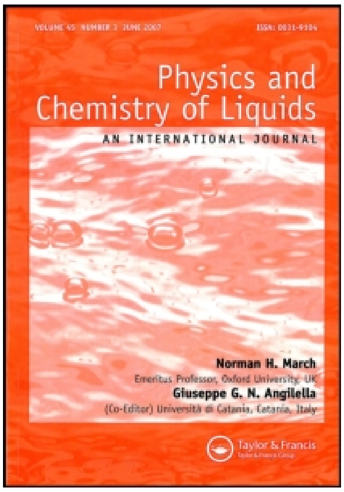

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M. Stockhausen[a]; H. Busch[a]
[a] Institut für Physikalische Chemie der Universität Münster, Münster, Germany

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DIELECTRIC RELAXATION OF BINARY MIXTURES OF THREE ALCOHOLS WITH DIMETHYLFORMAMIDE

M. STOCKHAUSEN and H. BUSCH

Institut für Physikalische Chemie der Universität Münster,
D-48149 Münster, Germany

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The dielectric spectra of binary liquid mixtures of the following alcohols with N, N-dimethylformamide (DMFA) have been measured between 5 MHz and 72 GHz at 20°C: 1-Hexanol, 1,2-hexanediol and 1,4-butanediol. The analysis of the spectra, which is particularly aimed at information on hetero-association, gives evidence for the formation of mixed aggregations, indicated by a minimum in the 'free' DMFA relaxation contribution at a mixture ratio of about 1:1 for hexanol/DMFA and about 1:2 in case of the dihydric alcohol/DMFA systems.

KEY WORDS: Association, binary mixtures, dielectrics.

1. INTRODUCTION

Binary mixtures of protic and aprotic liquids, as water or alcohols and, on the other hand, di-substituted amides, are not only of practical importance but attract also attention since, at the molecular level, their structural and dynamical characteristics can be rather complex and are not yet fully understood. Among other liquid mixtures consisting of interacting molecules, Kinart has studied alcohol/diamid mixtures[1,2], employing NMR data and various macroscopic physical properties to gain information on internal structures. For that purpose, excess quantities were determined, and their extrema occuring on variation of the mixture ratio were ascribed to the formation of definite associated 'complexes'. The conclusions drawn from most of the quantities considered are concurrent, but those drawn from static permittivity data deviate from others in some cases, exemplifying that the information contained in dielectric properties is not simply equivalent to that delivered by other physical parameters.

It seems worthwhile to study not only the static but also the dynamic dielectric properties of those mixtures. Dielectric spectroscopy is a useful technique of investigating association in polar liquids. The static permittivity reflects all the conceptually distinguishable fluctuations of local dipole moments only summarily, while, in principle, those processes appear spread out in the relaxation spectrum. Relaxation contributions at relatively low frequencies may originate in the association dynamics, being controlled by the lifetime of associated states. Higher frequency contributions relate to the tumbling motion of solitary polar molecules and, at still higher frequencies, eventually to intramolecular processes. Since the dominating relaxation mechanisms are of different nature, hydrogen bonding substances exhibit their overall relaxation region at appreciably lower frequencies than liquids where specific intermolecular interactions do not occur.

With regard to the dynamic dielectric properties of the protic/aprotic mixtures mentioned above, mainly aqueous systems with various amides have received attention (e.g.[3]). On the other hand, few studies have been performed on the dielectric relaxation of mixtures of alcohols and di-substituted amides[4].

In the present communication we report the dynamic dielectric properties of binary liquid mixtures of some aliphatic alcohols with N, N-dimethylformamide, DMFA, as aprotic component. Three alcohols of medium chain lengths were chosen to represent mono- and dihydric examples, the latter with either neighbouring or more distant hydroxy groups, namely 1-hexanol, HxOH, 1,2-hexanediol, $Hx(OH)_2$, and 1,4-butanediol, $Bu(OH)_2$. A major purpose of this work is to find out whether information on hetero-association (rather than self-association of the alcoholic component) can be extracted from the dielectric spectra.

2. EXPERIMENTAL

The complex permittivity of the mixtures was measured at a series of spot frequencies ranging from 5 MHz to 72 GHz, using different lumped circuit, coaxial and waveguide setups. The quantity of primary interest is the (negative) imaginary part $\varepsilon''(\omega)$ (dielectric loss) as already corrected for the (generally small) conductivity contribution $\varepsilon_c''(\omega) = \kappa/(\varepsilon_0 \omega)$, where κ is the conductivity and ε_0 is the permittivity of empty space. Further physical properties such as viscosity were determined, too. All measurements were carried out at 20°C.

