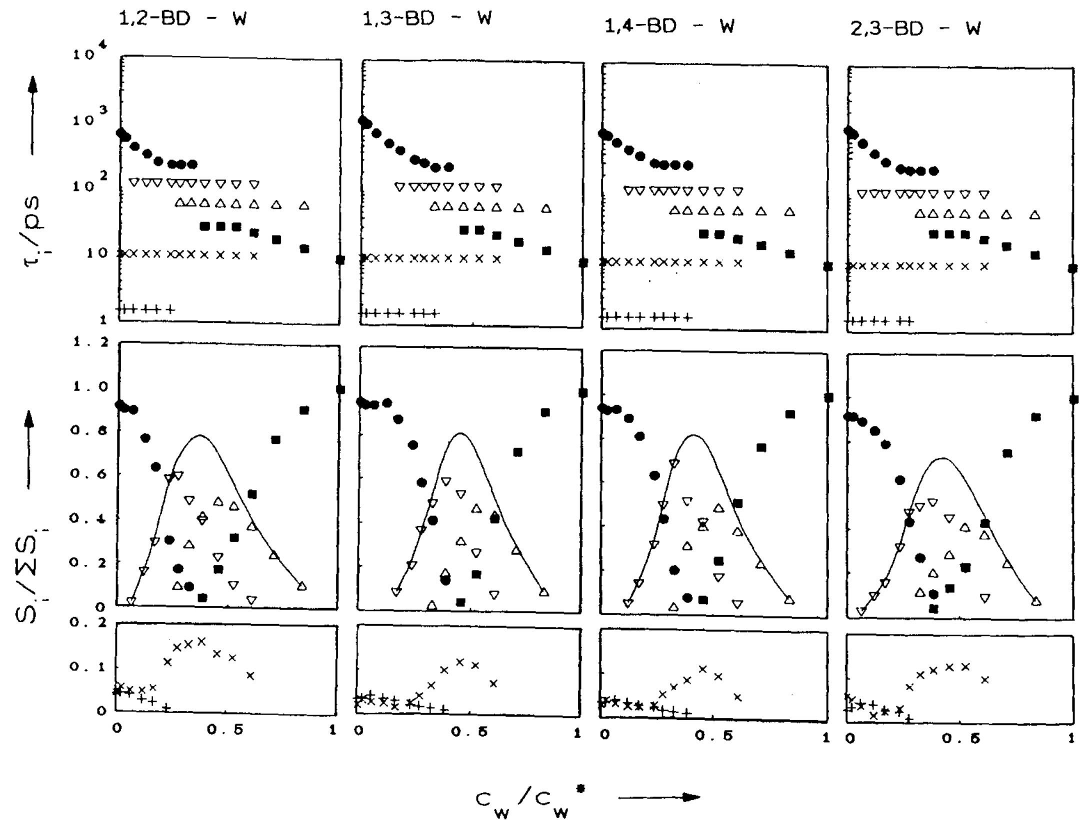

Figure 5 Relaxation parameters after discrete term analysis for aqueous mixtures of 1,2-, 1,3-, 1,4- and 2,3-butanediol. As Figure 4. For C_1 there is $\beta_{1,2} = 0.75$, $\beta_{1,3} = 0.77$, $\beta_{1,4} = 0.82$, $\beta_{2,3} = 0.75$. For 2,3-BD, the fit is improved by replacing C_1 by a further broadened Havriliak-Negami type component ($\alpha = 0.05$), which is disregarded in the text.

