Dielectric Properties of 1-Hexanol in Mesitylene Solution on Admixture of Aromatic Dihydric Alcohols

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Broadband dielectric relaxation spectra (at 20 to 40 °C) are reported for three liquid alcohol/non-polar solvent systems: Binary hexanol/mesitylene mixtures and two corresponding ternary mixtures, where 5 percent of hexanol are replaced by a dihydric alcohol, namely resorcinol (1,3-dihydroxybenzene) or 2,2'-dihydroxydiphenyl. The concentration of the polar substance(s) ranges from dilute solutions to pure alcohol(s). The lower frequency relaxation contribution, which generally is the more dominating the higher the alcohol concentration, is additionally enhanced by the diol admixture in the case of low and moderate concentrations. This can be understood as a hetero-association effect, the diol molecules playing a bridging role, which also leads to an increase in the mean lifetime of associated states.

Introduction

The structure and dynamics of hydrogen-bonded liquids can, among other methods, be studied by dielectric relaxation spectroscopy. Actually the latter measures the spectral density of polarization fluctuations of a sample, and these are related to the microscopic motional processes of the polar constituents of molecules. Structural peculiarities such as the orientational correlation of molecular dipoles due to association are discernible from the relaxation strength or, equivalently, the static permittivity εs, while dynamical characteristics are reflected in the relaxation time(s) and, in more detail, in the shape of the dielectric function ε(ω) = ε'(ω) − iε''(ω). In particular it is the absorption spectrum ε''(ω) which is directly related to the polarization fluctuation spectrum z(ω), since (at given temperature) ε''(ω) = ω · z(ω) [1].

Alcohols as a large class of associating liquids have been extensively studied by dielectric spectroscopy already for a long time, regarding the pure liquids as well as mixtures with nonpolar solvents. It is agreed that the lower frequency absorption, which predominates in pure alcohols but vanishes gradually on dilution is due to association in quite a broad sense. A number of structural models have been proposed to interprete the static dielectric properties which are often based on the assumption of a chemical equilibrium between distinct associated species [2–7], and dynamical models have been developed to picture the fluctuations process [8–20].

Binary mixtures of water with alcohols have attracted special attention as one can hope to elucidate the effects of self and hetero-association and structure formation in those systems [21–29]. In that connection also binary mixtures of dihydric and monohydric alcohols are of interest since, to a certain degree, dihydric alcohols resemble water in their dielectric behaviour [29]. Some investigations of those systems have been reported previously [30–33]. Further information might be gained by studying those polar/polar mixtures on dilution with a nonpolar solvent. Results have been reported for water/mono-alcohol/nonpolar solvent mixtures [34]. However, to the best of our knowledge, ternary dihydric/monohydric alcohol/non-polar solvent mixtures have not yet been considered. We have therefore examined the dielectric behaviour of some systems of that type with regard to the influence of diol admixture, and the present paper reports the first part of results.

This study deals with n-hexanol (1-hexanol) as mono-alcohol of moderate chain length. We have considered its binary mixtures with the nonpolar solvent mesitylene (1,3,5-trimethylbenzene) and the ternary systems obtained by adding a minor amount of dihydric alcohol. Two aromatic diols were used for that

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purpose, namely resorcinol (1,3-dihydroxybenzene) and 2,2'-dihydroxydiphenyl, which differ with respect to the distance of H-bonding sites. Moreover, internal hydrogen-bonding is impossible for steric reasons in resorcinol but is feasible in dihydroxydiphenyl. Static and dynamic dielectric properties of the three systems have been measured over the whole concentration range (total alcohol mole fraction \( x = 0.04 \ldots 1 \)) at different temperatures ranging between 20 and 50 °C.

**Experimental**

The measurement of dielectric properties over a large range of dielectric loss as well as over a broad frequency band, covering the absorption spectrum of the liquids under consideration as completely as possible, requires the use of different apparatus which are suited for certain limited absorption or frequency intervals. Therefore equipment at three laboratories (Cairo, Mainz, and Münster) was employed, which is briefly described in the following.

