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# Orientational Dynamics of Hydrogen-Bonded Liquids – A Comparative Study of Dielectric and Nuclear Magnetic Relaxation in n-Butanol-Tetrachloromethane Mixtures

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*Key Words:* Dielectrics / Hydrogen Bonding / Liquids / Nuclear Magnetic Relaxation / Solutions

Complex dielectric spectra up to 20 GHz are measured at 25 °C for n-butanol tetrachloromethane mixtures. Within this frequency range the spectra can be described by two Debye-processes. Their relaxation times  $\tau_1^{(1)}$  and  $\tau_1^{(2)}$  are compared with the hypothetical single-particle relaxation time of the dipoles  $\tau_1^s$  estimated from deuteron magnetic relaxation rates in these mixtures. The results indicate a collective nature of the primary relaxation time  $\tau_1^{(1)}$ , due to cooperative motion of several molecules. Although not accurate in detail, some theoretical models can reproduce major features of the concentration dependence of  $\tau_1^{(1)}$ . In these models,  $\tau_1^{(1)}$  is coupled to  $\tau_1^s$  via the Kirkwood correlation factor  $g_1$ , which can be determined independently from the static permittivity. There is no obvious interrelation between  $\tau_1^s$  and the secondary relaxation time  $\tau_1^{(2)}$ , the nature of which remains puzzling.

## 1. Introduction

Orientational dynamics influences many relaxation processes in liquids and plays an important role in the dynamics of chemical reactions in dipolar solvents such as electron transfer. Experimental methods can be subdivided into two groups which probe the reorientational dynamics of single molecules and cooperative motions of many molecules, respectively [1–3]. Intramolecular nuclear magnetic relaxation belongs to the former group, depolarized light scattering, dielectric relaxation and the magnetic relaxation of mono-atomic quadrupolar nuclei fall into the latter category. The relationship between the single-particle and collective motions is the subject of much theoretical debate [2, 3].

We report here on magnetic and dielectric relaxation of n-butanol (BuOH) dissolved in tetrachloromethane. Such mixtures are of interest as model systems for hydrogen-bonded liquids in solvents of low polarity [4–10]. Dielectric spectra of alcohols dissolved in inert solvents have been frequently studied. Although broad variety of models have been suggested to describe these spectra [10–13], they are not yet understood in detail. We consider here some aspects associated with the cooperative nature of the dielectric relaxation processes. From the experimental perspective, a comparative study of magnetic and dielectric relaxation seems to be particularly promising to study the relationship between the single-particle and cooperative motions.

## 2. Experimental

**Materials.** Solutions were made up by weight from dry BuOH and CCl<sub>4</sub> of the highest purity available (Baker). Deuterated n-C<sub>4</sub>H<sub>9</sub>-O<sup>2</sup>H was obtained from Sharpe and Dohme, Munich.

**Complex Dielectric Spectra.** Dielectric spectra were obtained with a microwave network analyzer (Hewlett-Packard HP 8720C). The probe (HP 85070B) was fixed in a glass cell thermostatted to (25±0.02) °C. Microwaves were introduced at about 1000 frequencies between 0.1 and 20 GHz. The reflected waves were sampled by the network analyzer and converted to complex dielectric spectra using software based on the Nicolson-Ross method [14]. Several spectra were recorded for each sample and were averaged. The calibration included measurements either with water [10, 15] or alcohols [10].

For alcohols, the complex permittivity  $\hat{\epsilon}(\omega)$  at angular frequency  $\omega=2\pi\nu$  can be represented by a superposition of three Debye-processes according to [10, 13]

$$\hat{\epsilon}(\omega) = \epsilon_{\infty} + (\epsilon - \epsilon_{\infty}) \sum_{k=1}^3 \frac{\Delta\epsilon^{(k)}}{1 + i\omega\tau_1^{(k)}} \quad (1)$$

$\epsilon$  is the static permittivity,  $\epsilon_{\infty}$  the limiting permittivity at high frequency which includes electronic and vibrational contributions.  $\tau_1^{(k)}$  is the relaxation time of the k-th mode. Subscript “1” recalls that dielectric relaxation refers to processes associated with the time dependence of ( $l=1$ ) spherical harmonics.  $\Delta\epsilon^{(k)} = \epsilon^{(k)} - \epsilon_{\infty}^{(k)}$  is the dispersion amplitude of the k-th mode;  $\epsilon_{\infty}^{(k)} = \epsilon^{(k+1)}$ . In the high-frequency limit, the permittivity should decay to  $\epsilon_{\infty} \cong 1.05 n_D^2$ , where  $n_D$  is the refractive index at the wave length of the Na<sub>D</sub>-line. In practice, higher values of  $\epsilon_{\infty}^{(3)}$  are found [13], indicating that not all contributions to  $\hat{\epsilon}(\omega)$  are covered in the range, where experiments are feasible.

