Interaction between cationic dyes and colloidal particles in a C_{60} hydrosol

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Strong interaction of cationic dyes with the dispersed phase of a C_{60} hydrosol results in the adsorption at the surface of colloidal particles and, finally, in coagulation of the sol.

To extend the area of application of fullerenes (C_{60}, C_{70} *etc.*), especially, to biophysics, biochemistry and medicine, it is important to have their aqueous solutions. Unfortunately, the equilibrium solubility of fullerenes in water was reported to be negligible.[1]

Recently, we prepared aqueous solutions of C_{60} without any stabilisers and chemical modification, which were reasonably concentrated (≥ 0.1 g dm^{-3}) and stable over at least several months. The procedure is based on transferring fullerene from toluene into water using sonication.[2] These solutions appeared to be colloidal systems.[2–4] The C_{60} hydrosol is found to be a typical ultramicroheterogeneous hydrophobic dispersion with negatively charged particles.[3,4] The C_{60} dispersions obtained by Scrivens *et al.*,[5] were much coarser and very dilute (0.001 g dm^{-3}). Presently, we can prepare colloidal solutions with C_{60} concentrations as high as 1.6 g dm^{-3}. Hence, the research into the colloid chemistry of the C_{60} fullerene seems to be necessary and rather promising.

Organic cations exert a strong coagulating effect on the sol; this effect increases with the surface activity of the cations.[3,4] As organic dyes are also known to be efficient coagulants for 'negative' sols,[6] we systematically studied the interaction of a C_{60} hydrosol with a number of cationic dyes. The general conclusion is following: the dyes are adsorbed at the surface of C_{60} colloidal particles, and this process finally results in coagulation of the sol. Here we report the data for the two dyes, which are prone to form dimers and other aggregates in aqueous media, Neutral Red and a methyl analogue of Pinacyanol.

The changes in the absorption spectra of Neutral Red as the C_{60} was added (Figure 1 shows a typical example) give evidence of the dye–fullerene interaction. The measurements were performed on a Specord UV-Vis or SP 46 instrument against solvent blanks containing the sol without the dye at pH $\leq$ 5. The spectral changes are typical of dimerisation of the Neutral Red cation.[7] Thus, the data in Figure 1 are indicative of the interaction between dye chromophores, which is induced by colloidal particles.

Pinacyanol is used as a probe for studies of surfactant micellisation.[8] At working concentrations (Figure 2), the dye 1,1′-dimethylquino-2-carbocyanine, used as the tosylate, is strongly dimerised in aqueous solution. The spectral changes observed upon addition of the C_{60} hydrosol are characteristic of the formation of H-aggregates of the dye.[9] We also detected effects of this kind in the Pinacyanol–sodium dodecylsulfate system (in the presence of 0.01 mol dm^{-3} NaCl), at surfactant concentrations somewhat below the critical micelle concentration. Under these conditions, the formation of mixed dye–surfactant micelles is typical.[8] If the number of homomicelles of the anionic surfactant became high enough, an intense band at 608 nm appeared. This band is typical of isolated solubilized dye monomers. Thus, in the colloidal C_{60} solution, coagulation takes place before the dye anions are adsorbed separately from each other.

The critical coagulation concentrations (*c.c.c.*) were obtained as described earlier.[3,4] Different aliquot portions of dye solutions were added to the sol; the final working concentration of C_{60} was always equal to 0.07 g dm^{-3}. For Neutral Red and 1,1′-dimethylquino-2-carbocyanine *c.c.c.* = 0.028 and 0.01 mmol dm^{-3}, respectively. The attempts to determine the *c.c.c.* values by titration of the sol with microamounts of concentrated dye solutions lead, in contrast to the case of inorganic salts, to much higher values. All of the experiments with 1,1′-dimethylquino-2-carbocyanine were performed in the presence of 1 vol% EtOH.

The presence of the dyes in the coagulates was detected by mass spectrometry. The mass spectra were obtained on a time-of-flight MSBC mass spectrometer using ^{252}Cf plasma

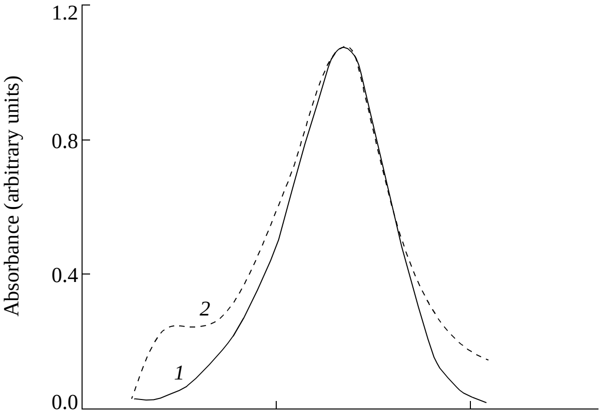

Figure 1 Absorption spectra of Neutral Red solutions (4.1×10^{-5} mol dm^{-3}) (*1*) in the absence of the hydrosol and (*2*) at a C_{60} concentration of 0.021 g dm^{-3}.

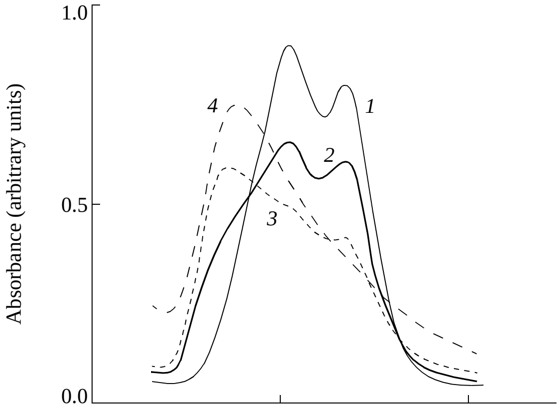

Figure 2 Absorption spectra of 1,1′-dimethylquino-2-carbocyanine (1.4×10^{-5} mol dm^{-3}) at the C_{60} hydrosol concentrations: (*1*) 0, (*2*) 0.0115, (*3*) 0.023 and (*4*) 0.0346 g dm^{-3}; 1 vol% EtOH.