The static permittivity \( \varepsilon_s \) was measured as \( \varepsilon' \) at 2 MHz using a WTW dipolemeter with an uncertainty of about 2%.

Concerning the measurement of the dynamic dielectric properties, which are expressed by \( \varepsilon''(\omega) \) in this work, two absorption ranges are roughly to be distinguished, corresponding to lower alcohol concentrations (alcohol mole fraction \( \leq 0.4 \)) and higher ones (\( \geq 0.4 \)).

For the lower concentrations, a swept-frequency transmission spectrometer \( (\nu_{\text{max}} = 18 \text{ GHz}) \) was used [35]. It could be utilized at frequencies between 100 MHz and 11 GHz, which is about the range of the absorption maximum. Leaving a gap of one order of magnitude on the frequency axis, four spot frequencies in the millimeter and submillimeter range were then available, namely 138, 238, 429, and 671 GHz. The 138 GHz frequency was generated by a Hughes impact oscillator, the other three frequencies were delivered by a methanol/methyl iodide laser system pumped by a CO\(_2\) laser [36, 37]. A differential method of absorption measurement was applied which makes use of two transmission cells in tandem, where the length of the chambers filled with solution and solvent, respectively, are continuously varied in opposite sense [38].

The higher concentration range was studied using different setups for spot frequencies between 10 MHz and 36 GHz. Up to 90 MHz a VHF bridge was employed. Above 300 MHz, the resonator perturbation method [39] was applied, except for 36 GHz, where the reflection of the sample cell was measured directly by a compensation method.

The \( \varepsilon'' \) values are on average accurate to about 5%.

Some non-dielectric properties were measured in conventional manner: Refractive index \( n_0 \) (Abbe refractometer), density \( \varrho \) (Mohr balance or pycnometer), and viscosity \( \eta \) (capillary viscosimeters).

Chemicals from Aldrich and Fluka were used as obtained (purity > 99% for the alcohols, > 98% for the solvent). For brevity, the mixture systems are denoted by a three letter code XYZ, indicating (in that order) the dihydric alcohol \( (X = o: \text{no diol, R: resorcinol, D: dihydroxydiphenyl}) \), the mono-alcohol \( (Y = H: \text{hexanol}) \) and the solvent \( (Z = M: \text{mesitylene}) \). Accordingly, the three systems regarded here are marked by oHM, RHM and DHM. The concentration of the polar components is always given as total alcohol mole fraction, \( x = x(X) + x(Y) \). In the ternary systems RHM and DHM, the diol as minor alcoholic component is held at a fixed mole ratio with respect to the mono-alcohol throughout the present work, which is \( x(X)/x(Y) = 5/95 \).

**Results**

**Static dielectric properties**

The static permittivity \( \varepsilon_s \) could be measured up to moderate concentrations only. Instead of reporting these values, it seems more informative to consider the apparent molecular moments \( \mu_{\text{app}} \) which are derived after the Onsager equation, assuming as usual that \( \varepsilon_x = n_0^2 \). The results are represented in Figure 1.

Regarding first the binary hexanol/mesitylene system \( (\text{oHM}) \), it is remarkable that \( \mu_{\text{app}} \) passes through a minimum. This minimum results from the application of the Onsager equation, while both the static permittivity \( \varepsilon_s \) and the static-optical dispersion step \( \varepsilon_s - n_0^2 \) increase monotonically with \( x \). We have observed a \( \mu_{\text{app}} \) minimum also for hexanol with n-heptane or decahydropaphthalene as solvent, and it has been reported for cyclohexane solutions as well [35]. Related monohydric alcohols (cyclohexanol, n-decanol and n-dodecanol) were found to behave similarly in cyclohexane solution [40]. Referring to Fig. 1, the \( \mu_{\text{app}} \) value of hexanol as extrapolated for \( x \to 0 \) is unexpectedly high in comparison to \( \mu_{\text{app}} \approx 1.65 \ldots 1.70 \text{ D} \).
as usually reported for n-alkanols in dilute solution, and it differs noticeably from the extrapolated $\mu_{\text{app}}$ values obtained with the other solvents mentioned. The extrapolation may, however, be questionable as data for still lower concentrations are lacking. The solvent effects behind these findings are not within the scope of the present work. For a qualitative comparison with the ternary systems it seems sufficient to state the occurrence of a $\mu_{\text{app}}$ minimum as a qualitative feature which points to an equilibrium of associate species characterized by preferably antiparallel or parallel molecular moment correlation (ring or chain structures, respectively [4–7]).

