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# THE POLARITY OF SOLUTIONS OF ELECTROLYTES

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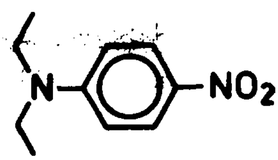
Abstract - The polarity of solutions of $LiClO_4$ in acetic acid has been investigated. However, polarity scales based on light absorption, e.g. the $\pi^*$-scale, are interfered by aggregation phenomena of the used solvatochromic dyes, whereas solvatochromic fluorescent dyes give proper results.

Salt containing solvents are used in mechanistic studies of solvolytic displacement reactions. The special salt effect of $LiClO_4$ in acetic acid, for example, is the experimental basis for the formulation of a solvent separated ion pair[1]. Although these reactions are strongly influenced by the solvent polarity, little is known about the effect of salts on the polarity of a medium[2].

The applied polarity scale mustn't be interfered by the formation of ion pairs. The well-known and widely applicated $E_T(30)$ polarity scale[3] as an independent scale cannot be applied in the case of acetic acid, for the corresponding pyridiniumphenolatebetaine is protonated under these conditions. Therefore we tested the $\pi^*$-scale[4] which is based on the solvatochromism of dye 1 having a lower basicity. In acetic acid $\lambda_{max}$ of the absorption of dye 1 is only little shifted



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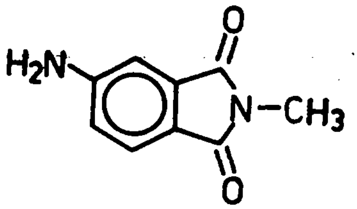

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on addition of increasing amounts of $LiClO_4$. However, a new absorption band is formed at shorter wavelength. This spectral change is shown in fig. 1a for concentrations in the order of $10^{-2}$ mol/l $LiClO_4$. With higher concentrations, up to 1 mol/l, a third, even more hypsochromic absorption band is formed, with an iso-