Chemicals from Aldrich and Fluka were used as obtained.

3. RESULTS AND DISCUSSION

3.1. Qualitative Description

The $\varepsilon''(\omega)$ spectra of the pure alcohols resemble those of other alcohols. They appear (on the log ω scale) asymmetrically broadened in comparison to a Debye function, with the indication of a weak shoulder on the high frequency side. The dielectric function of pure DMFA, on the other hand, is (over the experimental frequency range) practically of Debye type. Examples are shown in Figure 1a.

For the alcohol/DMFA mixtures there is a gradual shift of the loss maximum and an apparently monotonous variation of the spectral shape with the mixture ratio. Closer inspection, however, reveals that the shape of the $\varepsilon''(\omega)$ curve changes in non-monotonous manner such that broadening is particularly marked for medium mixture ratios. This can readily be recognized normalized spectra, Figure 1b. Qualitatively, this feature is a strong indication of hetero-association.

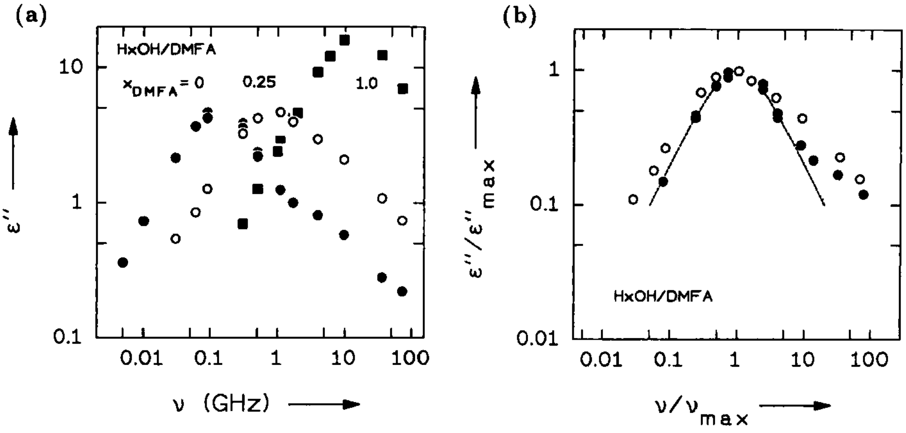

Figure 1 Typical spectra, ε'' against frequency ν (double log plot), illustrating the mixture series HxOH to DMFA; $x_{DMFA} = 0$ ●, 0.25 ○ and 1 ■. (a) Absolute scales. (b) Scales normalized to the ε'' maximum; the dotted line indicates a Debye function (applicable for $x_{DMFA} = 1$).

All ε''(ω) spectra observed can formally be described as a superposition of up to four Debye type spectral components C_i:

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

However, a plausible assessment of the relaxation times τ_i and the relaxation strengths S_i is difficult and leads to somewhat ambiguous conclusions. Therefore we desist from reporting those relaxation parameters but change to a modified scheme of analysis which includes a reasonable constraint. That method has successfully been applied already to similar mixture systems[5].

3.2. *Method of Analysis*

Liquids consisting of aprotic, quasi-rigid molecules, where single molecule rotational tumbling motion is the dominating relaxation process, show often dynamic dielectric properties which are characterized by some rough estimation rules for relaxation time and relaxation strength, applicable to the whole range from dilute solutions to pure liquids. DMFA is among the liquids exhibiting this 'normal' relaxation behaviour[6,7]. The constraint introduced into the analysis of the present spectra consists in the presupposition that DMFA, *if not* involved in specific interactions, should relax as usually found, so that for this case an 'expected' relaxation time $^e\tau$ and an 'expected' relaxation strength ^eS can be estimated. Accordingly, a spectral component C_0, with $\tau_0 = {}^e\tau$ kept constant for each mixture, is introduced into the analysis of the spectra, which then is carried out according to Eqn. (1) with a minimum number of additional spectral components C_i. Besides the parameters of the latter, the fit yields also the relaxation strength S_0 of the starting component, which then can be compared with its 'expected' value ${}^eS_0$.

