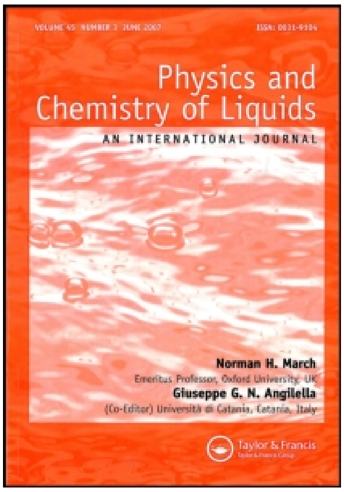

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DIELECTRIC RELAXATION OF BINARY MIXTURES OF GLYCEROL WITH THREE MONOHYDRIC ALCOHOLS

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The dielectric spectra of the following liquid mixture systems have been measured over the whole absorption region: Glycerol (Gly)/*n*-butanol, Gly/*t*-butanol (both at 20°C) and Gly/guaiacol (20, 40 and 60 °C). The results are comparatively discussed with regard to hetero-interactions, taking into consideration the possibility of internal hydrogen bonding in the case of guaiacol and, generally, of steric constraints.

Keywords: Dielectrics; hydrogen bonding

1. INTRODUCTION

The dielectric relaxation properties of liquid alcohols have been extensively investigated for a long time. These studies have provided substantial information about the dynamics of intermolecular interaction *via* hydrogen bonding and the occurrence of associated structures. Alcohols are a class of compounds comprising a broad variety of molecular structures, so that the influence of molecular peculiarities, *e.g.* steric conditions, can be studied without changing the character of the predominating interaction mechanism. In that respect mixtures of different alcohols have attracted interest, and recently systems containing a dihydric and a monohydric alcohol have drawn particular attention [1 – 11]. They have been studied both as binary mixtures of the alcoholic components and as ternary systems

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with a nonpolar diluent as third component. It appears, however, that little work has been performed so far on binary mixtures of trihydric with monohydric alcohols. In the present communication we report results on three systems of that kind. Glycerol (Gly) is the common trihydric component. The monohydric components are 1-butanol (*n*-butanol, *n*B), *tert*-butanol (*t*-butanol, *t*B) and guaiacol (*o*-methoxyphenol, Gu). The latter was chosen as an example with competing *intra*molecular hydrogen bonding, which is known to result in a relaxation behaviour of the pure liquid resembling that of non-associating substances [12].

2. EXPERIMENTAL

We have measured the dielectric relaxation spectra of the binary systems for their whole mixture ranges at up to 17 spot frequencies between 5 MHz and 72 GHz. The temperature was 20°C. For the guaiacol system (Gly/Gu), 40 and 60°C data were measured in addition. The viscosity was determined at the same temperatures.

3. RESULTS

The loss spectra $\varepsilon''(\omega)$ can satisfactorily be described in most cases as a sum of a Cole-Davidson plus a minor Debye function, except for Gly/Gu in the medium mixture range where a superposition of only Debye functions is suitable. For better comparability, it seems appropriate to use Debye type spectral components C_i without exception, *viz.*

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

(indexed in the order of decreasing τ_i). Such a description is formal in character, the terms do not necessarily correspond to distinguishable physical processes. Three terms are required to obtain fits within the limits of experimental error. The fit parameters, *viz.* relaxation times τ_i and relaxation strengths S_i, are represented graphically in

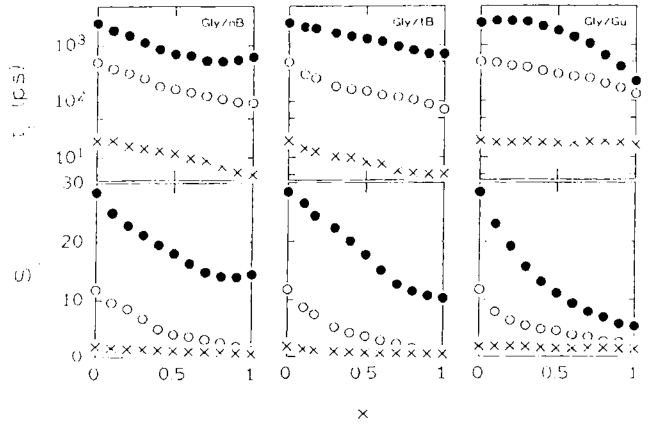

FIGURE 1 Relaxation parameters τ_i and S_i vs. mole fraction x of monohydric alcohol for the systems (left to right) glycerol/*n*-butanol, glycerol/*t*-butanol and glycerol/guaiacol; 20°C. Symbols for spectral components: ● C_1, ○ C_2, × C_3.

