

## Abstract

Ionic organic dyestuffs show a rather complex behavior of aggregation, particularly in aqueous solution. To elucidate this behavior different measuring techniques are used, which provide consistent results for either method, but in comparison to each other they seem to contradict themselves.

In the present Ph.D. thesis the influence of concentration, temperature, and pressure on the aggregation behavior of the ionic azo dye acid red 266 was investigated using three very different measuring techniques.

The results of  $^{19}\text{F}$ -NMR- and UV/VIS-spectroscopy, respectively, can be interpreted as a monomer/dimer-equilibrium. The free enthalpies of dimerization determined by both methods are in the same order of magnitude of roughly  $-20 \text{ kJ}\cdot\text{mol}^{-1}$ .

The enthalpy and entropy of dimerization determined by UV/VIS-spectroscopy point to a synergism of enthalpic and entropic contributions. The positive dimerization entropy ( $+7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) suggests an involvement of hydrogen bonds between dye and solvent. Using exciton theory, the UV/VIS-spectroscopy provide information about the twist angle ( $\sim 50^\circ$  in the presence and absence of electrolyte). Furthermore, the interplanar distance between adjacent monomeric units in a dimer are revealed.

The results of static light scattering on acid red 266 yielded aggregation numbers far above small dimers. The explanation is that the method of static light scattering registers the „global structure“, whereas the aforementioned methods „only“ detect dimers because of nearest neighbours‘ interaction. Thus, the methods used give insight into different levels of aggregates‘ organisation, hence, the results found do not contradict, but advantageously complete each other. The detailed analysis of the light scattering data led to the following picture:

Without electrolyte the aggregates can be described as wormlike species having molecular weights of about  $10^5 \text{ g}\cdot\text{mol}^{-1}$  and contour lengths of roughly 300 nm, respectively, whereas the addition of electrolyte leads to aggregates which are best described as rigid rods. In the last case the molecular weights are increased by a factor of ten, whereas the length is roughly doubled in comparison to the electrolyte-free solutions. These differences in the presence of electrolyte can be interpreted as a growth in aggregates‘ length and cross section.

Aggregation phenomena of ionic cyanine dyes is indicated by the appearance of a new absorption band, the so called J-band, having a very small half width. For this reason the investigations were expanded on pseudoisocyaninechloride (PIC) and DYE A under high pressure. The spectroscopic studies under high pressure required the design of special inner cells. These cuvettes allow the extraordinarily accurate recording of UV/VIS-spectra up to 3000 bar. The determination of the pressure-dependence of the absorption, additionally to the dimerization enthalpy via temperature-dependence, moreover, the volume contraction of dimerisation  $\Delta V$  was accessible. The discussion of the  $\Delta V$ -values, together with the twist angles from the deconvolution of spectra at atmospheric pressure, point to column-like or herringbone structures, rather than linear or brickwall aggregate structures.

The significant differences in the  $\Delta V$ -values of both dyes can be explained by the likewise significantly different twist angles which mutually corroborate the experimental results:

A larger twist angle corresponds to a smaller overlapping area between adjacent molecules, which finally results in a smaller  $\Delta V$ -value.

In the case of PIC a temperature-concentration-, and for the first time a pressure-concentration- diagram was determined just as well.

The appearance of the J-band is frequently explained in the literature by an abrupt increase of the aggregation number, however, in the present thesis this is explained by a change of the tilt angle  $\alpha$  within the aggregates. Therefore, the aggregates' geometry is of more importance than their length. With increasing pressure or decreasing temperature the equilibrium of H-aggregates shifts to the J-aggregates.

In addition to the above mentioned investigations, pressure induced spectral shifts were examined to check the method suggested by Chan and Lindrum to determine the dipolar coupling constants of J-aggregates. Some assumptions of this method were proved to be unjustified, hence, this method cannot be applied.

For the azo dye congo red, the observed increase of intensity of the  $n \rightarrow \pi^*$ -band with increasing pressure can be interpreted as a trans  $\rightarrow$  cis configurational change.