Concerning the relaxation time, we refer to the empirical finding that, in cases of 'normal' relaxation behaviour, relaxation times obey a good mcorrelation with molecular size and viscosity[6,8,9]. From this, the 'expected' relaxation time for unaffected DMFA is estimated as

$$ {}^e\tau_0 = \tilde{\tau}\left(\frac{\eta}{\tilde{\eta}}\right)^{(r_{\text{eff}}/\tilde{r})-\tilde{k}}, \tag{2} $$

where the radius r_{eff} characterizes the size of the tumbling molecule, η is the viscosity of the liquid and the quantities marked by a tilde are empirical parameters. For the present systems, r_{eff} is determined from the relaxation time and the viscosity of pure DMFA to be $r_{\text{eff}} = 0.36$ nm. The relaxation times τ_0 for the mixtures are calculated with that value and the measured viscosities, which vary monotonously with mixture composition.

The relaxation strength in case of 'normal' behaviour is, due to the absence of orientational correlation effects, roughly proportional to the concentration c of the polar species. Thus

$$ {}^eS_0 = \frac{c_{\text{DMFA}}}{c^*_{\text{DMFA}}} S^*_0 \tag{3} $$

(where the asterisk denotes pure DMFA). It has been found for all mixtures considered here that $S_0 < {}^eS_0$, indicating that less DMFA behaves 'normal' than expected. The 'missing' fraction must be assumed to contribute to more slowly relaxing hetero-associates. To take into account the change in the number density of polar molecules over the mixture range, the (negative) 'excess' $S_0 - {}^eS_0$ is divided by the total (alcohol plus amide) concentration c_{tot}. The quantity

$$ \delta_0 = \frac{S_0 - {}^eS_0}{c_{\text{tot}}} \tag{4} $$

is given below together with the relaxation parameters.

3.3. *Results of the Model Supported Analysis*

Apart from the starting component C_0, the fit requires two ($Bu(OH)_2$) to four (HxOH) additional components. The sum of these *additional* components resembles in all cases spectra as shown in Figure 1, *viz.* of broadened shape with a minor high frequency shoulder. This is not unreasonable for a spectral contribution which is likely to reflect essentially self- as well as hetero-association. The relaxation times τ_i of the additional components differ sufficiently (by a factor of >2, with a few exceptions) from τ_0. Thus it can be hoped that C_0 reflects mainly the relaxation of unaffected DMFA as presumed.

For some alcohol rich mixtures, the fit is improved by allowing for a Cole Davidson (CD) type spectral component C_1, characterized by the skewness parameter β_1 (where $\beta_1 = 1$ means Debye type).

Relaxation times τ_i, relaxation strengths S_i, CD parameter β_1 and excess parameters δ_0 obtained in that manner are represented graphically in Figure 2. (Within the acceptable variability ranges of fit parameters, the values shown have been smoothed. The additional spectral components C_i are indexed in the order of increasing frequency by $i = 1 \ldots 4$. For easy comparison, corresponding indices are used even if not all numbers are required.)

3.4. *Discussion*

The relaxation times appearing in Figure 2 suggest that one should distinguish three ranges, that is (i) $\tau_i > \tau_0$ as represented by spectral components C_1 to C_3, (ii) the DMFA component C_0, and (iii) the higher frequency component C_4. The latter is a minor contribution, which is likely to reflect internal motion, e.g. the flexibility of alcohol chains or the rotation of 'free' OH groups. Since not related to the question of association, C_4 can be left out of consideration.