In detail, our experiments yielded data triples  $\{\epsilon', \epsilon'', \nu\}$  for the real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of  $\hat{\epsilon}$  which had to be fitted to Eq. (1). Fig. 1 shows plots of  $\epsilon'(\nu)$  and  $\epsilon''(\nu)$  for pure BuOH. Two modes are observable up to 20 MHz, which are denoted as “primary” ( $k=1$ ) and “secondary” ( $k=2$ ) relaxation. The high-frequency mode ( $k=3$ ) is beyond the available range. Such high-frequency

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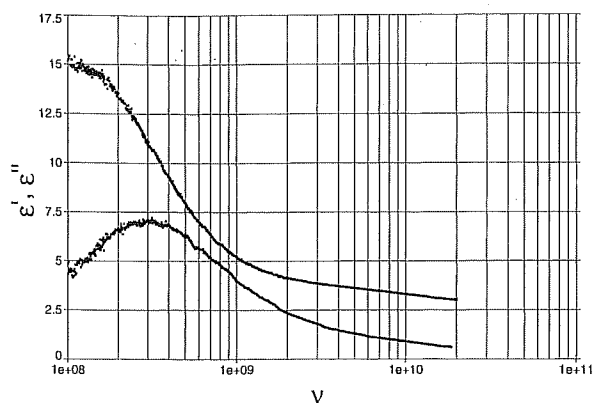


Fig. 1  
Real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of the dielectric spectrum of pure n-butanol at 25°C. The frequency is given in Hz

processes are often accounted for by an effective value of  $\epsilon_\infty$ . After due consideration of literature data [10, 13, 16], we preferred to model this mode by concentration-independent parameters  $\tau_1^{(3)} = 2$  ps, and  $\epsilon_\infty^{(3)} = 2.30$ . Variations of these parameters within reasonable ranges had a comparatively large effect on  $\Delta\epsilon^{(2)}$ , while the other parameters were not markedly affected. The resulting fit parameters are summarized in Table 1.  $x_A$  is the mole fraction of BuOH.

Absolute errors of the data in Table 1 can only be estimated from the reproducibility of literature data [13] and the quality of the fits.  $\tau_1^{(1)}$  should be accurate to within  $\pm 2\%$  in pure BuOH and  $\pm 5$ –10% in dilute mixtures. Errors of  $\tau_1^{(2)}$  should be larger, because of the lower amplitudes. The fitted values of  $\epsilon$  agree with static permittivities reported in [17] to within  $\pm 2\%$  or better. For  $\Delta\epsilon^{(1)}$  errors between 5 and 20% seem realistic.  $\Delta\epsilon^{(1)}$  depends on the assumption about the ( $k=3$ ) mode, and thus represents only a fit parameter.  $\Delta\epsilon^{(1)}$  and  $\Delta\epsilon^{(2)}$  will not be considered further in this paper.

**Magnetic Relaxation.**  $^2\text{H}$  magnetic relaxation rates were measured at 46.1 MHz with a Bruker pulsed FT-NMR-spectrometer, using techniques described elsewhere [18]. Results are summarized in Table 2. Estimated errors of the relaxation data are  $\pm 2\%$ .

$^2\text{H}$  relaxation is caused by interaction of the nuclear electric quadrupole moment with the intramolecular electric field gradient at the nucleus, as described by the standard relation [19]

$$\left(\frac{1}{T_1}\right)_{2\text{H}} = \frac{3}{2} \pi^2 \chi^2 \tau_2^s, \quad (2)$$

where  $\chi$  is the nuclear quadrupole coupling constant and  $\tau_2^s$  is the rotational correlation time of the OH-axis in the BuOH molecule. Superscript "s" and subscript "2" denote that  $\tau_2^s$  is a single-particle quantity, associated with the time dependence of ( $l=2$ ) spherical harmonics.