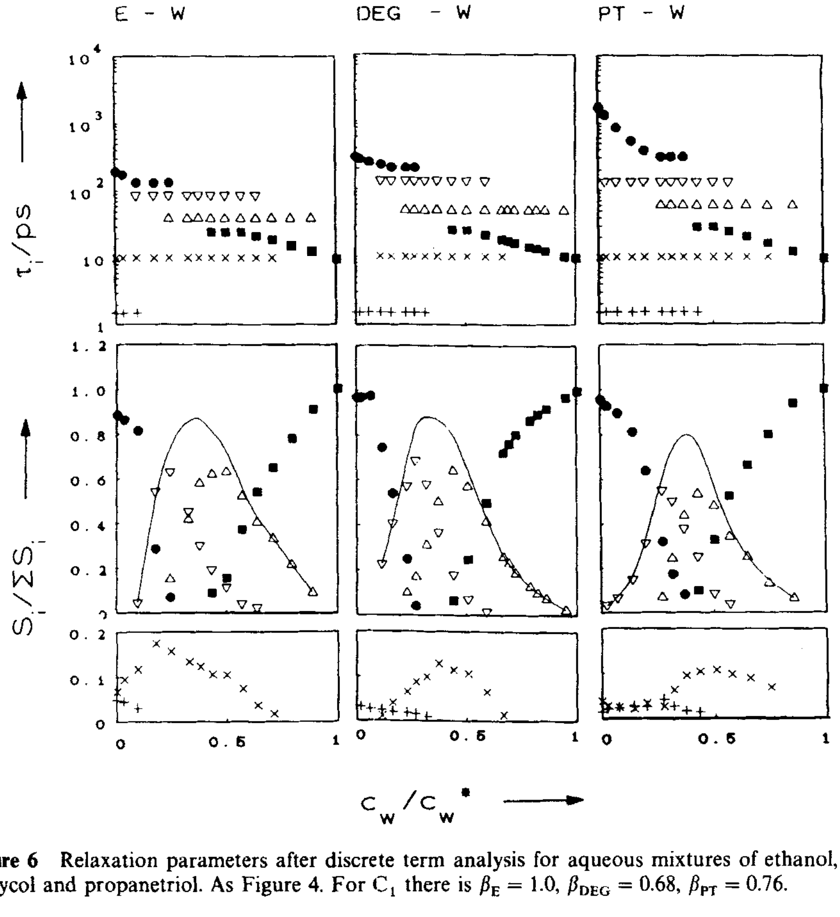

Figure 6 Relaxation parameters after discrete term analysis for aqueous mixtures of ethanol, diethyleneglycol and propanetriol. As Figure 4. For C_1 there is $\beta_E = 1.0$, $\beta_{DEG} = 0.68$, $\beta_{PT} = 0.76$.

Table 4 Alcohol-water mixtures: Maximum values Z^{max} (Eq. (10)), and parameters $\bar{\tau}_{2,3}$ and $\sigma_{2,3}^{max}$ characterizing the intermediate terms (Eqs. (11) and (12), respectively).

	Z^{max}	$\bar{\tau}_{2,3}$ ps	$\sigma_{2,3}^{max}$		Z^{max}	$\bar{\tau}_{2,3}$ ps	$\sigma_{2,3}^{max}$
ED	0	51	0.91	E	0.2	52	0.87
1,2-PD	0.5	84	0.81				
1,3-PD	0.7	82	0.84	DEG	0.4	93	0.88
1,2-BD	0.3	84	0.78				
1,3-BD	0.8	93	0.81	PT	0.2	86	0.80
1,4-BD	0.6	92	0.82				
2,3-BD	0.5	92	0.73				

analysis. Consequently τ_1 (equivalent to τ_{CD} of Eq. (1)), τ_4 and the relaxation strengths S_1 to S_6 are to be determined by the fitting procedure.

The results obtained in that manner are graphically represented in Figures 4–6. Note that *relative* relaxation strengths $S_i/\sum S_i$ are depicted. Concerning the absolute values, it should be mentioned that S_1 in the alcohol rich region mostly increases as the water content and passes through a maximum, which cannot be recognized in the normalized form (Figures 4–6). This looks like a water contribution to spectral component C_1, while otherwise water is suspected to establish component C_4. In order to obtain comparable values for that increase we shall convert it into an approximate number Z of water molecules contributing to C_1 (instead of C_4) per alcohol molecule, assuming for that purpose 'ideal' conditions (although these are actually not given here). Accordingly the excess contribution ΔS_1 would be

$$\Delta S_1 = S_1 - S_1^* \frac{c_a}{c_a^*}, \tag{8}$$

and the water concentration contributing to C_1

$$\Delta c_w = \frac{\Delta S_1}{S_4^*} c_w^*. \tag{9}$$

Using this, the quantity Z is calculated as

$$Z = \frac{\Delta c_w}{c_a}. \tag{10}$$

At low water contents, Z increases proportional to c_w/c_w^* and then passes through a maximum, beyond which its determination becomes rather uncertain. The maximum values Z^{max} are summarized in Table 4. Since depending on the parameters chosen for the subsequent spectral component C_2, they are only rough estimates in character. The Z^{max} values of Table 4 are attained at medium water mole fractions, $x_w \approx 0.3 \ldots 0.5$.

