Dielectric Relaxation of 2-Amino-1-butanol

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The dielectric relaxation spectrum of the title substance in mixtures with 1,4-dioxane or benzene (pure liquid to moderate mixture ratios) is measured between 5 MHz and 36 GHz at 20 °C. The static permittivity is determined over the whole mixture range. The results are discussed in particular with respect to the possibility that different types of hydrogen bonded aggregations may contribute to the main relaxation.

The 2-amino-1-butanol molecule offers several hydrogen bonding possibilities. One may expect intramolecular H-bonds as known for similar molecules (2-amino-ethanol), where preferably the N···H–O bond is established by the isolated molecule [1] and occurs also in dilute solution [2]. In the pure liquid state a variety of intermolecular H-bonds is feasible, the N···H–O or O···H–N as well as the O···H–O type. The dielectric relaxation spectrum of pure 2-amino-1-butanol [3] indicates a correspondingly complex association behaviour by exhibiting a comparably broad main absorption region, which is just the region usually related to self-association, while the high frequency side of the spectrum resembles that normally found with alcohols, its moderate slope indicating subsequent but less intense relaxation contributions. There is no influence of the stereoisomeric composition on the spectrum [3]. It is a question whether the main absorption incorporates overlapping absorptions ascribable to dielectrically distinguishable types of self-association (so that its formal description by discrete spectral components rather than by a continuous distribution of relaxation times would be appropriate). Information in that respect may be gained from the eventual alteration of the relaxation spectrum on dilution of the alcohol by a nonpolar solvent. We have therefore studied the relaxation behaviour and the static dielectric properties of 2-amino-1-butanol in mixtures with 1,4-dioxane and benzene.

The absorption quantity $\varepsilon''(\omega)$ was measured at 10 spot frequencies ranging between 5 MHz and 36 GHz. The temperature was 20 °C. For reasons of sensitivity the alcohol mole fraction $x_{alc} > 0.4$. The static permittivity ε_s, on the other hand, was measured over the whole mixture range ($x_{alc} \geqq 0.01$), either at 1.5 kHz (with a Wayne-Kerr B 330 bridge) or 5 MHz (with a Wayne-Kerr B 801 B bridge), depending on the alcohol content being lower or higher than $x_{alc} \approx 0.4$, respectively. The density ϱ, viscosity η and refractive index n_D were determined in addition.

The $\varepsilon''(\omega)$ data (after correction for the conductivity contribution) were fitted by a sum of discrete Debye type spectral components C_i. A minimum number of four components is necessary for satisfactory fits covering the experimental frequency range. Their parameters, i.e. relaxation times τ_i and relaxation strengths S_i, are represented graphically in Figs. 1 a and 1 b. The relaxation strenghts are normalized to the alcohol concentration, viz. $S_i\, c^*_{alc}/c_{alc}$, the asterisk indicating the pure liquid. In Figs. 1 a, b the size of the symbols corresponds roughly to the acceptable variability range of the parameters (only the minor high frequency component C_4 is somewhat less accurately defined). From the static ε_s data we calculated the apparent dipole moment μ_{app} according to the Onsager equation, with $\varepsilon_\infty = n_D^2$. These moments appear in Figure 1 c. The applicability of the Onsager equation is questionable at higher x_{alc}, so the absolute μ_{app} values should be considered with some caution in that region.

The results show some conspicuous features. All the parameters (except for S_1 at most) differ only insignificantly between the dioxane and the benzene mixture systems. This is not usually the case with simpler alcohols. For example, we found clear differences between

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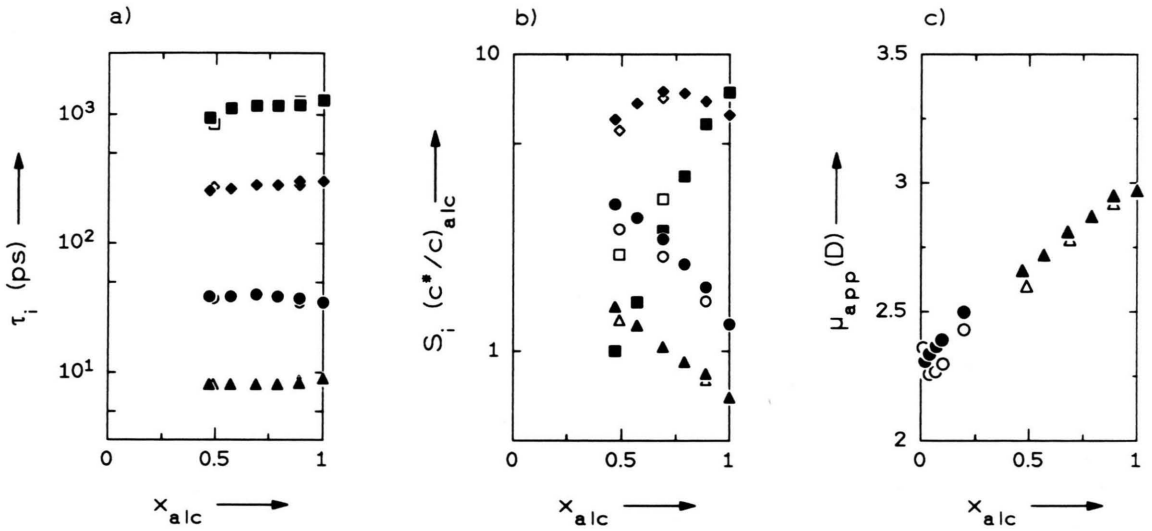