Experimental data for the coupling constant vary almost linearly from  $\chi = 192$  kHz for pure BuOH to

Table 1

Parameters describing dielectric relaxation in BuOH- $\text{CCl}_4$  mixtures at 25°C

$x_A$	$\tau_1^{(1)}/\text{ps}$	$\tau_1^{(2)}/\text{ps}$	$\epsilon$	$\Delta\epsilon_1$	$\Delta\epsilon_2$
1.00	478	26.2	17.0	13.2	0.86
0.800	474	23.3	13.2	9.52	0.83
0.600	436	22.4	9.45	6.01	0.72
0.500	388	21.9	7.07	3.75	0.67
0.401	312	19.7	5.40	2.15	0.64
0.356	262	17.6	4.50	1.37	0.60
0.300	220	16.6	3.98	0.86	0.62
0.250	167	14.2	3.45	0.52	0.52
0.200	152	14.7	3.10	0.40	0.45
0.148	75.5	10.7	2.89	0.40	0.44
0.100	37.5	9.3	2.71	0.30	0.30

Table 2

$^2\text{H}$  magnetic relaxation rates and reorientational correlation times  $\tau_2^s$  in n-butanol- $\text{CCl}_4$  mixtures at 25°C

$x_A$	$(1/T_1)_{2\text{H}}/\text{s}^{-1}$	$\tau_2^s/\text{ps}$
1.00	27.0	49.5
0.80	26.5	43.9
0.60	25.0	37.6
0.40	21.9	30.0
0.20	17.2	21.4
0.10	13.0	15.7
0.05	10.6	12.5
0.03	8.3	9.8

236 kHz for at  $x_A = 0.2$  [8], thus allowing an accurate determination of  $\tau_2^s$  in this concentration range. No coupling constants are available below  $x_A = 0.2$ . If the concentration dependence is smoothly extended to infinite dilution, we obtain the results summarized in Table 2. From data obtained for dilute solutions of methanol in  $\text{CCl}_4$  [6] there is, however, evidence for a maximum of  $\chi$  near  $x_A = 0.1$ . If this holds true for BuOH as well, the correlation times at  $x_A = 0.05$  and  $x_A = 0.03$  Table 2 may be too low by about 10%. This is negligible at the level of sophistication of the analysis given below.

#### 4. Results and Discussion

**Magnetic Relaxation.** For pure BuOH we find  $\tau_2^s = 49.5$  ps, in comparison with a value of 51 ps quoted in Ref. [8]. Detailed discussions of correlation times for pure methanol [6, 20, 21] and higher alcohols [7, 8] are concordant with the comparatively slow molecular reorientation in pure BuOH, caused by association in hydrogen-bonded chains. For methanol, there is some indication for moderately anisotropic reorientation [20], but the motion of the OH-axis appears to be a good measure for the motion of the dipolar axis in the molecules [21].

Fig. 2 shows that upon dilution in  $\text{CCl}_4$ ,  $\tau_2^s$  decreases to about 9 ps at  $x_A = 0.03$ . Based on data for methanol and

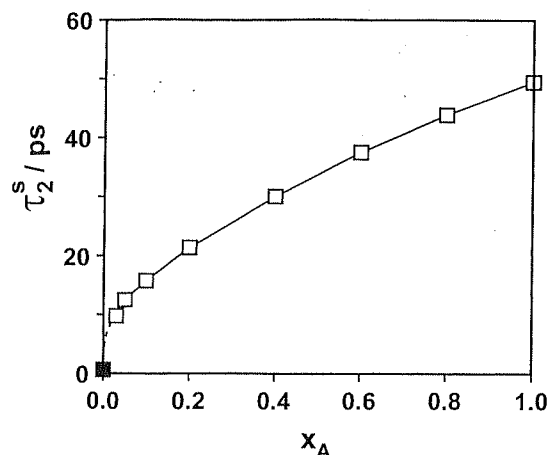


Fig. 2

Correlation times  $\tau_2^s$  in mixtures of n-butanol with  $\text{CCl}_4$  at 25°C deduced from  $^2\text{H}$  magnetic relaxation data in Table 1.  $x_A$  is the mole fraction of the alcohol. The extrapolation value at  $x_A \rightarrow 0$  is estimated from data for methanol and ethanol

ethanol [5, 9], a further pronounced decrease of  $\tau_2^s$  is expected below  $x_A = 0.03$  to a limiting value well below of 1 ps. The data obviously reflect enhanced mobilities due to a breaking of the molecular associates by added  $\text{CCl}_4$ . It may be noted that methanol shows a maximum in the concentration dependence of  $\tau_2^s$  [6] which vanishes for the higher homologues [7, 8].

