

TRANSFER OF ELECTRONIC ENERGY IN MICELLAR SOLUTIONS

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The tendency of detergent molecules to form micelles, i.e. colloidal aggregates, can be exploited to investigate unusual energy transfer phenomena. Aqueous solutions containing ionic micelles can be considered as two phase systems in which the micelles are droplets of liquid paraffin with an appreciable surface charge. Water insoluble substances like hydrocarbons are incorporated in the hydrophobic interior of the micelles while ions are either enriched or depleted (depending on their charge) in the electric double layer defining the micellar surface. Thus the location of donor and acceptor in dipole-dipole energy transfer is determined by the solution properties of the individual molecular species. Accordingly, electronic energy transfer can take place within the micelle, across the phase boundary, and within the surface of the micelle. The rate of transfer is determined in all cases by the specific structure of the micellar solution.

As an example, we have studied the fluorescence of micellar solutions containing pyrene (donor) and fluoresceine (acceptor), because the anionic dye fluoresceine cannot enter the micelle, whereas pyrene practically occurs only solubilized in the micelles because of its extremely low solubility in water. Following flash excitation of pyrene, the emissions of pyrene, of pyrene excimer, and of fluoresceine were observed. The rate of transfer was determined by monitoring the fluorescence decay of the donor. It turned out to depend on the surface charge of the micelle. Cationic detergents like cetyl trimethyl ammonium bromide, CTAB, form micelles which attract the fluoresceine anions so that energy transfer is fast. Conversely, a repulsion of fluoresceine anions takes place in solutions containing anionic micelles, e.g. sodium dodecyl sulfate, SDS. Here energy transfer can no longer compete with the radiative transition from the pyrene excimer.

In further experiments we have studied energy transfer between two anionic dyes, fluoresceine (donor) and eosine (acceptor) in CTAB solutions. Since these dyes are not incorporated into the micellar core, they should have no influence on shape or size of the micelle and thus are ideal probe molecules.

Furthermore, the maximum of the emission band of fluoresceine coincides almost exactly with the maximum of the absorption band of eosine, which allows energy transfer to compete effectively with the spontaneous emission at separation distances comparable to the external dimensions of the micelles. Keeping the concentrations of the dyes and of CTAB sufficiently low, it is possible to establish conditions such that the average distance between micelles is large and energy transfer occurs only when donor and acceptor anions are located in the Stern layer of the same micelle. Experimentally, the energy transfer was monitored by studying the fluoresceine emission yield as a function of the average number of acceptor molecules in the environment of a micelle. Because of the peculiar nature of the solutions this can be done either by varying the concentration of the acceptor at constant concentration of donor and of micelles, or by varying the concentration of micelles at constant dye concentration. Stern-Volmer plots of the data turned out to be linear in both cases and to furnish the same rate constant ratios.

Although the mechanism of energy transfer does not necessarily imply Stern-Volmer kinetics, this finding enables us to define an effective separation distance which is a weighted average over all the possible donor-acceptor separations in the electric double layer surrounding the micelle. This distance depends directly on the diameter of the micelle core and on the extent of the Stern layer. The value obtained from the data was 6 nm. This information is not obtainable by small angle x-ray diffraction or light scattering methods that were used previously to determine micelle diameters and yielded a significantly lower value, i.e. about 5 nm. Therefore, our results indicate that the anionic dyes are distributed in the diffuse layer surrounding the micelle rather than rigidly adsorbed on its core.