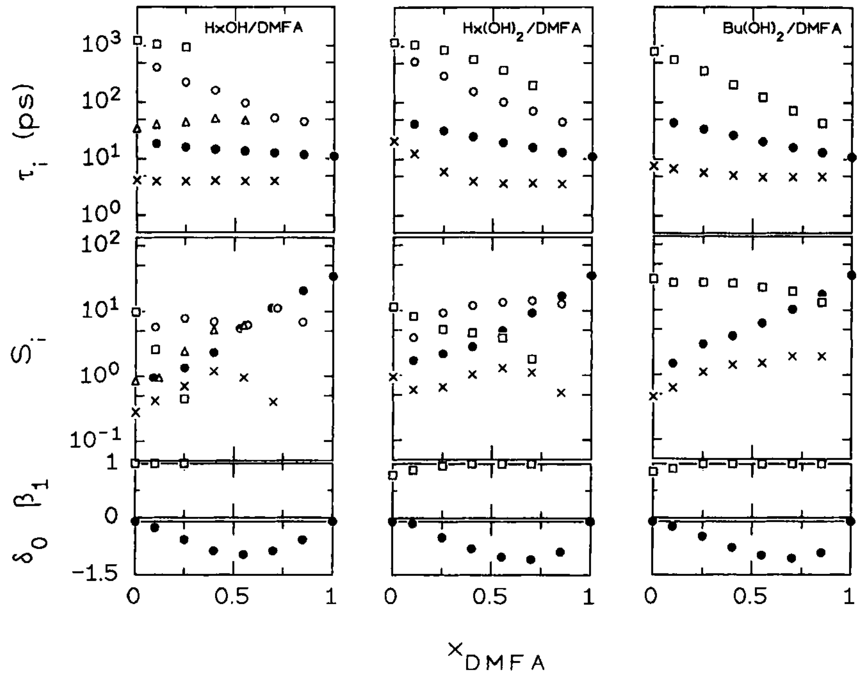

Figure 2 Relaxation times τ_i, relaxation strengths S_i, skewness parameters β_1 (for component C_1) and (negative) excess δ_0 of component C_0 (in units of l·mol^{-1}), against DMFA mole fraction x_{DMFA}, for the three mixture systems HxOH/DMFA (left), Hx(OH)$_2$/DMFA (middle) and Bu(OH)$_2$/DMFA (right). Symbols for the spectral components: C_0 ●, C_1 □, C_2 ○ C_3 Δ, C_4 ×.

(i) The relaxation parameters of C_1 to C_3 show that the interplay of self- and hetero-association leads to a behaviour which obviously depends on the individual properties of the alcohol involved. However, it seems unavailing to discuss the formally obtained spectral components in detail with respect to distinguishable physical processes. Merely the sum $\Sigma_1^3 S_i$ (which is practically not affected by fit uncertainities of the single values since these are coupled in opposing sense) shall briefly be regarded in a qualitative manner; a quantitative discussion would require model assumptions on the multitude of associates formed. With increasing x_{DMFA}, the sum passes through a maximum at medium DMFA content but shows a noticeable decrease only at high x_{DMFA}, finally vanishing for pure DMFA. This again is an indication of intensified association, very probably involving DMFA, and since the dipole moment of the amide is much higher than that of the alcoholic hydroxy groups, it is understandable that $\Sigma_1^3 S_i$ stays at a relatively high level until the mixture composition approaches pure DMFA.

(ii) The advantage of the model supported analysis is that C_0 can be ascribed to a well-defined species, that is to non-associated DMFA molecules. As already mentioned, there is a noticeable deficiency in the relaxation strength S_0, expressed by δ_0, Figure 2. It is the dependence of δ_0 on the mixture ratio x_{DMFA} which may give a hint as to what associated species exist. The minimum of δ_0 is at $x_{\mathrm{DMFA}} \approx 0.5$ for HxOH/DMFA and at $x_{\mathrm{DMFA}} \approx 0.7$ for both $\mathrm{Hx(OH)_2}$/DMFA and $\mathrm{Bu(OH)_2}$/DMFA.

These values compare quite well with those obtained by Kinart from the static permittivities of similar binary mixtures. He found extrema at $x_{\mathrm{DMFA}} \approx 0.5$ for methanol/DMFA[2] and $x_{\mathrm{DMFA}} \approx 0.6$ for 1,2-propanediol/DMFA[1]. Altogether, static and dynamic dielectric data seem to indicate some characteristic concentration of $x_{\mathrm{DMFA}} \approx 0.5$ for monohydric alcohols but clearly >0.5 for dihydric alcohols in DMFA mixtures. They do not give any evidence of peculiarities on the alcohol-rich side, in contrast to several other physical parameters in the case of the diol/DMFA system studied by Kinart[1].

Conclusions on the composition of hetero-associates cannot be drawn without model assumptions on the equilibria involved. On the simplifying assumption of only hetero-association (thus disregarding competing self-association), the position of the δ_0 minimum on the x_{DMFA} scale (Fig. 2) would directly yield the mean alcohol: DMFA ratio of the hetero-associates, that is about 1:1 in case of the monoalcohol and about 1:2 for the diols.

Summing up, hetero-association effects in the dynamic dielectric properties of binary alcohol/DMFA mixtures (although not as remarkable as in corresponding aqueous systems) can at least semi-quantitatively be revealed by an appropriate analysis of the relaxation spectra.

Acknowledgements

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