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

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Static Permittivity has been measured for \( n \)-hexanol and \( n \)-dodecanol in heptane solution on admixture of a monomer (fixed) fraction of a dihydric alcohol (ethanediol, \( 1,6 \)-hexanediol or \( 1,12 \)-dodecanediol) from low to medium total alcohol concentrations. The \( 20 \degree C \) 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 permittivity has been determined at \( 2 \) MHz using a WTW dipolemeter with an uncertainty of 2%. The refractive index \( n_0 \) was measured with an Abbe refractometer. We consider the normalized dispersion step

\[
S/N = \frac{\Delta \varepsilon_1}{n_0^2} = \frac{S}{N},
\]

where \( \Delta \) 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 the \( 20 \degree C \) values. The data for \( \text{oohH}, \text{oHHH}, \text{oEDH}, \text{oHDH} \) are taken from [12].

The results are represented in Figure 1. The quantity \( S/N \) is related to the apparent molecular moment squared, \( \mu_{app}^2 \), 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 Figure 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. This 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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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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