**Static Permittivity.** Before discussing the dielectric relaxation processes, it is convenient to consider the static permittivity.  $\epsilon$  is usually discussed in terms of the Kirkwood-Fröhlich theory, which considers permanent dipoles embedded in a continuum with the permittivity  $\epsilon_\infty$  [22]. Due to correlations between the dipoles, the effective squared dipole moment differs from that in the gaseous phase ( $\mu$ ) by the Kirkwood factor  $g_1 = \mu_{\text{eff}}^2 / \mu^2$ . If there are no correlations, one has  $g_1 = 1$ , and the Kirkwood-Fröhlich equation reduces to the well-known Onsager equation for  $\epsilon$  [22]. For dipoles of type A in a non-polar solvent B one finds

$$g_1 = \frac{9k_B T \epsilon_0}{x_A L \mu_A^2} \frac{(\epsilon + \epsilon_\infty)^2}{(\epsilon_\infty + 2)^2 (\epsilon + 1)} \left\{ \frac{\bar{V}(\epsilon - 1)}{\epsilon} - \frac{3x_B M_B (\epsilon_B - 1)}{(\epsilon + \epsilon_B) \rho_B} - \frac{3x_A M_A (\epsilon_\infty - 1)}{(\epsilon + \epsilon_\infty) \rho_A} \right\}, \quad (3)$$

where  $k_B$  is the Boltzmann constant,  $L$  the Avogadro constant,  $\epsilon_0$  the absolute permittivity of the vacuum, and the  $\bar{V}$  the molar volume of the mixture.  $M_i$ ,  $\rho_i$  and  $\epsilon_i$  are the molecular mass, density and permittivity of the pure components ( $i = A, B$ ).

If the orientational distribution in the liquid were known, e.g. from scattering experiments or computer simulations, the calculation of  $g_1$  could be carried through completely, because there is a rigorous relation between  $g_1$  and the angular dependent distribution function of the

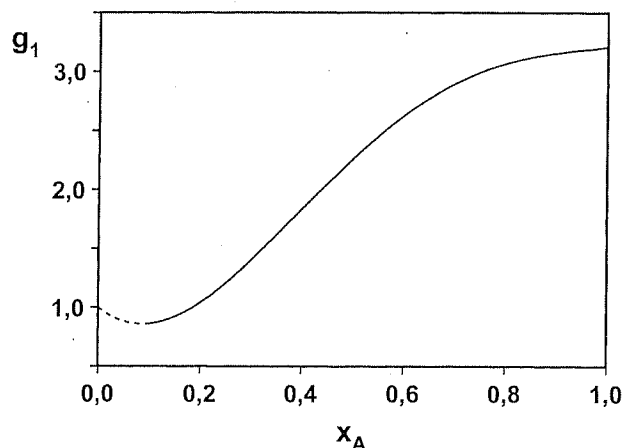


Fig. 3

Composition dependence of the Kirkwood factor  $g_1$  in mixtures of n-butanol with  $\text{CCl}_4$  at 25°C

dipoles [23]. Without this information, it is only possible to discuss  $g_1$  on a qualitative level in terms of possible molecular configurations.

In practice, calculated values of  $g_1$  depend on the choice of  $\epsilon_\infty$ , which is subject to some debate, because the values of  $\epsilon_\infty$  derived from dielectric data do not agree with those deduced from refractive index data. After consideration of various possibilities, we followed the procedures for estimating  $\epsilon_\infty$  from refractive index data, as described in detail in Ref. [17]. Fig. 3 shows the smoothed curve of  $g_1$  of BuOH- $\text{CCl}_4$  mixtures, calculated from the  $\epsilon$ -values in Table 1 and Ref. [17], refractive index data in and molar volume data in Ref. [17].

