

THE DESCRIPTION OF THE POLARITY OF ALCOHOLS AS A FUNCTION OF THEIR MOLAR CONTENT OF OH GROUPS

Heinz Langhals

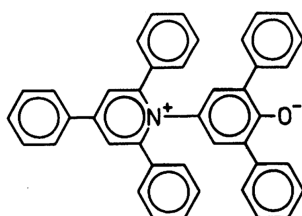
*Chemisches Laboratorium der Universität Freiburg,
Albertstr. 21, D-79104 Freiburg i.Br. (R.F.A.).
Presently: LMU University of Munich, Department of Chemistry,
Butenandtstr. 13, D-81377 Munich, Germany,
E-Mail: Langhals@lrz.uni-muenchen.de.*

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ABSTRACT. -The two-parameter equation which is described for the polar behavior of binary solvent mixtures can also be applied to pure liquids. In the case of *n*-alcanols it is shown that the polarity of binary mixtures and pure alcanols is described by the same formula in which the molar concentration of OH groups is the essential term. Applications e.g. to intramolecular effects are discussed.

ABRISS. — Die für das Polaritäts-Verhalten binärer Lösungsmittelgemische beschriebene Zwei-Parameter-Gleichung lässt sich auch auf reine Flüssigkeiten anwenden. Am Beispiel homologer *n*-Alkohole wird gezeigt dass sowohl die Polaritäten der Reinsubstanzen als auch die von binären Gemischen der gleichen Gesetzmäßigkeit folgen, bei der die molare Konzentration der polaren OH-Funktion die wesentliche Kenngröße ist. Anwendungsmöglichkeiten der gefundenen Gesetzmäßigkeiten werden u. a. für intramolekulare Effekte diskutiert.

RÉSUMÉ. - L'équation à deux paramètres qui décrit le comportement des mélanges de solvants binaires peut également s'appliquer aux liquides purs. Dans le cas des *n*-alcanols, on montre que la polarité des mélanges binaires et des alcanols purs est représentée par la même formule dans laquelle la concentration molaire en groupements OH est le terme essentiel. Des applications aux effets intramoléculaires sont discutées.



1

In previous work¹⁻⁵, using dye **1** (CAS RN 10081-39-7), it was shown that the empirical polarity of a binary mixture according to the $E_T(30)$ scale⁶⁻⁷ developed by Dimroth and Reichardt is quantitatively described by the two-parameter equation (1):

$$E_T(30) = E_D \cdot \ln \left(\frac{c_p}{c^*} + 1 \right) + E_T^0(30) \quad (1)$$

where $E_T(30)$ is the polarity⁴ of the mixture and c_p is the molar concentration of the more polar component. $E_T^0(30)$ is the $E_T(30)$ value of the less polar component. E_D (energy penetration) and c^* (appearance concentration) are the parameters of the equation.

The polar properties of monosubstituted hydrocarbons are in many cases dominantly influenced by the functional groups, so the polarities of these substances should be determined essentially by the molar concentrations of these groups, calculated from density and molecular weight. For alcohols, for example, this is the OH function. It is known that the polarity of *n*-alcohols decreases with increasing chain length^{6,7}. It can also be seen from literature data⁶ that the decrease in polarity is smaller for long-chain alcohols than for their shorter-chain homologs. This relationship will now be investigated in more detail.

Results

In Figure 1, the polarity according to $E_T(30)$ scale⁶ for various binary mixtures of *n*-alcohols with 1,4-dioxane has been plotted against the molar concentration of alcohol component (cf. also ref.³). It is noteworthy that the measured values for all the alcohols investigated follow a common curve. Since the polarity of 1,4-dioxane is low compared to the alcohols, the common curve of Figure 1 should largely reflect the properties of the alcohol function alone, at least in the range of high polarity

values, and thus describes the concentration-polarity behavior of this group.

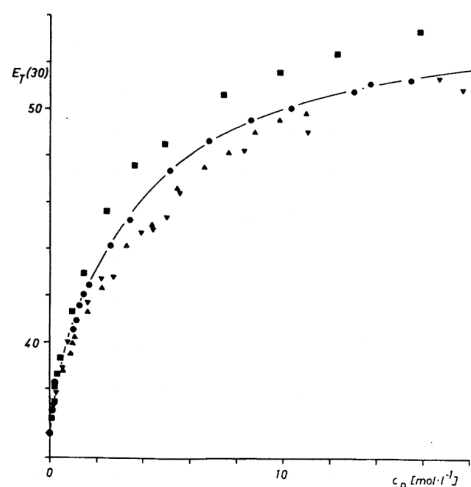


Figure 1. - Polarities of mixtures of *n*-alcohols and 1,4-dioxane as a function of molar concentration of alcohol component (c_p). ▼ water; ■ methanol; ● ethanol; ▲ 1-butanol.

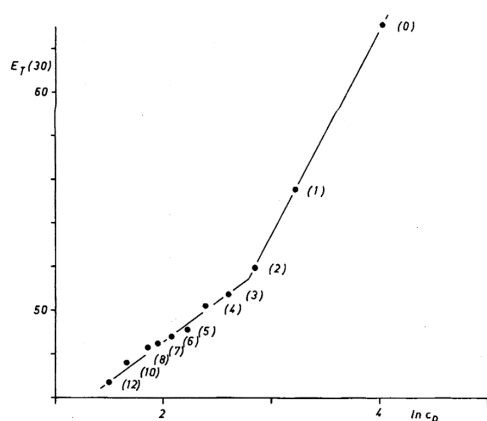


Figure 2. - $E_T(30)$ ⁶ as a function of $\ln c_p$ for the homologous *n*-alcohols. The numbers in parentheses indicate the chain length: E.g. (0) = H₂O, (1) = CH₃OH.

