Dielectric Spectroscopy of Binary Liquid Mixtures of Methanol with Morpholine, Pyrrolidine and some of their Derivatives

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Dielectric spectra (up to 72 GHz) have been measured at 20 °C for mixtures of methanol and one of the following substances: morpholine, N-methyl morpholine, N-cyano morpholine, pyrrolidine and N-cyano pyrrolidine. The composition dependence of the relaxation parameters shows close similarities for the morpholines and, on the other hand, for the pyrrolidines, which indicates that a structure breaking effect on methanol is exerted by the former but not by the latter group of substances.

The heterocyclic molecule morpholine can act as proton acceptor via the ring oxygen as well as the ring nitrogen. These potential hydrogen bonding sites enable interactions with other, proton donating molecules. Morpholine, which is a liquid at ambient temperature, may therefore, apart from self association, show hetero association effects in mixtures with protic components. Dielectric spectroscopy is a suitable tool to reveal those interactions in the liquid state. Indeed, in a previous dielectric relaxation study [1] on morpholine and some of its N-substituted derivatives we have observed clearcut features in the relaxation behaviour of aqueous mixtures which are due to hetero interactions. The purpose of the present note is to study whether those effects occur also with other protic mixture components such as alcohols. Methanol has been considered for that purpose. In addition, the question may be raised which of the two hydrogen bonding sites is responsible for effects observed in the dielectric relaxation spectra. It is another objective of the present note to answer this question by comparison with an analogous molecule which, however, does not contain oxygen in the heterocycle, namely pyrrolidine. Also this substance and some of its N-substituted derivatives have previously been studied dielectrically as pure liquids and in mixtures with nonpolar components [2]. Therefore the present note focuses on the mixtures, looking in particular at the methanol relaxation as affected by the addition of the second mixture component.

We have carried out dynamic dielectric measurements at 20 °C, covering the frequency range between some ten MHz and 72 GHz, on mixtures of methanol (MeOH) as common component and one of the following substances as second component:

morpholine (Mo),
N-methyl morpholine (MeMo),
N-cyano morpholine (CyMo),
pyrrolidine (Py),
N-cyano pyrrolidine (CyPy).

Mo, in contrast to MeMo, is known to show self association effects [1], so both substances were studied in MeOH mixtures in order to see whether this fact leads to noteworthy differences in the respective overall relaxation behaviour. The cyano derivatives of both morpholine and pyrrolidine were chosen because of their relatively high dipole moment, which in mixtures with MeOH might allow for a better discrimination of the relaxation contributions than in case of the unsubstituted (weakly polar) compounds.

The frequency dependence of the complex permittivity, primarily of its imaginary part $\varepsilon''(\omega)$, was formally analyzed into a conductivity contribution, which is of no interest here, and a sum of Debye type spectral components C_i, each characterized by the parameters relaxation time τ_i and relaxation strength S_i. The spectral shapes are close to the Debye function in all cases, so a two term analysis is sufficient, the higher frequency term being of minor relaxation strength. Only for two systems (CyMo/MeOH and Py/MeOH) the fit could significantly be improved by applying three terms.

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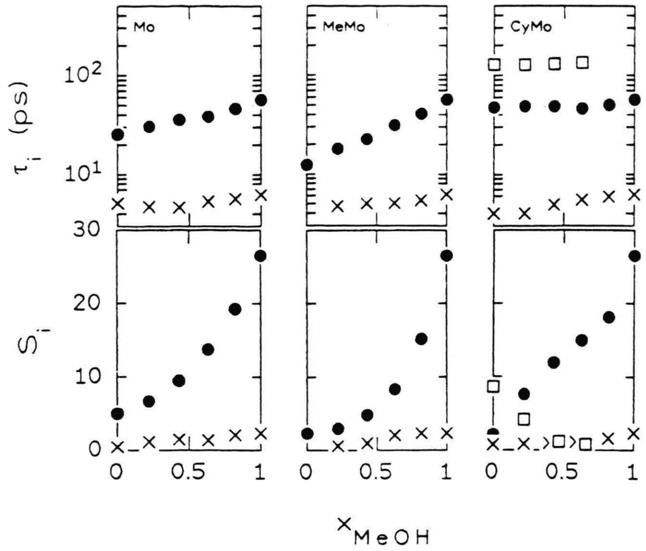

Fig. 1. Relaxation times τ_i and relaxation strengths S_i according to a two or three term fit with Debye type components, against mole fraction x_{MeOH} for the mixture systems Mo/MeOH (left), MeMo/MeOH (middle) and CyMo/MeOH (right). The spectral components are differentiated by the symbols used.