It is known that pure alcohols exhibit unusually high  $g_1$ -factors of around 3 [22], as expected for preferred parallel orientations in chains of hydrogen-bonded molecules. In dilute solutions  $g_1$  decreases to values below unity, probably caused by the existence of cyclic dimers [6]. For an isolated dipole at infinite dilution one expects  $g_1$  to approach unity, so that the existence of a minimum in the concentration dependence of  $g_1$  below  $x_A = 0.1$  can be assumed for the BuOH- $\text{CCl}_4$  system. The existence of such minima is well established experimentally for a variety of similar systems, where experimental data extend to lower concentrations than obtained here [22]. We note that a broad variety of models have been suggested to explain this peculiar shape of the concentration dependence of  $g_1$  in terms of the self-association of alcohol molecules to dimers and higher clusters. We mention here as an illustrative example the work of Brot [24].

**Dielectric Relaxation.** The slowest mode ( $k=1$ ) dominates the spectrum. The resulting concentration dependence of  $\tau_1^{(1)}$  is shown in Fig. 4.  $\tau_1^{(1)}$  indicates a cooperative nature of the relaxation process, because it is much longer than estimated for single molecules, e.g. from magnetic relaxation data. Agreement that the  $\tau_1^{(1)}$ -process relates to cooperative motions of molecular associates was achieved a long time ago [11, 12].

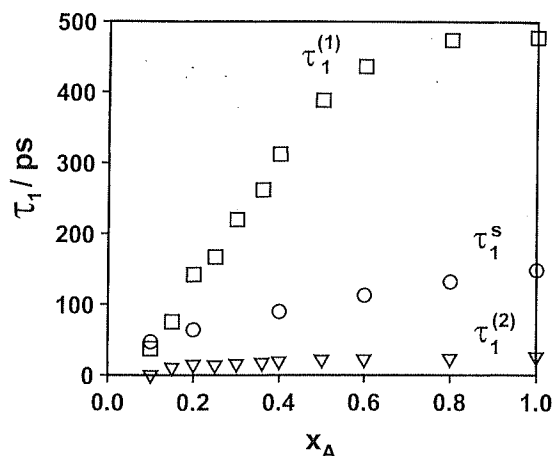


Fig. 4  
Dielectric relaxation times  $\tau_1^{(1)}$  and  $\tau_1^{(2)}$  in mixtures of n-butanol with  $\text{CCl}_4$  at 25 °C in comparison with correlation times  $\tau_2^s$  deduced from  $^2\text{H}$  magnetic relaxation data

In solutions in inert solvents  $\tau_1^{(1)}$ , like  $\tau_2^s$ , reflects the breaking-down of hydrogen bonds by the solvent. It is interesting to note that for the lower alcohols in  $\text{CCl}_4$ , maxima are found in the concentration dependence of  $\tau_1^{(1)}$  [10, 25]. Obviously, the addition of  $\text{CCl}_4$  initially results in an increasing self-association of the alcohol molecules due to solvophobic forces [4, 10]. The general shape of the concentration dependence of  $\tau_1^{(1)}$  in  $\text{BuOH-CCl}_4$  mixtures is still reminiscent of these maxima.

For examining the presence of cooperative motions, it is suitable to estimate the hypothetical dielectric relaxation time  $\tau_1^s$  of single dipoles by the formula

$$\tau_1^s = 3\tau_2^s. \quad (4)$$

Eq. (4) assumes small-step diffusion for the conversion of NMR data ( $l=2$ ) to dielectric data ( $l=1$ ) [21] which is well established for liquids of normal fluidity [1]. Thus, the ratio  $\tau_1^{(1)}/\tau_1^s$  can be taken as a direct measure of the cooperativity of the dielectric relaxation process. It is seen from Fig. 5 that, for  $\text{BuOH-CCl}_4$  mixtures, these ratios deviate from unity over large parts of the concentration range, indicating the cooperative nature of  $\tau_1^{(1)}$ . Towards infinite dilution,  $\tau_1^{(1)}/\tau_1^s$  should decay to unity, because correlations between the dipoles vanish. Of course, this is difficult to confirm, as at the same time  $\Delta\epsilon_1$  vanishes.

