Static Permittivity and Association in Mixtures of Mono- and Dihydric Alcohols

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The static permittivity has been measured for *n*-hexanol and *n*-dodecanol in heptane solution on admixture of a minor (fixed) fraction of a dihydric alcohol (ethanediol, 1,6-hexanediol or 1,12-dodecanediol) from low to medium total alcohol concentrations. The 20 °C dispersion steps are reported. They show a more or less pronounced intensification due to the additive, which unexpectedly is smaller on addition of two diols together than of only one diol. Probably this reflects competing self- and hetero-association equilibria.

The static dielectric properties of monoalcohols have often been used to obtain information on their self-association [1–9]. Recently we reported results of static and dynamic measurements on *ternary* systems containing a monohydric and (as minor component) a dihydric alcohol together with a nonpolar diluent [10, 11]. It was found that, at low and medium total alcohol content, the admixture of the diol leads to an intensification of the lower frequency relaxation contribution which can generally be ascribed to increased self- and hetero-association via hydrogen bonding. The intensification by ethanediol is smaller than that by 1,6-hexanediol. It seems worthwhile to consider the difference between these additives closer in order to find out whether it is simply a monotonous diol chain length effect. For that purpose it is sufficient to regard the static permittivity ε_s which reflects the intensification effect summarily.

The present note reports results for systems containing, as dihydric component, either ethanediol or 1,6-hexanediol (as quoted above) or both diols at the same time. Thus, we deal with up to *quaternary* systems. Also mixtures where hexanediol was replaced by 1,12-dodecanediol were studied for comparison. The monohydric alcohols are *n*-hexanol and *n*-dodecanol, the nonpolar component is *n*-heptane in all cases. The X_1X_2YZ code will be used for the systems, where X_1 and X_2 stand for the dihydric alcohols (E: ethanediol, H: 1,6-hexanediol, D: 1,12-dodecanediol; o: no diol), Y for the monohydric alcohol (H: hexanol, D: dodecanol) and Z for the nonpolar component (H: heptane). The ten systems regarded are:

Hexanol systems:
ooHH, oEHH, oHHH, HEHH, DEHH,
dodecanol systems:
ooDH, oEDH, oHDH, HEDH, DEDH.

The molar ratio of the diols (if two) is kept the same in all cases, $x(X_1)/x(X_2)=1/4$. Also the dihydric/monohydric ratio (if any diol) is fixed, $x(X_1+X_2)/x(Y)=1/9$. Only the *total* alcohol mole fraction x is varied, covering the range between about $x=0.07\ldots0.40$. Instead of x, the number density N of dipoles, that is of OH groups, shall serve as a measure for the total alcohol content.

The static permittivity ε_s was determined at 2 MHz using a WTW dipolemeter with an uncertainty of 2%. The refractive index n_D was measured with an Abbe refractometer. We consider the normalized dispersion step

$$S/N = (\Delta\varepsilon_s - \Delta n_D^2)/N\,,$$

where Δ denotes the difference between solution and pure solvent heptane. Measurements were made at three temperatures. However, since the results are closely similar, we restrict ourselves to regarding the 20 °C values. The data for ooHH, oHHH, oEDH and oHDH are taken from [12].

The results are represented in Figure 1. The quantity S/N is related to the apparent molecular moment squared, μ_{app}^2, as obtainable e.g. by use of the Onsager equation. It should be stressed that a representation of the latter (or likewise of the "reduced permittivity" after [13]) does not change the qualitative features of Fig. 1, which are also unaffected by the choice of the concentration scale (e.g. x instead of N).

An increase of S/N with alcohol content is common to all systems studied. It indicates the increasing association tendency as usually observed with alcoholic solutions. With respect to the introductory question, there are the following two features which are worth noting.

(i) As mentioned before, the increase of S/N on admixture of a diol to hexanol or dodecanol is remark-

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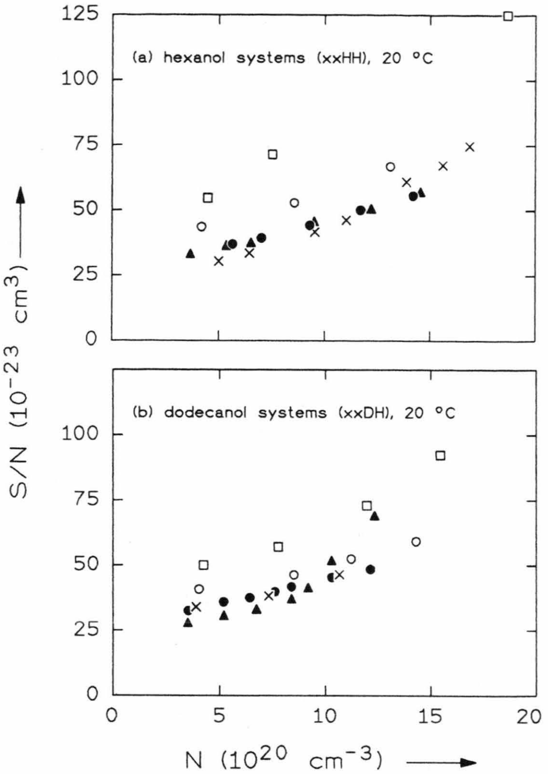

Fig. 1. Normalized dispersion steps S/N against number density N of dipoles, 20 °C. (a) Hexanol systems, (b) dodecanol systems. Symbols denote the diol admixture: × no diol (ooHH, ooDH), ○ ethanediol added (oEHH, oEDH), □ hexanediol added (oHHH, oHDH), ▲ hexanediol plus ethanediol added (HEHH, HEDH), ● dodecanediol plus ethanediol added (DEHH, DEDH).

ably larger when hexanediol is added (oHHH and oHDH) rather than ethanediol (oEHH and oEDH as compared to ooHH or ooDH, respectively). The *simultaneous* effect of hexanediol plus ethanediol (HEHH and HEDH), however, is found to be smaller than that of only one diol, even that of ethanediol, except for the region regarded below (ii). The same holds for the simultaneous effect of dodecanediol plus ethanediol (DEHH and DEDH).

(ii) For the quaternary system HEDH (but not for DEDH), the region of highest concentrations measured shows that S/N tends to approach the oHDH values. This unexpected intensification appears to be peculiar to the monoalcoholic component dodecanol as it is not observed with hexanol.

Obviously the effect of the dihydric additive is *not monotonously* related to its mean chain length. Thus diol-diol interactions are likely to be involved which may preferably lead to the formation of weakly polar (e.g. closed) associates. On the other hand, there is also an influence of the chain length of the monohydric component, which points to mono-diol interactions leading to more polar (e.g. chain like) aggregations. The interplay of both processes cannot sufficiently be elucidated by measurements with constant molar ratios of the alcoholic components as in the present case but will be subject to future studies.

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