Figure 1 *vs.* the mole fraction x of the monohydric mixture component (20°C; pure *t*-butanol could be measured as undercooled liquid at that temperature [13]).

4. DISCUSSION

Spectral component C_1 is predominating in all cases and may therefore primarily be regarded when comparing the relaxation behaviour of the mixture systems. Qualitatively, that component reflects the dynamics of association, τ_1 being a measure for the mean lifetime of a molecule in an associated state [14], assumedly with the exception of the Gu rich side of the Gly/Gu system. The common overall trends of C_1 (Fig. 1) are as to be expected. The relaxation times τ_1 decrease with increasing mole fraction x, corresponding to the considerable decrease of viscosity η from glycerol to the pure monohydric components. The relaxation strengths S_1 decrease at the same time, an effect which is qualitatively consistent with the decreasing concentration of polar groups. More specific features will be detailed in the following.

The x dependence of the main relaxation time τ_1 is found to show a slight minimum in the case of Gly/*n*B, while it changes monotonously for Gly/*t*B and exhibits a slight maximum for Gly/Gu. The extrema appear in spite of the monotonous decrease of viscosity, establishing examples of the rare situation that dielectric relaxation time and viscosity vary in opposite sense. In order to illustrate the variation of viscosity with mixture composition, Figure 2 shows, instead of η, the excess viscosity η^E defined by

$$\eta^E = \eta - \exp(x_A \ln \eta_A^* + x_B \ln \eta_B^*),$$

where the subscripts A, B refer to glycerol and the monohydric component, respectively, and the asterisk denotes the pure substances. The maximum excess increases by more than an order of magnitude in the sequence Gly/*n*B — Gly/*t*B — Gly/Gu. In the case of Gly/Gu, the maximum coincides approximately with that of τ_1.

The composition dependence of the main relaxation strength S_1 is paralleled by that of the minor contribution S_2 and S_3, and therefore it may suffice to regard the total relaxation strength $\sum S_i$. In order to eliminate, at least for the most part, its dependence on the concentration of polar groups, it is useful to normalize it with respect to an effective OH concentration $c_{\text{eff}} = c_{A,\text{eff}} + c_{B,\text{eff}}$ as contributed by both mixture components A, B. For that, the following simplifying assumptions are made. Glycerol OH moments are supposed to be independent in their orientation, so $c_{A,\text{eff}} = c_{\text{OH}} = 3_{c_A}$. For $B = n$B, tB there is $c_{B,\text{eff}} = c_{\text{OH}} = c_B$. In case of $B = \text{Gu}$, the effect of moment alteration due to the presence of the methoxy group has to be taken into account. Assuming that the guaiacol molecule behaves as rigid

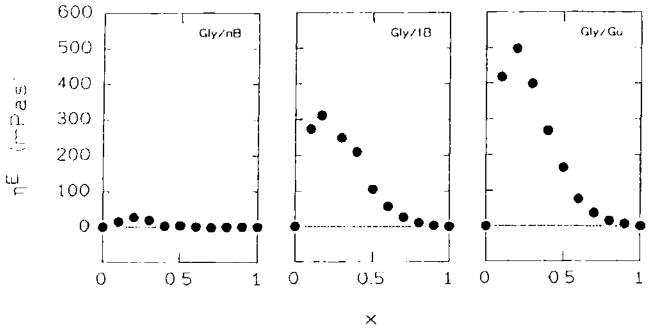

FIGURE 2 Excess viscosities η^E for the same systems as Figure 1; 20 °C.

entity, we have $c_{B,\mathrm{eff}} = (\mu^2_{\mathrm{Gu}}/\mu^2_{\mathrm{OH}})c_B$, with the approximate values $\mu_{\mathrm{Gu}} \approx 2.4$ D and $\mu_{\mathrm{OH}} \approx 1.6$ D [12]. The $\sum S_i/c_{\mathrm{eff}}$ values obtained in that manner are shown in Figure 3. They are a measure for the Kirkwood g-factor, qualitatively indicating the orientational correlation of moments although disregarding quantitative details of the underlying relations which are model dependent.

The value for pure guaiacol ($\sum S_i/c_{\mathrm{eff}} \approx 0.4$) is known to correspond to $g \approx 1$ [12]. Consequently a positive orientational correlation of moments is likely to occur in all systems over the whole mixture range, varying, however, remarkably in magnitude with mixture composition. As before, also the features of Figure 3 change in the order of Gly/*n*B — Gly/*t*B — Gly/Gu. A similarly curved dependence on composition as found for Gly/*n*B (Fig. 3) has been reported for the g-factor of propanediol/*n*-propanol mixtures [15]. This shape seems to be common for mixtures of polyhydric with linear short chain mono-alcohols.