The relationship between collective relaxation times ( $\tau_1$  or  $\tau_2$ ) and the corresponding single-particle relaxation times ( $\tau_1^s$  or  $\tau_2^s$ ) has been a subject of much discussion [2, 3]. Madden and Kivelson arrived at an interrelation of the form [2, 26]

$$\tau_1^{(1)} = \frac{3k_B T \epsilon (\epsilon - 1)}{\rho \mu^2 g'} \quad (59)$$

where  $\rho$  is the dipole density and  $g'$  a coupling parameter. Some conceptual problems arise, when applying this rela-

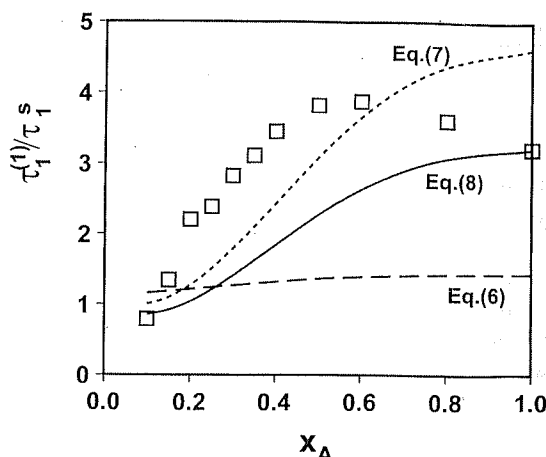


Fig. 5  
Comparison of the ratios  $\tau_1^{(1)}/\tau_1^s$  with theoretical predictions

tion to spectra with more than one mode but, in the present case, these may be of minor importance, as the primary relaxation is by far dominating.

For determining the coupling parameter, models have to be introduced. In the simplest case, one extends the Onsager model of the static permittivity to describe dielectric relaxation. In this case, one obtains [3]

$$\tau_1^{(1)} = \frac{3\epsilon}{2\epsilon + \epsilon_\infty} \tau_1^s, \quad (6)$$

as first mentioned by Glarum [27]. The Onsager-Glarum estimate is shown in Fig. 5 as a dashed line. The model reflects to some degree the increase of the cooperative contributions to the dielectric relaxation with increasing  $\text{BuOH}$  concentrations, but fails to describe the data in detail. This failure is well-known [3]. In fact, Eq. (6) cannot account for ratios  $\tau_1^{(1)}/\tau_1^s > 1.5$ .

As correlations between dipoles are neglected in the Onsager theory, it is intriguing to look for the dynamical analogue of the Kirkwood-Fröhlich theory which accounts for a non-statistical dipole distribution. In this case, one obtains an expression suggested a long time ago by Powles [28]

$$\tau_1^{(1)} = \frac{3\epsilon}{2\epsilon + \epsilon_\infty} g_1 \tau_1^s, \quad (7)$$

which reduces to the Onsager-Glarum relation for  $g_1 \rightarrow 1$ . Now, the overall increase of  $\tau_1^{(1)}/\tau_1^s$  from unity to a value above 3 is predicted, and there is at least a weak indication of the maximum in the experimental data by a plateau in the alcohol-rich regime. Remarkably, both the experimental data and the Kirkwood-Powles model show ratios  $\tau_1^{(1)}/\tau_1^s$  smaller than unity at low  $x_A$ . In the Kirkwood-Powles model this behavior can be traced back to the minimum of  $g_1$ . In view of the experimental uncertainties, we hesitate to take the existence of a range with  $\tau_1^{(1)}/\tau_1^s < 1$  for granted.

Additionally, we tried the simple relation

$$\tau_1^{(1)} = g_1 \tau_1^s \quad (8)$$

with the bare Kirkwood factor  $g_1$  as a coupling factor. A relation of this form is suggested by a similar expression widely used in the analysis of depolarized light scattering data [29, 30]. For hydrogen-bonded liquids like water [31] and alcohols [32] it is also born out by the results of computer simulations. Fig. 5 shows that, in total, predictions with Eqs. (7) and (8) are of about the same quality.

The intensity of the ( $k=2$ ) mode in alcohols is very weak compared with the primary mode, and also weaker than the ( $k=3$ ) mode [10, 13]. It is not observed with other hydrogen-bonded liquids such as water or amides [13]. Fig. 4 shows the concentration dependence of  $\tau_1^{(2)}$  which gradually decreases upon dilution in  $\text{CCl}_4$ .

In earlier work [16, 33],  $\tau_1^{(2)}$  has been attributed to free alcohol molecules, e.g. seen in infrared spectra [34]. There exist quite elaborate models which demonstrate that in the case of "free" and "bound" states two or more modes are expected in the dielectric spectrum, possibly associated with  $\tau_1^{(1)}$  and  $\tau_1^{(2)}$  [35]. This would justify an interpretation in which  $\tau_1^{(2)}$  is assigned to free alcohol molecules, while  $\tau_1^{(1)}$  reflects motions of molecules in the associated state. There are however arguments against this picture [10]. Buchner and Barthel [10, 13] have suggested that, in addition to free molecules, the terminal molecules in hydrogen-bonded chains may have a sufficiently increased mobility to explain  $\tau_1^{(2)}$ .