On addition of a diol, the dispersion step and, consequently, $\mu_{\text{app}}$ is clearly increased (Figure 1). The depth of the minimum appears to be reduced. The effects of both diols do not significantly differ.

**Dynamic dielectric properties**

The dielectric absorption spectra exhibit some features which depend on the alcohol concentration and additionally on the admixture of the minor diol component. These may first be described in a qualitative manner. For illustration, some characteristic results are displayed in Figure 2. All spectra are broader than a Debye curve, as commonly found with alcoholic systems. For medium and higher alcohol concentrations and for the undiluted alcohols (upper part of Fig. 2), there is a relatively slight deviation from the Debye character due to a rather weak but significant “shoulder” on the high frequency side of the main absorption band. On dilution, the latter contribution continues to exist in about the same frequency region, while the lower frequency absorption is reduced in its relative intensity, so that the overall absorption spectra appear now appreciably broadened (lower part of Figure 2). The effect of diol admixture is rather small at high alcohol content, but on dilution it becomes increasingly noticeable as a particular absorption in the low frequency region. One is confirmed in that qualitative description by a closer comparison of the shape of spectra for stepwise changed concentrations. It shows that the $\varepsilon''$ values in the lower frequency region change nonlinearly with alcohol content $x$ and are moreover affected by the admixture of a diol. In the higher frequency region, on the other hand, $\varepsilon''$ is roughly proportional to $x$.

Aiming at a quantitative description of these findings, we have chosen a fitting function according to
the following considerations. The absorption curve \( \varepsilon''(\omega) \) of concentrated alcoholic solutions and pure alcohols is often found to be formally describable by a Cole-Davidson (CD) function. Depending on the accessible frequency range, that fit may be improved by adding a further spectral component on the high frequency side \([29]\). Just this procedure is suggested also for the present systems by the shape of spectra at higher concentrations (see for example the upper part of Figure 2). An additional spectral component of Debye character, however, is not sufficient to describe also the lower concentration examples because they exhibit very broad spectra, but a succession of a few Debye type components is required. Accordingly we have fitted our data by a superposition of up to four spectral components \( C_1 \) to \( C_4 \) (indexed in the order of increasing frequency). Here, \( C_1 \) is the CD component characterized by relaxation time \( \tau_1 \), relaxation strength \( S_1 \) and skewness parameter \( \beta \) (\( \beta = 1 \) corresponds to the Debye case). It should be reminded for the following that the absorption maximum of the CD function corresponds to an “effective” relaxation time \( \tau_1 \beta \). The remaining three Debye terms are characterized by \( \tau_i \) and \( S_i \), where \( i = 2 \ldots 4 \). The experimental frequency gap mentioned above is arbitrarily “bridged” by an approximately linear \( \varepsilon''(\omega) \) dependence in the double log representation as indicated by the straight line in Figure 2. That frequency range concerns mainly component \( C_3 \) which is accordingly uncertain. Component \( C_4 \) need not be taken into account for cases where the experimental frequency range is restricted to 36 GHz maximum.