The relaxation strength S_4 attributed to water decreases on increasing alcohol content on the relative (Figures 4–6) as well as on the absolute scale. Thus obviously the addition of water to alcohol cannot be treated as equal to the addition of alcohol to water.

Table 4 gives also some values characterizing the intermediate terms C_2 and C_3, which numerically repeat information from Figures 4–6. These are the weighted relaxation time

$$\bar{\tau}_{2,3} = \exp\left(\frac{S_2 \ln \tau_2 + S_3 \ln \tau_3}{S_2 + S_3}\right) \tag{11}$$

and the maximum normalized relaxation strength

$$\sigma_{2,3}^{\max} = \left(\frac{S_2 + S_3}{\sum S_i}\right)^{\max} \tag{12}$$

3.3 *General Discussion*

Taking the formal point of view, the discrete term analysis (Section 3.2) should be given preferential attention because of the better fit quality in comparison to the CD analysis (Section 3.1). From this the inference appears that one should reckon with correspondingly distinguishable physical relaxation processes rather than a uniform collective relaxation mechanism, even if a precise evaluation of the spectral components might be questionable. The minor high frequency spectral components C_5 and C_6 may relate to single molecule or internal motion[42]. These, however, will not be regarded in the following. The other spectral components (C_1 to C_4) are to be ascribed to relaxators consisting of hydrogen bonded aggregations or 'clusters', the dynamics of which are, generally speaking, responsible for relaxation. The rotational tumbling of long-lived 'clusters' on the one hand, and the internal fluctuation or association-dissociation dynamics on the other hand, may be taken into consideration as limiting cases.

It is remarkable that the plots of Figures 4–6 look closely alike for all mixture systems considered here. Individual differences are merely discernible in the alcohol rich region (see also Table 3). This finding answers the introductory question as to whether the different systems might be describable by use of one and the same scheme, and it suggests that analogous relaxation processes are operative in all these hydrogen bonded mixture systems in spite of mono-, di- and trialcohols being involved. Those processes are likely to differ in detail according to the differentiation between alcohol rich, intermediate and water rich mixture regions. The concentration dependence of the relaxation strengths of the three main contributions (accentuated in Figures 4–6 by full symbols or by lines) points to a 'chemical' equilibrium between relaxators which are distinguished by their structural and/or dynamical properties.

It has been observed with some other mixture systems which are likely to form distinct hetero-associates that the relaxation contributions assigned to these associates appear at frequencies $\omega_{\max}$ clearly *lower* than those of the pure mixture partners[43,44]. In contrast, the present systems exhibit those contributions which are ascribable to hetero-interactions in a frequency range *intermediate* between the alcohol and water contributions. This is a hint at essentially similar dynamical behaviour of the relaxators in the three mixture regions.

Turning now to the individual features which can be observed in the alcohol rich mixture region, we should at first recall the different influence of water added to members of the mono-, di- or trihydric alcohol 'family' as evident from Figure 2. This is obviously related to the structural and dynamical differences of already the pure alcohols which, for example, are recognizable from the g_{OH} factors (Table 2). Note that, on average, g_{OH} for n-ols decreases as n increases, probably since the mean structure changes from chain to network character. However, individual differences in the effectof added water are much less obvious if viscosity is left out of consideration as in Figures 4–6. At the most, the Z^{max} values (Table 4) seem to indicate steric influences in being remarkably small for alcohols with neighbouring OH functions, e.g. ED and PT, but it is no longer possible to differentiate between the 'families'.

