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POLARITY OF LIQUID MIXTURES WITH COMPONENTS OF LIMITED MISCIBILITY

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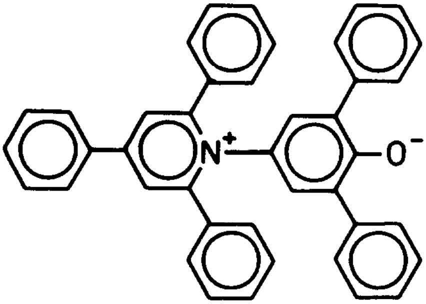
Summary: *Binary mixtures of organic solvents with limited miscibility are investigated by a two parameter equation which reliably describes the polarity of mixtures as a function of their composition. A relation is found between limited miscibility and critical change of solvent structure.*

The polarity of liquid mixtures of organic solvents has been quantitatively investigated in preceding papers[1-6]. It was shown that the polarity of a mixture defined by empirical polarity scales, e.g. the $E_T(30)$ scale of Dimroth and Reichardt[7], is quantitatively described by the two parameter equation (1). $E_T(30)$ in (1) is the $E_T(30)$ value of the mixture obtained by

$$E_T(30) = E_D \cdot \ln (c_p/c^* + 1) + E_T^0(30) \qquad (1)$$

$$E_T(30) = 28590[\mathrm{kcal \cdot nm}]/\lambda_{max} \qquad (2)$$

use of the solvatochromism of dye 1 and eq. (2). c_p in eq. (1) is the molar



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concentration of the more polar component and $E_T^O(30)$ is the $E_T(30)$ value of the pure component with lower polarity. E_D and c^* are the parameters of the equation.

Eq. (1) holds with high precision for all investigated examples (about 80) without exception and therefore can be used to study interactions between the components of liquid mixtures. In some mixtures, as mentioned before[1-6], eq. (1) holds up to a critical concentration c_k with a point of inflection at this concentration. For $c_p > c_k$ eq. (1) holds too, but with different parameters E_D and c^*. This experimental fact (double straight lines) is interpreted in terms of a change in solvent structure.

The subject of investigation is the phenomenon of double straight lines (two solvent structures) in relation to limited miscibility of liquids. Therefore good model systems are binary mixtures between water and n-alkanols for one can get from systems with complete miscibility to systems with more or less limited miscibility by stepwise lenghthening the alkyl group of the alkanol.

The results are shown in Fig. 1. With water as the more polar component and dye <u>1</u> as a polarity probe eq. (1) holds for the binary mixtures water/methanol up to water/1-butanol. Double straight lines are obtained in each case. With water/butanol the concentration region of limited miscibility lies between the two straight lines. The parameter c^* in the region with low concentration of water characterizes the degree of the interaction of the water molecules in the used solvent. c^* drops from about 150 $mol \cdot l^{-1}$ in methanol to 38.1 in ethanol and 4.22 in 1-propanol to 1.89 $mol \cdot l^{-1}$ in 1-butanol. The interactions of water molecules come into account at lower concentrations as the alkyl chains of the alkanols are growing. This will finally cause the formation of two liquid phases in the case of butanol. On the other hand, the shorter the alkyl chains are the more similar the solvents will be in comparison to water. This effect is demonstrated by Fig. 1. The slopes of the two straight lines become more and more similar in the series butanol/water to methanol/water. One might conclude that generally in the case of small similarity of two liquids there are two different solvent structures and in a certain concentration region two phases. On becoming more similar the components show complete miscibility, but the two solvent structures (double straight lines) will be retained. Finally in the case of even more similar components there is a continiuous change in solvent properties in binary mixtures (only one straight) line, as one observes for most binary solvent mixtures.

Therefore the phenomenon of limited miscibility is in close relation to the fact of double lines indicating a change in solvent structure. Responsible, however for the formation of two liquid phases is the surface tension between the two solvent structures. In the case of low surface

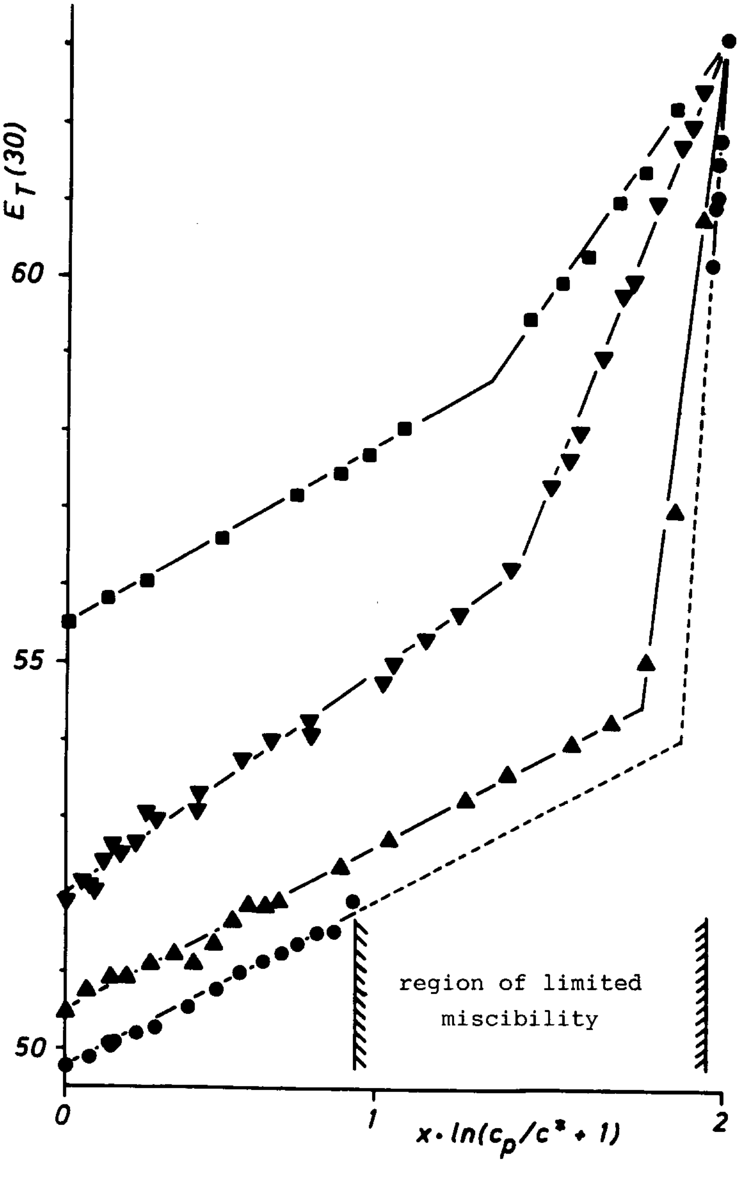

Fig.1: $E_T(30)$-values of binary mixtures between n-alkanols and water as a function of $\ln(c_p/c^* + 1)$ according to equation (1)

■: Water/methanol (X = 0.157); some values are taken from ref.[7a)]
▼: Water/ethanol (X = 0.318); some values are taken from ref.[7a)]
▲: Water/1-propanol (X = 1.349)
●: Water/1-butanol (X = 1.705)

tension on structure changes to the other at c_k without forming a second liquid phase. With high surface tension however a second liquid phase is formed. Substances which lower surface tension, detergents, therefore should have a profound influence on phase separation. Their key part in micell formation is in accord with these results as well as the aggregation behaviour of surface active oxazole merocyanine dyes[8)] which form J-aggregates in solvent mixtures with low contents of water and turn to H-aggregates in solvent mixtures with high contents of water (hydrogen bonding structure of water).

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