The relaxation parameters obtained by that fitting procedure are displayed in Figs. 3 – 5 for two temperatures, 20 and 40 °C. Data for 30 °C have been analyzed, too, but are not shown since, as to be expected, the parameters obtained lie intermediate to those for the two temperatures depicted. The relaxation strengths \( S_i \) are given in normalized form as \( S_i/x \). The alternative normalization to the molar concentration ratio \( c/c^* \) (the asterisk denoting the pure alcohol) would cause only little changes: As \( x \) decreases, \( S_i/(c/c^*) \)
The fitting results shown in Figs. 3–5 are in accord with the qualitative findings mentioned above. Relaxation times of at least spectral components $C_3$ and $C_4$, but in some regions even of $C_2$, are nearly independent of $x$. Also, the normalized relaxation strengths of these spectral components are approximately independent of $x$. Taking into consideration the variability range of fitting parameters, components $C_2$ to $C_4$ behave thus nearly "normal" in the sense that such behaviour is known for non-associating liquids. It is the combined increase of $\tau_1$ and $S_1/x$ which causes the development of the pronounced lower frequency absorption when going from dilute to concentrated solutions. Consequently the overall maximum of $\varepsilon'' (\omega)$ is mainly determined by $C_1$ at higher alcohol concentrations while at lower concentrations also the subsequent component $C_2$ must be taken into account. It is obvious that self and hetero-association effects are reflected in $C_1$. Since we are interested in just these effects, it will suffice to regard mainly that low frequency component.

For better comparability, “effective” relaxation times $\tau_1 \beta$ and normalized relaxation strengths $S_1/x$ are compiled in Figure 6. It may be noted that resorcinol and dihydroxydiphenyl lead to practically the same increase in $S_1/x$, while their influence is different with respect to the “effective” relaxation time $\tau_1 \beta$. The temperature dependence of $\tau_1 \beta$ can formally be expressed as an activation enthalpy $\Delta H$ according to an Arrhenius law. The fitting results for 20, 30, and 40 °C lead to the averaged $\Delta H$ values given in Figure 7. These are fairly uncertain due to the variability range of parameters resulting in the fit procedure, as indicated by an error bar in the figure. Only for the lowest concentration there is a significant difference between $\Delta H$ for the binary system oHM on the one hand, and the systems containing diol (RHM and DHM) on the other hand.
Discussion

It should be stressed that the above analysis is purely formal in character, so that the spectral components need not necessarily correspond to physically distinguishable relaxation processes. The use of Debye type components, for example, would not be justified for the submillimeter region if one aims at a physical interpretation (instead, spectral functions of the Rocard-Powles type might be appropriate). The present analysis, however, shall mainly provide a comparison of the three systems. For that purpose it seems permissible to retain the qualitative distinction of contributions being related or not to association, viz. \( C_1 \) at lower frequencies and \( C_2 - C_4 \) at higher frequencies, respectively.

Before discussing the influence of diol admixture on the relaxation parameters of \( C_1 \), an at least qualitative picture concerning the circumstances which govern the dielectric spectrum should be at hand. There is a continuing debate in the literature on dynamical models describing the dielectric spectra of alcoholic systems. The interpretation schemes are prevailingely based on the assumption of a dominating process consisting in fluctuations within associated clusters and exchange with “free” molecules rather than the tumbling motion of whole clusters. Qualitatively, exchange models yield absorption curves as found in experiment, although they may not allow for a sharp dividing line between certain well defined species \[41, 42\]. In a simple model of the one particle time correlation it is supposed that a dipole moment rests alternately in an “associated” and fluctuates in a “free” state, in the former occasionally undergoing rotational jumps \[43\] or staying even motionless \[44\]. In the case of slow exchange between these states, a lower frequency spectral component results with a relaxation time which is determined by the residence time of the particle in its associated state. The relaxation strength of that component is a measure of the fraction of molecules being “associated” on average, depending of course also on the degree of orientational moment correlation. A higher frequency component appears in addition which reflects the relaxation of “free” particles. This lifetime picture may be taken as a basis of discussion.

It is a common property of the systems studied here that \( \beta \) is small at low concentration, thus \( C_1 \) is very broad, possibly since quite different “associated” relaxors are operative independently. On increasing \( x \), also \( \beta \) increases, thus \( C_1 \) is narrowed. This has been considered a hint at an increasing degree of cooperativity \[8, 9, 16\], so that indeed it seems no longer meaningful to reckon with well defined associated species.