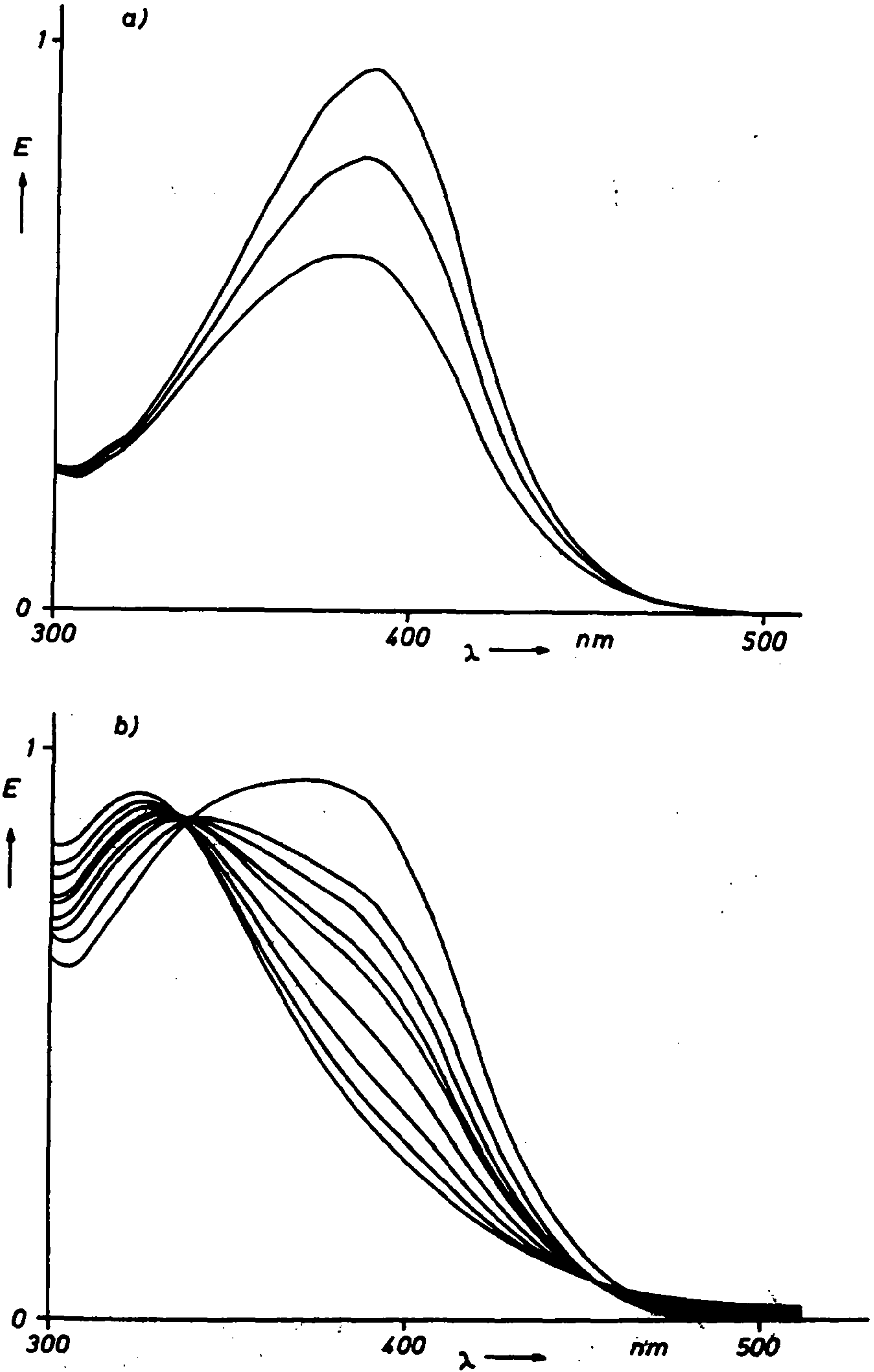

Fig.1: Absorption spectra of dye 1 in acetic acid with increasing amounts of $LiClO_4$ - a) about 0.01 mol/l - b) about 1 mol/l $LiClO_4$

sbestic point at 338 nm between the second and the third one, as shown in fig. 1b. We are interpreting the spectral changes of 1 in acetic acid on addition of