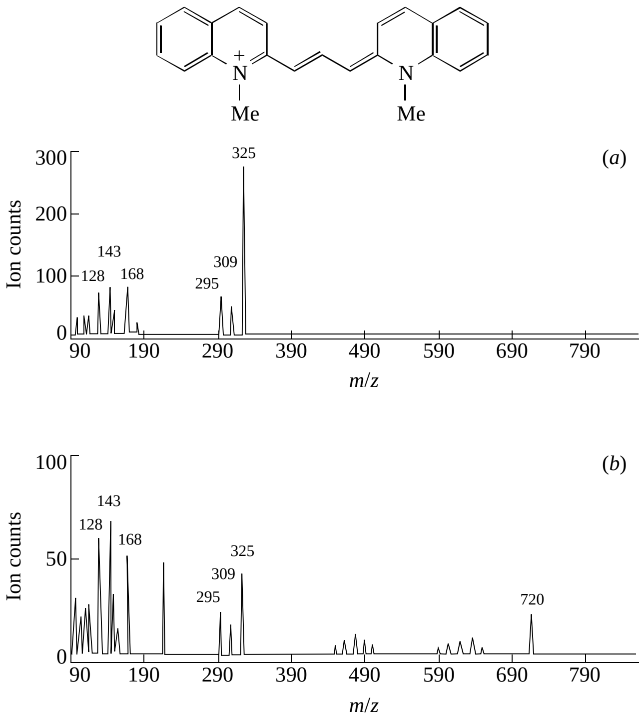

Figure 3 ^{252}Cf PD mass spectra of 1,1′-dimethylquino-2-carbocyanine (*a*) in the absence and (*b*) in the presence of the C_{60} hydrosol.

desorption (PD) ionisation. Additional evidence of dye–fullerene interactions was obtained from the mass spectra of systems with dye concentrations somewhat lower than *c.c.c.* according to a previously developed approach.[10] Essential differences in the peak intensities were found in the presence of colloidal C_{60} as compared with pure 1,1′–dimethylquino–2–carbocyanine (Figure 3, the same phenomenon was observed with Neutral Red). The mass spectrum of the latter compound is consistent with the reported data.[11] Besides, the mass spectra show that the dye adsorption on the fullerene particles facilitates the formation of cluster ions in the region *m*/*z* 632–646 and of fragment ions in the region *m*/*z* 447–474.

Transmission electron micrographs of the solid phase obtained from the sols after supporting on nitrocellulose and drying in air give an indication of the colloidal particles (Figure 4). The samples were examined using an EMV 100 AK electron microscope (voltage 75 kV, vacuum, 3 Pa). This study provides support for the ultramicroheterogeneous and polydisperse character of the system, which was found earlier.[3,4] Isodiametrical particles from 7 to 40 nm in size, which consist of smaller spherical particles, are prone to further cluster formation. Note that the associates of amino acids and dipeptide derivatives of the C_{60} fullerene in solutions are larger by approximately two orders of magnitude.[12] Thus, the specific surface area is about $(1–5)\times10^2$ m^2 g^{-1}. It is likely that individual C_{60} molecules are detected in some regions of the micrographs. Electron diffraction patterns show the ordered (crystal-like) character of the primary aggregates.

Thus, under conditions of changing absorption spectra of the dyes (Figures 1 and 2), and at the threshold of coagulation, the number of dye ions is one or two orders of magnitude higher than that of the colloidal particles of C_{60}. Hence, it becomes apparent that the dye ions are concentrated at the surface of fullerene particles, resulting in interactions between the dye chromophores. Spectral effects of this type are referred to as ‘metachromasy’.[13]

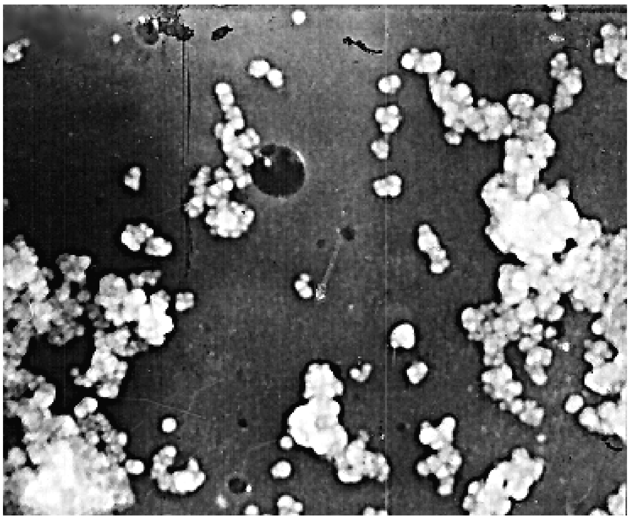

Figure 4 Transmission electron micrograph of C_{60} colloidal particles (×70000) obtained from a sol with a fullerene concentration of 0.13 g dm^{-3} (negative image).

On the other hand, this surface condensation of cations leads to neutralization of the negative surface charge and to further hydrophobization of the colloidal particles. Both of these effects cause coagulation of the C_{60} hydrosol. As a result, the coagulating power of the dyes is approximately 3×10^3 times higher than that of NaCl.[3]

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