In a plot of binary mixtures between alcohols and acetone analogous to Figure 1, a common curve is also observed for all the alcohols studied, except that there the polarity range is smaller than for mixtures with the considerably less polar 1,4-dioxane. The curve in Figure 1 thus describes a polarity phenomenon and does not represent a peculiarity of the solvent 1,4-dioxane.

It is further noteworthy that in Figure 1 the polarity values for the pure alcohols are also points on the common curve and in this respect no longer occupy a special position. This polarity behavior of the pure *n*-alcohols is shown in Figure 2, where the $E_T(30)$ values are plotted against $\ln c_p$ of various *n*-

alcohols calculated from density and molecular weight.

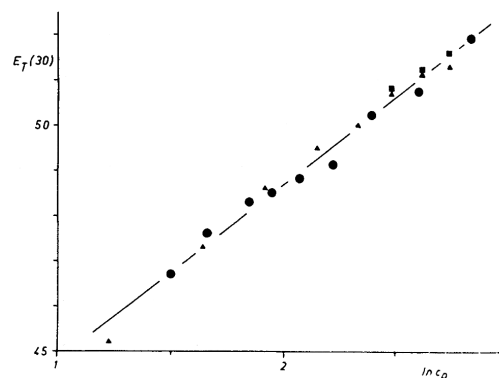


Figure 3. - Comparison of the polarities [$E_T(30)$ values] of pure alcohols with those of binary mixtures with ethanol as a function of the molar concentration of the alcohol function. ● Pure *n*-alcohols; ▲ mixtures ethanol/1,4-dioxane; ■ mixtures ethanol *n*-heptane.

For ethanol and its higher homologues, a straight line with the slope $E_D = 3.7 \text{ kcal} \cdot \text{mol}^{-1}$ results. From this linear relationship, the validity of Eq. (1) also follows for the series of pure *n*-alcohols with c_p as the molar concentration of alcohol (see also Ref. ¹). Consequently, Eq. (1) also describes intramolecular effects. Pure alcohols can then be regarded as binary mixtures of the polar OH function with the less polar alkyl chains. If the alkyl chains are lengthened, the molar concentration of OH groups is reduced and should disappear at infinitely long alkyl chains. If one approximates for this case ($c_p = 0$) the known $E_T(30)$ value of the pure hydrocarbon *n*-hexane of $30.9 \text{ kcal} \cdot \text{mol}^{-1}$, then with the help of Eq. (1), an c^* value for the mixture alkyl chain/OH-functionality of $0.06 \text{ mol} \cdot \text{L}^{-1}$ can be estimated. Similar E_D and c^* values are generally found for binary liquid mixtures with *n*-alcohols ³. The relationship becomes particularly clear if, as shown in Figure 3, the lower branch of the curve in Figure 2 is plotted not only with the polarities of the pure alcohols but also with the polarity values of mixtures between ethanol and substances of low polarity, such as 1,4-dioxane or *n*-heptane. (Because of the low solubility of 1, only large concentrations c_p are accessible when mixing with *n*-heptane). Since all points in Figure 3 lie on a common straight line within the limits of experimental uncertainties, it must be concluded that for both pure alcohols and the mixtures with low polar components, the molar concentration of the OH function is essentially polarity determining.

In the literature³⁻⁴ it is often observed for mixtures with water that above a critical concentration (c_k) the straight line according to Eq. (1) abruptly changes into a second steeper one, which has different E_D and c^* values. This feature is also present in Figure 2 for $c_p > 16 \text{ mol}\cdot\text{L}^{-1}$ (c_k) with $E_D = 9.6$ and $c^* = 1.9$ and includes the solvents water and methanol. Thus, it can be assumed that the transition at c_k is characteristic of the alcohol function and possibly represents a transformation point in the liquid structure. Using the linear relationship in Figure 2 for $c_p < c_k$, the virtual polarity values of 55.9 and 53.0 can be calculated for water and methanol, which are smaller than the actual values (63.1 and 55.5⁶). An indication that these virtual values are valid for water and methanol in the range $c_p < c_k$ is provided by Figure 1, in which completely similar behavior of water, methanol, ethanol and 1-butanol is observed in this range with respect to the molar concentrations.

From these results it can be concluded, among other things, that the large polarity of water compared with most organic solvents is not a peculiarity, but is essentially due to its high density in relation to its molecular weight.

The regularities found with alcohols can also be applied to other classes of compounds. This will be reported in another context. In general, it can be concluded that the polarity values of pure liquids can be composed of group increments. Polar groups such as the alcohol function play a key role in this process. However, the increments do not behave additively, as is assumed in many other fields, but follow a logarithmic function. This must also be considered in the linear correlation of the polarity scales. A quantitative description of intramolecular polarity effects is of interest in many areas of chemistry and has particular importance in polymer chemistry. Since intra- and intermolecular processes are now based on a common model, copolymerization parameters can be understood on the one hand, and processes such as chain entangling and interactions between chain segments on the other. This will be reported elsewhere. On the basis of Eq. (1), steric interactions with OH functions, for example, can also be studied.

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Experimental section

The determination of E_D and c^* of Eq. (1) has been performed at 25°C using the UV spectrometer DMR21 from Zeiss completely analogous to Ref.

^{1,3}. The calculation of the published data was carried out by means of the computer program Polar¹ at the computer center of the University of Freiburg.

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