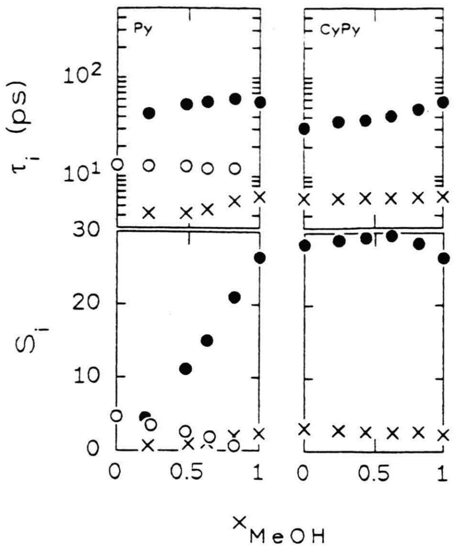

Fig. 2. Relaxation times τ_i and relaxation strengths S_i for the mixture systems Py/MeOH (left) and CyPy/MeOH (right). As Figure 1.

The relaxation parameters τ_i and S_i found for the morpholine/MeOH mixture systems are represented in Fig. 1, and those for the pyrrolidine/MeOH systems in Figure 2.

The main spectral component (the role of which is passed to another one only in the $x_{\mathrm{MeOH}} \rightarrow 0$ limit in case of the three term analyses, viz. CyMo/MeOH and Py/MeOH), is denoted in the figures by full symbols. Its relaxation time changes monotonously with mixture composition, but seems to be uncorrelated to the viscosity η of the mixtures. For example, for Mo/MeOH the main relaxation time (termed τ_1) increases slightly with x while η decreases monotonously, and for MeMo/MeOH τ_1 increases remarkably though η stays nearly constant. This is a consequence of the fact that, at least in the case of the two term analyses, the main component must be considered a superposition of unresolved contributions. Obviously it is the MeOH contribution which yields the increase in τ_1 for $x_{\mathrm{MeOH}} \rightarrow 1$. This can be understood as resulting from an increasing self association tendency, if the relaxation time is interpreted as reflecting the lifetime of MeOH molecules in their associated state [3]. In the three term cases, all relaxation times appear to be nearly constant. This is worth mentioning in particular for the CyMo/MeOH system, where η changes considerably between 6.7 and 0.59 mPa s for $x_{\mathrm{MeOH}} = 0$ to 1, respectively. A weighted mean of the two spectral components with the longest relaxation times would exhibit an 'effective' relaxation time which changes in the same sense as η.

With regard to the introductory questions, it is not necessary to try for an analysis into spectral components which allow for an unambiguous physical interpretation. Rather it seems sufficient to consider the variation of the parameters of the main spectral component on the MeOH rich side, where this can be ascribed to merely MeOH. Especially the initial change of S_1 on addition of the second mixture component is informative. The relatively high relaxation strength of pure MeOH reflects the positive orientational correlation of dipole moments (Kirkwood factor $g > 1$), that is the assumedly chain like association in this alcohol. If this should stay unaltered in the mixtures, viz. if both mixture components would not affect each other, S_1 would change in proportion to the alcohol content. Now looking from the pure MeOH side, S_1 is found to behave differently for morpholine and pyrrolidine mixture systems.

In all morpholine mixtures (Fig. 1), the initial decrease of S_1 is steeper than expected from the MeOH mole fraction. This means that the orientational correlation of moments is reduced, which may be considered a structure breaking effect. The τ_1 variation mentioned above is in accord with this inference.

On the other hand, for Py/MeOH (Fig. 2) S_1 changes proportional to x_{MeOH} over the whole mixture region. Concerning the 12 ps term which is characteristic for pure Py (and is therefore ascribable to Py also in the mixtures), it is remarkable that its relaxation strength changes proportional to x_{Py}. The second pyrrolidine system, CyPy/MeOH, is peculiar in showing rather similar relaxation parameters for both pure liquids. These stay nearly unchanged over the whole mixture range. Consequently it is possible to split the spectrum into a CyPy and a MeOH contribution (which practically are undistinguishable) such that the relaxation strengths of both change in proportion to the respective mole fractions, just as found with the Py/MeOH system.

These qualitative features do not depend on the presence of substituents, neither in the morpholine nor the pyrrolidine case. The substituents determine of course the relaxation parameters of mixtures in the limit of low alcohol content, which, however, have been discussed already in previous work.

Summing up, the addition of morpholines to MeOH leads to an alteration of the MeOH relaxational contribution which indicates hetero interactions of structure breaking character. That effect is absent when pyrrolidines are added to the alcohol. Consequently it appears to be related to interactions of the alcoholic hydroxy group with the oxygen site of morpholines rather than with the common nitrogen site.

Acknowledgements

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