For monoalcohols a noticeable change of relaxation behaviour on addition of small amounts of dialcohols has been reported, which has been ascribed to an alteration of cluster properties as mediated by molecules offering two associogenous sites[10,45]. Those 'bridging' effects have also been observed with polyethers in the presence of water or a dihydric alcohol[43]. For the present systems, these findings may correspond to the initial increase of S_1 on addition of water which may alternatively be termed a structure making effect.

The individual differences depending on the kind of alcoholic mixture component tend to vanish in the medium concentration range where the spectral components C_2 and C_3 become dominating. For example, the $\bar{\tau}_{2,3}$ values (Table 4) for all mixtures are similar although the relaxation times of the respective pure alcoholic components differ appreciably, which means that dynamical properties converge. On the other hand, some individual features are still discernible in a quantity such as $\sigma_{2,3}^{max}$ (Table 4) which reflects structural properties. Within the series of isomers the $\sigma_{2,3}^{max}$ values increase in the same order as the parameters g_{OH} and β obtained by the CD analysis of pure alcohols (Section 3.1). Such an influence of steric factors has been reported also by other workers[22,46,47].

The water rich region is peculiar in exhibiting a relaxation pattern which is practically independent of the kind of alcohol added, as already indicated by the similarity of the θ_w values (Table 3). It should be mentioned that this holds if mixtures are compared on the c_w/c_w^*, viz. the volume fraction (rather than the mole fraction) scale. On increasing the alcohol content of water, the principal water relaxation (C_4) is slowed down (τ_4 increases) while at the same time the initial water structure seems to decay (S_4 decreases drastically). As shown in a previous paper, this can equivalently be described in terms of 'affected' and 'unaffected' water[19].

Finally we shall briefly remark on conceivable relaxation mechanisms. The limiting assumption that rotational tumbling motion of well defined clusters be the dominating process is hardly tenable for several reasons. The main one is the difficulty to picture clusters of reasonable size on the basis of a comparison with the relaxation times and viscosities of liquids where relaxation originates in the tumbling motion of rigid or quasi rigid molecules[34,48]. On the other hand, fluctuation models which relate the relaxation time to characteristic times of stochastic alterations within a 'cluster' (residence time or lifetime models) seem, in a general sense, to be consistent with the experimental findings.

On the single particle level, various models have been proposed to describe the fluctuation of a molecular dipole moment component. Their common feature is the distinction between phases of 'free' rotational fluctuation and, on the other hand, fluctuation in a hindered ('associated') situation. The 'associated' situation may simply be characterized at motionless. With the additional assumption of exponentially distributed residence times and slow exchange between both situations the appearance of nearly Debye type spectral components becomes understandable, the effective relaxation time being governed by the mean residence time in the 'associated' situation[49,53]. An additional jump motion may be introduced for the 'associated' phase[50] which can be interpreted as 'switch' process of the OH dipole from one hydrogen bond direction to another[20]. Somewhat differently pictured is the structural relaxation model which already implies cooperative behaviour. It takes into account the translational motion of unstructured regions which allow for 'free' tumbling motion[46,51]. The single dipole models are suited to interprete the shape of the dielectric spectrum and the effective relaxation time but by no means the relaxation strengths since these depend essentially on the orientational correlation of dipoles. The models have therefore been developed further to different degrees of cooperativity. For the switch mechanism[20] it was considered possible that on breaking a hydrogen bond not only one dipole switches to another position but that all (orientationally correlated) dipoles of a cluster (or, for monohydric alcohols, a chain like associate structure) are cooperatively reoriented[20,52].

In a qualitative sense, a switch process[20] in combination with a cage effect, which means that a broken hydrogen bond will preferably be re-established unless a sufficient alteration in its neighbourhood allows for formation of a new bond, could account for the relaxation behaviour found with the present systems. It would also meet the requirement that the relaxation mechanism should not be *directly* coupled to viscous flow (cf. Figure 1) which, instead, is related to the translational motion of whole molecules. Similar inferences were previously drawn from studies on monoalcohols[47,54]. We feel, however, that more extensive conclusions which would enable a distinction between various models cannot be gained by only dielectric spectroscopy.

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