Looking from the glycerol side it appears from Figures 1, 3 that the perturbation of glycerol structure and dynamics is least by *n*B and worst by Gu. On the other hand, looking from the complementary side, the fall in the normalized relaxation strengths of two of the *B* components, namely *n*B and *t*B (Fig. 3), indicates a structure breaking effect of Gly on these self-associating mono-alcohols, an explanation which has similarly been given for the addition of diols to normal

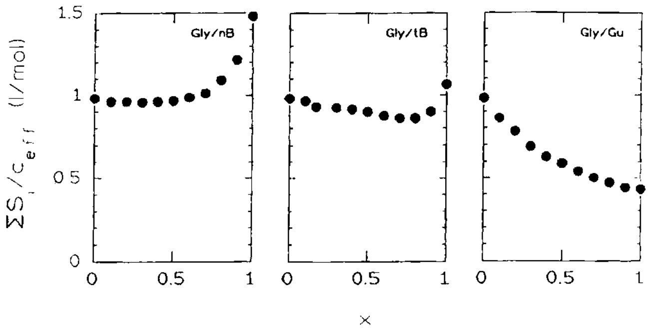

FIGURE 3 Normalized total relaxation strengths $\sum S_i/c_{\mathrm{eff}}$ for the same systems as Figure 1; 20 °C.

alcohols [2]. A tendency to form hetero-complexes with a molar A:B ratio of about 1:3 may be inferred from the plots.

The third example, Gly/Gu, deserves closer examination. As mentioned earlier, the dielectric properties of guaiacol in the pure liquid state and also in solution with a non-polar solvent are similar to those of non-associating molecules [12]. That behaviour is likely to relate to intramolecular hydrogen bonding as well as steric conditions. Since now Gly is present as second hydroxy compound, the question arises as to whether hetero-interactions may enter into competition with the intramolecular effect.

A hint in that regard is given by the temperature dependence of the relaxation parameters of the Gly/Gu system. We desist from reporting details but consider only the Arrhenius activation enthalpy $\Delta H_{\tau 1}$ derived from relaxation time τ_1. This is shown in Figure 4 together with the activation enthalpy for viscous flow, ΔH_η. Looking from the guaiacol side, both quantities increase considerably even on addition of only small amounts of glycerol. This behaviour is quite different from that found with normal, self-associating alcohols. Two examples may be mentioned: On admixture of 1, 2-propanediol to n-propanol [15] or of aromatic diols to n-hexanol [9], $\Delta H_{\tau 1}$ starts from a higher value but it is, however, not significantly changed by addition of

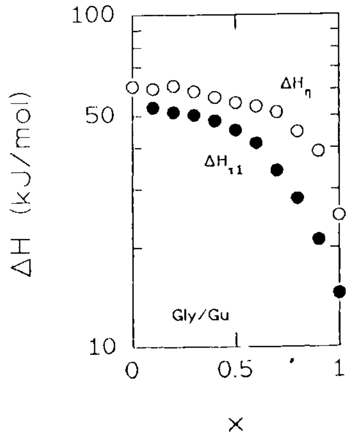

FIGURE 4 Arrhenius activation enthalpies $\Delta H_{\tau 1}$ (full symbols) and ΔH_η (open symbols) from relaxation time τ_1 and viscosity η, respectively, for the system glycerol/guaiacol (20–60 °C).

the diol. For the Gly/Gu system under consideration (Fig. 4), the (logarithmic) slope of both ΔH_{T1} and ΔH_{η} becomes smaller on the glycerol rich side. The intersection of limiting slopes may be considered indicative of a 1:3 molar ratio in the Gly-Gu interaction, in that respect resembling the other two mixture systems.

Finally it is worth emphasizing that the observed Gly/*n*B — Gly/*t*B — Gly/Gu sequence of properties, irrespective of *intra*molecular *H*-bonding in Gu, can qualitatively be explained by the assumption that *inter*molecular interaction is controlled by steric requirements. It is obvious from a comparison of the linear molecular structure of *n*-butanol and the compact structure of *t*-butanol that the accessibility of the hydroxy group is reduced in that order, and similarly the hydroxy oxygen of guaiacol may partly be screened by any (even inert) group in *o*-position which is equivalent in size to the methoxy group. In that situation the OH group will more probably act as proton donor rather than proton acceptor. The donor function is presumably put into effect if another mixture component, glycerol in the present examples, offers acceptor sites.

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