Let us regard now the increase in relaxation strength \( S_1/x \) caused by the addition of diol. It cannot simply be ascribed to the higher moment per molecule of diol in comparison to a monohydric alcohol since the diol fraction is only 5%. For the most part, it must be related to intensified association as due to increased orientational correlation within clusters existing also in the absence of diol, and/or formation of additional associates. Let tentatively the latter be assumed to be the dominating effect. Then the finding that the relative increase of \( S_1/x \) is appreciable at low concentration \( x \) but tends to vanish as \( x \) increases (Fig. 6) could be readily understood as a result of competing self and hetero-association processes. Regardless of detailed assumptions concerning species involved, the observed tendency will always result if the equilibrium constant for hetero-association is large enough with respect to that for self-association of the major alcoholic component (hexanol). According to the different number of H-bonding sites per molecule, the self-association of n-alkanols is usually assumed to be chain-like, whereas dihydric alcohols are presumably capa-
ble of forming associated networks. For the present systems, diol molecules may act as connectors between hexanol molecules. We infer therefore that hetero-association by "bridging" could account for the remarkable effect of the only minor diol component in particular at low total concentration.

It may be added at this point that the rather small effect at high concentration is possibly related to the aromatic nature of the diols used here. For \( x = 1 \) (viz. the binary dihydric/monohydric alcohol mixture), the effect of aliphatic diols has been found to be clearly larger than observed for the present systems (according to own data for 1,6-hexanediol and to literature data for some 1,2-alkanediols [31]).

The differences in self-associate structure of monohydric and dihydric alcohols are known to influence dielectric relaxation and viscous flow. In a \( \tau - \eta \) plot, pure n-alkanols and dihydric alcohols appear as clearly separated "families" [29]. Figure 8 shows such a plot for the present systems. For comparison, values for a series of n-alkanols are also shown. (The diol "family" would be found at higher viscosities outside the figure's frame). Restricting ourselves for the moment to the binary oHM system, we notice that the points for the concentration series of oHM resemble remotely those for the series of pure n-alkanols, but not in any case there is a similarity to the behaviour of diols. It may be noted that at low concentrations \( \tau_1 \beta \) increases with increasing \( x \) while \( \eta \) stays nearly unaffected, which is indicative of not too large associated clusters. Turning now to the ternary systems containing also diol, it is remarkable that RHM behaves as oHM to within uncertainty of relaxation parameters, while DHM, at low concentrations, deviates significantly due to the relatively long relaxation time \( \tau_1 \beta \) (which may also be recognized by comparing \( \tau_1 \) in Figs. 4 and 5).

The question remains how to understand that the addition of resorcinol and dihydroxydiphenyl leads to about the same alteration of relaxation strengths \( S_1/\chi \) but has differing influence on the relaxation times \( \tau_1 \) as well as \( \tau_1 \beta \). The former is explainable by the assumption that the diol is almost quantitatively involved in hetero-associates, in accordance with the conclusion drawn above that the respective equilibrium constant is likely to be relatively large. The latter indicates that, in quite a broad sense, the characteristic times of the fluctuation process in the "associated" state of polar molecules, particularly of the majority (hexanol) molecules, are related to the size and structure of the "bridging" diol molecules. Several processes are conceivable to picture this interrelation in a rough fashion. For instance, if small hetero-associates should be present at low concentration, their relaxation by rotational tumbling would depend on the size of the diol molecules involved as observed. On the other hand, one may invoke the "switch" process within an associated cluster as proposed by Sagal [12], the relaxation time of which depends on the probability of moment jumps and also on the jump angle. If switching between the two hydrogen bonding sites of a diol molecule should play a noticeable role, the relaxation time due to this particular process would depend on the structure of the diol. For the two diols used here the observed tendencies of \( \tau_1 \) (or \( \tau_1 \beta \)) are not implausible in view of the different distances of OH sites. Lastly the possibility of intramolecular O−H⋯O hydrogen bonding in the case of dihydroxydiphenyl [45] may be taken into account as a competing process (while O−H⋯π bonds are unlikely to cause the differences since possible in all systems).
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