

Electronic Supplementary Information

Monomer/dimer dependent modulation of reduction of cationic dye methylene blue in negatively charged nanolayers as revealed by mass spectrometry

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Evaluation of the ratio of SDS to Methylene Blue dye in the surface layer, observed under secondary ion mass spectrometric conditions

It is of interest to estimate the efficiency of Methylene Blue dye cations (MB⁺) adsorption at the SDS anions monolayer at the liquid-gas interface on the basis of mass spectrometric data. Since the molar ratio of the components in the initial solution is preset during liquid sample preparation, the deviations from this ratio in the matter sputtered from the surface layer of the sample would point to formation of certain self-assembled structures in the (SDS + MB) system.

Rough quantitative estimates only can be made on the basis of the intensities of the peaks recorded in desorption mass spectra, since a number of factors which either facilitate or hamper the evaluation must be accounted:

- 1) It is believed that the direct transfer to the gas phase of the so-called “preformed” or “performed” ions of the dissociated ionic compounds takes place under desorption mass spectrometric conditions. This favourable effect permits to avoid ambiguities caused by differences in ionization potentials or proton affinities characteristic of neutral compounds.
- 2) It is necessary to account of contribution of MB⁺ cation and all its reduction products, so intensities (I) of all peaks in the peaks envelope of MB, as well as all isotopic peaks of SDS are to be summarized for determination of the MB to SDS ratio **R**:

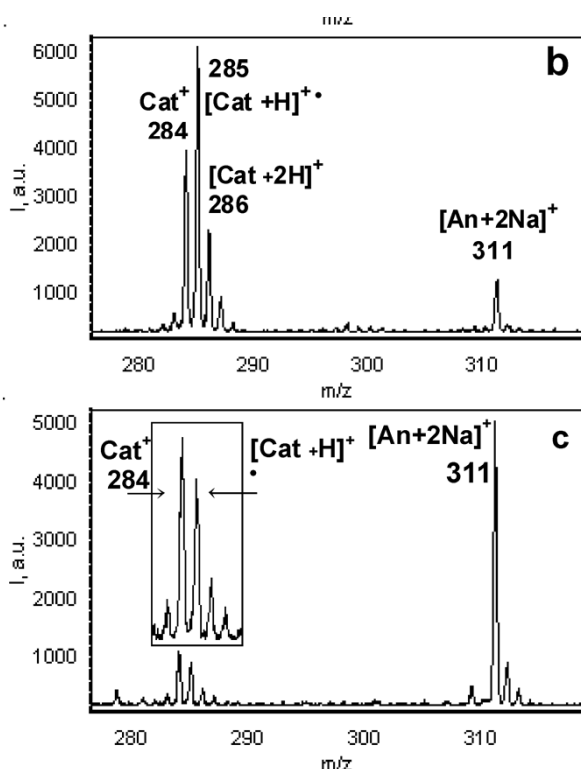
$$R = \sum I(\text{MB})_i / \sum I(\text{SDS}) \quad (1)$$

- 3) The peculiarities of formation of the SDS-related An⁻•2Na⁺ cluster ion is to be accounted. Independently of the exact pathways of its formation, two SDS salt “molecules” 2(An⁻•Na⁺) are involved in its formation. (Since both positive and negative ions are generated in the excited zone on particle bombardment, the second An⁻ is recorded in the negative ion mode.) In this connection the An⁻•2Na⁺ yield should be multiplied by a factor of two:

$$R = \sum I(\text{MB})_i / 2 \sum I(\text{SDS}) \quad (2)$$

- 4) Production of An⁻•2Na⁺ clusters may be distorted by depletion of Na⁺ cations in the surface layer due to their replacement of the adsorbed MB⁺ cations. It can be accepted that one MB⁺ cations displaces at least one Na⁺.

The estimates were made using the data of the FAB mass spectra presented in Fig. 2 in the main text:



Extract from Fig. 2. FAB mass spectra of the surface layer of (SDS + MB) system in glycerol matrix:

- b) a mixture of 10^{-1} M SDS and 10^{-2} M MB;
- c) a mixture of 10^{-1} M SDS and 10^{-4} M MB.

While the ratio of MB to SDS in the initial solution in the system described in Fig. 2b is 1 to 10, the R value calculated using equation (1) is about 10 to 1; the correction with account of the factor from paragraph 3 in equation (2) gives 5 to 1. This ratio seems to be unrealistic; it points either to the MB^+ cations adsorption in the form of aggregates larger the dimers or, which is more probable, noticeable underestimate of the SDS content due to the factor mentioned in the paragraph (4).

In the system described in Fig. 2c the initial ratio of MB to SDS is 1 to 1000, while equation (1) gives 2 to 5 and equation (2) 1 to 5. These values are more realistic, since they do not contradict geometrical possibilities of MB^+ cations allocation at the surface layer.

Thus, although the R values calculated on the basis of peaks intensities in the mass spectra for the both above systems are obviously overestimated, they definitely point to the increased concentration of MB^+ in the surface layer as compared to the bulk solution, which agrees with the notions of self-assembly of the SDS surfactant monolayer doped by MB^+ at the liquid-gas interface.