Fig. 1. Dielectric parameters against aminobutanol mole fraction x_{alc} for mixtures with 1,4-dioxane (full symbols) or benzene (open symbols). – (a) and (b): Relaxation times τ_i and normalized relaxation strengths $S_i\, c^*_{alc}/c_{alc}$ (log scales). Symbols for the spectral components: ■ C_1, ◆ C_2, ● C_3, ▲ C_4. – (c) Apparent moment μ_{app}. (Circles and triangles refer to the measuring devices mentioned in the text.)

corresponding ethanol mixture systems. A second peculiarity is the approximate constancy of the relaxation times, which contrasts with the considerable decrease of viscosity on dilution ($\eta = 42.8$ mPa s for the pure alcohol, but 4.3 mPa s at $x_{alc} = 0.47$ in dioxane and 3.2 mPa s at $x_{alc} = 0.49$ in benzene). It may be reminded that in those cases where the relaxation process consists in the tumbling motion of quasi-rigid, non-associating molecules one observes a regular change of tumbling time with viscosity. Even associating liquids, where the relaxation may be governed by another characteristic time (viz. the molecular residence time in the associated state) often show a similar τ vs. η correlation. It has not been found possible, however, to modify the minimal 4-term fit to such a degree that an according viscosity dependence could be reproduced. Considering the absolute values of relaxation times τ_i (Fig. 1 a), only τ_3 is in an order to be probably related to the reorientational motion of single molecules.

Let now the main absorption region be considered, which is composed of spectral components C_1 and C_2. As with other alcohols, it is doubtless due to some fluctuation within associated aggregations. The introductory question can be answered by regarding the concentration dependence of C_1 and C_2. For the pure substance $S_1 \approx S_2$ so that both terms could be replaced by one symmetrically broadened component. On dilution, however, the normalized relaxation strength $S_1\, c^*_{alc}/c_{alc}$ is found to decrease drastically, while $S_2\, c^*_{alc}/c_{alc}$ increases and passes through a maximum. This behaviour is likely to reflect (at least) two absorption contributions attributable to physically distinguishable processes rather than to a uniform (collective) mechanism. The $S_i\, c^*_{alc}/c_{alc}$ vs. x_{alc} plots (Fig. 1 b) resemble the tendencies expected in case of a stepwise association equilibrium. From this the conclusion appears that C_1 and C_2 are probably due to differentially associated aggregations. One may speculate that these are distinguished by the type of H-bonds.

From their relaxation times the components C_3 and C_4 are likely to relate to monomeric alcohol molecules. The relaxation time τ_4 is already so short that it may be connected with the internal mobility of the molecule. The latter assignment is suggested also by the only slight change of the ratio S_3/S_4. The relaxation strengths S_3 and S_4 give no hints with regard to the question as to whether or not the monomeric molecules form intramolecular hydrogen bonds.

Lastly the static dielectric properties may be taken into consideration. For medium and higher alcohol contents the monotonous concentration dependence of μ_{app} (Fig. 1 c) is in accord with the picture of stepwise association provided that higher aggregation states are characterized by greater (positive) orientational moment correlation. However, further discus-

sion as on the types of H-bonds in the aggregations which are suspected to cause C_1 and C_2 would be purely conjecture. The range of low alcohol content may yield some information on the monomeric molecules. The dilute solution limit of the apparent moment is (average of both mixture series) $\mu_{app}^0 = 2.30 \ldots 2.32$ D. This value is rather close to the total moment $\mu \approx 2.15$ D expected for the case of independently oriented group moments ($\mu_{NH_2} \approx 1.3$ D, $\mu_{OH} \approx 1.7 \ldots 1.75$ D), so this possibility cannot be ruled out. On the other hand, even assuming that only one well defined species be present, conformations which would allow for internal H-bonds and, at the same time, approximately the above molecular moment are conceivable as well. Thus group moment considerations are not decisive for the present case. One may compare μ_{app}^0 to the experimental moment of 3.05 D which is reported for the internally H-bonded conformation of the related molecule 2-aminoethanol in the gaseous state [2]. If a corresponding conformation with about the same moment should exist for the present alcohol, this cannot play an essential role in comparison with other, less polar conformations in dilute solution.

In conclusion it should be mentioned that the present systems, even though details of their relaxation behaviour are still left in need of clarification, exhibit some features of significance for the assessment of dielectric properties of associating liquids. The occurrence of distinguishable relaxation contributions with roughly viscosity independent relaxation times closely resembles the dynamic dielectric properties of polymer solutions [4]. Aminobutanol provides an example of a small molecule showing such a behaviour which is ascribable to a microheterogeneous structure of the liquid, based on aggregations with distinctive relaxation dynamics.

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