From our data for  $\tau_1^{(2)}$ , no direct relation to the NMR data can be found. Buchner and Barthel have pointed out that in methanol- $\text{CCl}_4$  mixtures  $\tau_1^{(2)}$  is of the same magnitude as the NMR correlation time  $\tau_2^s$  [10]. Fig. 5 shows that this coincidence is not obtained for BuOH- $\text{CCl}_4$  mixtures. Anyway, it would be difficult to explain such a coincidence in view of the fact that conversion from  $l=1$  to  $l=2$  processes inevitably introduces a factor of three into any comparison of this type.

Finally, it is interesting to examine consequences of the fact that NMR experiments only yield  $\tau_2^s$  from an integral over the spectrum, while the spectrum itself remains unknown. The reason is that the accessible frequency range in NMR is limited to frequencies well below 1 GHz, e.g. 46.1 MHz in our actual experiments for the  $^2\text{H}$  resonance. Thus, it cannot be excluded that  $\tau_1^{(2)}$  has a counterpart in the NMR spectral density which, due to its low amplitude, is hidden in the integral time constant. It may be more meaningful, therefore, to compare  $\tau_2^s$  with an integral dielectric relaxation time  $\langle \tau_1 \rangle$  averaged over the total dielectric spectrum.  $\langle \tau_1 \rangle$  can be easily derived from the amplitudes and relaxation times of the single modes (Table 1) but bears a comparatively large uncertainty as the amplitudes are uncertain.

Fig. 6 shows the resulting ratios  $\langle \tau_1 \rangle / \tau_1^s$  which in this case definitely become smaller than unity at low concentrations. Now, Eq. (8) yields a better representation of the experimental data than Eq. (7). Although not accurate in

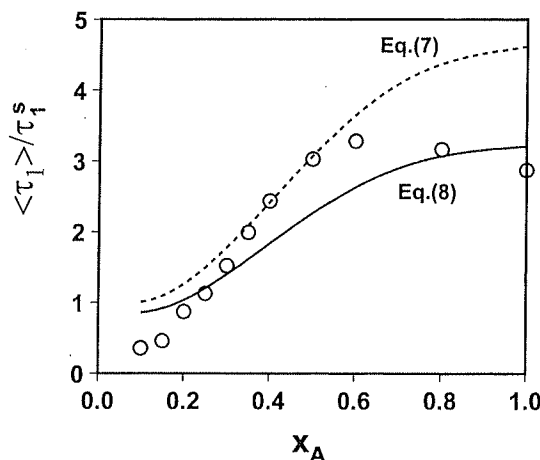


Fig. 6  
Comparison of the ratios  $\langle \tau_1 \rangle / \tau_1^s$  with theoretical predictions

detail, Eq. (8) reproduces major features of the concentration dependence of  $\langle \tau_1 \rangle / \tau_1^s$ , including the minimum at low and the plateau at high concentrations.

## 5. Conclusions

The comparison of magnetic and dielectric relaxation data confirms the collective nature of the primary relaxation and suggests that an expression of the general form

$$\tau_1 \propto g_1 \tau_1^s, \quad (9)$$

with the Kirkwood factor  $g_1$  as a coupling factor, may account for the relation between the dielectric relaxation time and the single-particle relaxation time of the dipoles. Possibly, this relation even is of the simple form of Eq. (8), where the bare factor  $g_1$  only is needed to relate collective and single-particle properties.

For  $l=2$  processes, the analogous relation  $\tau_2 = g_2 \tau_2^s$  [36] has been successfully applied to relate the cooperative correlation time observed in depolarized light scattering to NMR data [29, 30]. In analogy to  $g_1$ , the coupling factor  $g_2$  depends only on the equilibrium structure of the solution, and has often been denoted as "generalized Kirkwood factor".

Further tests of Eq. (7) or (8) are desirable, above all with purely dipolar liquids, where the absence of specific hydrogen-bonded interactions should largely facilitate theoretical computations. Unfortunately, most dipolar liquids exhibit Kirkwood factors  $g_1 < 1$  which do not differ sufficiently from unity to allow clear-cut conclusions. In this respect, alcohols (and some amides) are unique.

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