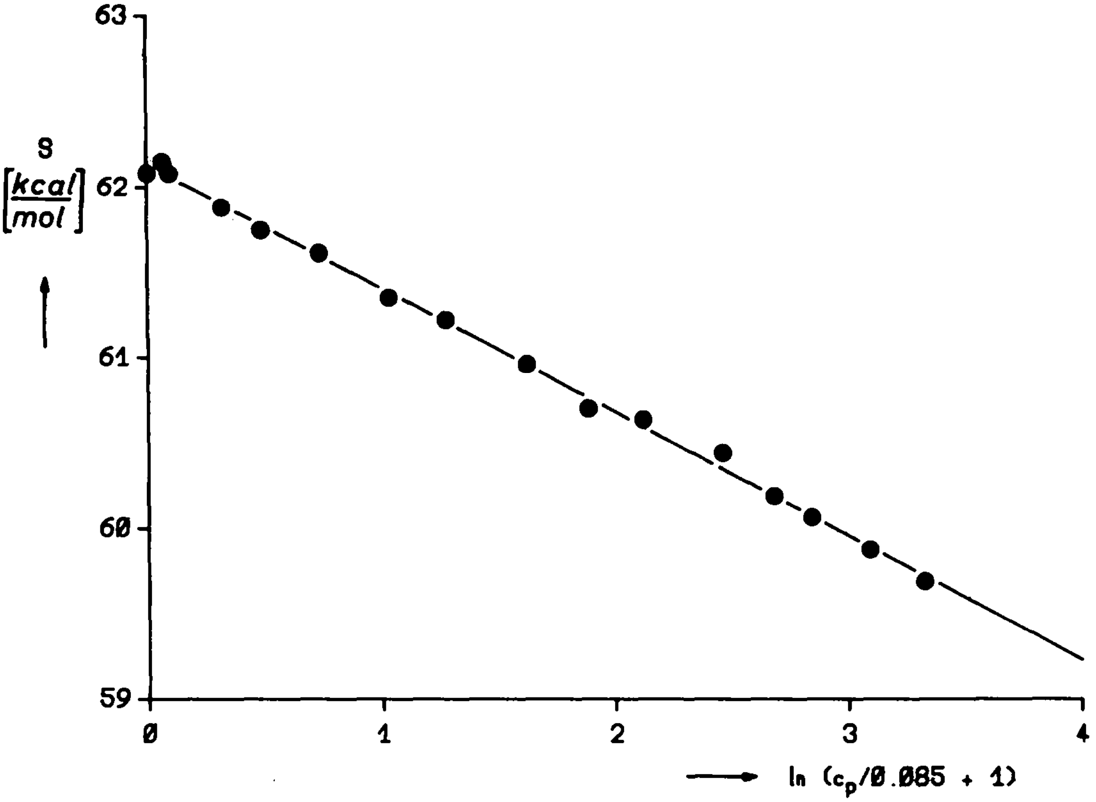

Fig. 2: Linear relationship between S and ln ($c_p/c^*$ + 1) for $LiClO_4$ in acetic acid according to eq. (2): $E_D$ = -0.724 and $S^o$ = 62.1 kcal/mol, correlation factor r = -0.9987 with 16 points, $c_p$ and $c^*$ in mol/l

$LiClO_4$ in terms of aggregation of dye 1. The hypsochromic shift indicates the formation of H-type aggregates[5] as well as the line shape, which is more Lorentzian than Gaussian[6], especially with high salt concentrations. The isosbestic point gives an experimental evidence for the interconversion of one distinct species to some other. Therefore, the $\pi^*_1$-polarity scale cannot be used with the system $LiClO_4$/acetic acid and more generally with other salt containing solutions which give similar results. The aggregation of 1 is remarkable, for the dye chromophore is very small.

In order to overcome the problems with dye aggregation (the dye of the $E_T$(30)-scale aggregates too, as indicated by a change in line shape) we used the solvatochromic fluorescent dye 2 which is the basis of Zelinskii's[7] polarity scale S. Dye 2 aggregates in $LiClO_4$/acetic acid forming a H-type aggregate which is indicated by a hypsochromic shift and a change in line shape as with dye 1. However, the solvent polarity is derived from $\lambda_{max}$ of the fluorescent spectrum according to eq. (1), and fluorescence will not be obtained from H-aggregates,

$$S/(\text{kcal}\cdot\text{mol}^{-1}) = 28590 \cdot \frac{1}{\lambda_{max}/\text{nm}} \qquad (1)$$

$$S = E_D \cdot \ln(c_p/c^* + 1) + S^o \qquad (2)$$

but from the not aggregated dye molecules in equilibrium, as was pointed out by

Förster[5]. This is verified with dye 2 in $LiClO_4$/acetic acid which gives a continuous bathochromic shift of the fluorescent spectrum without changing the line shape on increasing salt concentration. Therefore, the S-values indicate the polarity of salt solutions. A 2 molar solution of $LiClO_4$ in acetic acid increases the polarity of solvent from S = 61.1 to S = 59.8. This corresponds to 2 units within the $E_T(30)$-scale[8].

The polarity of the binary mixture $LiClO_4$/acetic acid as a function of composition is quantitatively described by eq. (2) as with other binary mixtures[9]. S in eq. (2) is the polarity of the mixture defined by eq. (1), $S^o$ is the S-value of the pure component with lower polarity (acetic acid), and $c_p$ the molar concentration of the more polar component ($LiClO_4$). $E_D$ and c* are the parameters of the equation. The validity of eq. (2) tested up to a concentration of more than 2 molar is shown in fig. 2. Therefore, a salt acts like other polar additive components. The c*-value is rather low so that the solvent polarity is considerably increased by addition of small amounts of $LiClO_4$. This must be taken into account with solvolytic displacement reactions. On the other hand, extrapolation of the straight line in fig. 2 up to the concentration of pure $LiClO_4$ leads to an S-value value of 58.1 which is, for example, higher than the value of water (S = 47.2).

## EXPERIMENTAL

The following instruments were used for spectroscopic measurements - UV/VIS absorption spectra: Bruins Instruments OMEGA-10;- fluorescent spectra: Perkin Elmer 3000. $LiClO_4$ was dried at 140°C in vacuo. For the used polarity scales see ref.[9]. $\lambda_{max}$ of absorption and fluorescent spectra are determined by use of Mathias rule[9].

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