

# Colloidal Dispergation In Micelle Solutions Of Colloidal Surface-Active Substances (CSAS)

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## Abstract

The colloidal surface-active substances (CSAS) are capable to form molecular solutions only at very small concentrations. The greatest possible concentration, when CSAS is still in solution in the molecular (ionic) form, for the CSAS majority lies in the limits of 10<sup>-5</sup>-10<sup>-3</sup> mol/l. More concentrated of them gain colloidal structure owing to formation in a volume of solution of aggregates - micelles. This phenomenon makes up the CSAS most important distinctive singularity, many practically valuable properties of their solutions are connected with which one.

It is shown, that at an adsorption of CSAS on technical carbon and magnetite a formation of resistant suspensions, at concentrations exceeding critical concentration of micelleforming is observed. It is established, that in micelles of CSAS depending on nature of the used adsorbent one and more fragments of the adsorbent can be colloidal dispersed.

Higher than some definite for everyone CSAS of critical concentration of micelleforming (CCM) separate molecules (ions) of CSAS spontaneously are aggregated: the hydrocarbon radicals, sticking together for the score of Van-der-Vaalces power, will form an internal part (core) arising micelles, and the polar groups reduce to aqueous phase. Thus, each micelle is as though ultra micro drip of hydrocarbon concluded in a shell of hydrated polar groups, connected by chemical powers with hydrocarbon core chains.

At micelleforming it is sharply changes volume properties of solutions of CSAS: density, electrical conductivity, factor of an interception, osmotic effects, optical behavior (turbidity) etc. On isotherms «property - the concentration of CSAS» a change of an inclination in the very narrow concentration region, practically in the point, corresponding to CCM is observed. Change of these properties, as well as surface tension, lies in the base of miscellaneous methods of CCM definition.

Micelleforming, similarly to an adsorption, flows past spontaneously, as reduces a free energy of a system. Really, the powers of cohesion between polar molecules of water are much higher, than powers of interplay between hydrocarbon chains and water. Therefore any process, connected with the transition of hydrocarbon radicals of CSAS molecules in close phase on polarity, is energetically expedient. In very weak solutions (up to CCM) the aiming of a system to decrease of a free energy is contented at the

expense of excess accumulation of solute in a surface layer and pushing hydrocarbon chains from water in non-polar phase. As soon as the saturated adsorptive layer will be formed, such capability is depleted. With further increase of the concentration of CSAS in solution the minimum free energy can be realised only at the expense of structural changes in the volume of solution by the way of formation of micelles. Thus the hydrophilic chains are popped from water in hydrocarbon cores of micelles, just as they are displaced from the volume on a water surface during formation of an adsorptive layer.

Due to hydrated polar groups the surface of micelles has hydrophilic properties and very small interphase free energy. It creates an affinity of micelles to a dispersing medium and informs a system about property of liophilic colloids. The indicated features of a condition of CSAS solutions which are higher then CCM allow to consider them as two phase disperse systems, which represent by themself an example thermodynamic stable lyophilic colloidal systems. In such solutions colloidal dissolved CSAS is in a thermodynamic equilibrium with true dissolved part.

The micelles are thermodynamic stable convertible formations, which appear at CCM and disintegrate from dilution of solution. It distinguishes solutions of CSAS from other colloidal systems.

Though the micellar solutions of CSAS also are two-phase, the micelles can be considered only as germs of a new phase. They are not capable to boundless growth with the formation of macro phase. The growth of micelles and the installation of the equilibrium in the micelle solution is adjusted by three main factors.

Van-der-Vaalces powers of adhesive hydrocarbon chains and conditioned by them gain of energy at an aggregate promote formation and growth of micelles.

Electrostatic repulsing of ionized polar groups in surface layer of micelles and reduction of a system entropy, owing to increase of a degree of order at packaging separate molecules (ions) in micellar aggregates, limit growth of micelles. Increasing of the electrical energy of repulsing of micelleforming ions and the entropic factor indemnify the decrease of energy at an aggregate of chains. In solution the equilibrium sizes of micelles are established. In the final accounting this moment depends on a ratio of all three indicated factors.

The capacity of CSAS to micelleforming appears at a definite ratio (balance) of hydrophilic properties of molecules conditioned by the nature and quantity of polar groups, and hydrophobic properties, connected with the presence of a hydrocarbon radical. The optimal balance of these properties is characteristic for CSAS, in molecules of which sharply hydrophilic, more often ionized polar group are connected with a developed hydrocarbon radical. The balance upset of properties in this or that side makes micelleforming impossible. So, the alkaline salts of the lowest fatty acids are not capable to micelleforming hydrophilic properties, conditioned by an ionized polar group at a short hydrocarbon chain prevail for them. It appears energy of aggregates of short chains at the expense of adhesive Van-der-Vaalces powers is insufficient to indemnify disaggregating operating of heat motion. Micelleforming becomes possible only at the sufficient length of a hydrocarbon radical, i.e. at strengthening of hydrophobic properties of molecules.

The optimal hydrophilic - lyophilic balance in a series of colloidal solutions of fatty acids is reached, if there are 15-18 carbon atoms in the chain. It is exhibited in a high surface activity and micelleforming capacity of the corresponding homologues, in sharp strengthening their detergent, stabilizing and other properties.

The submissions about hydrophilic - lyophilic balance of CSAS are very relevant for the solution of the question about efficiency of their application. However, unfortunately, quantitative idealized substantiation of this concept is not designed, and remains only empirical by now.

Micelleforming in water solutions takes place at the expense of hydrophobic interplays, at which the lyophilic segments of molecules of CSAS are displaced by molecules of water. It results to formation of adsorptive layers, and at achievement of CCM - micelles, the formation which probably is higher of the definite for everyone CSAS temperature. The size of micelles can be within the limits from 3 up to 100 nm. In contrast to process of micelleforming in water solutions, in organic solvents the aggregation of molecules of CSAS takes place at the expense of interplay of polar groups of diphylic molecules. Considerable quantity of hydrocarbon and others slightly soluble in water of matters are capable to pass in micellar solutions CSAS.

Suspension stability is possible to rise using for this purpose CSAS and polymers. At an adsorption of these matters a modification of a surface of a disperse phase takes place. On the surface of fragments the adsorptive layer, which will update a surface of a hydrophobic adsorbent, is formed.

The adsorption cation - fissile, anion - fissile and nonionic CSAS on technical carbon from water solutions is conducted. It is showed, that at depositing into solution of CSAS highly dispersive adsorbents the spontaneous formation of steady suspensions exists, that has a place at achievement of CCM. It testifies that the most highly dispersive fragments of adsorbents penetrate in micelles of

CSAS. Thus there is a process of a colloidal dispersion in micelles. Quantity of colloiddally dispersed adsorbent in micellar systems is determined. In a Fig. 1 and 2 the dependence of a highly dispersive adsorbent quantity on equilibrium concentration of solutions of CSAS are adduced.

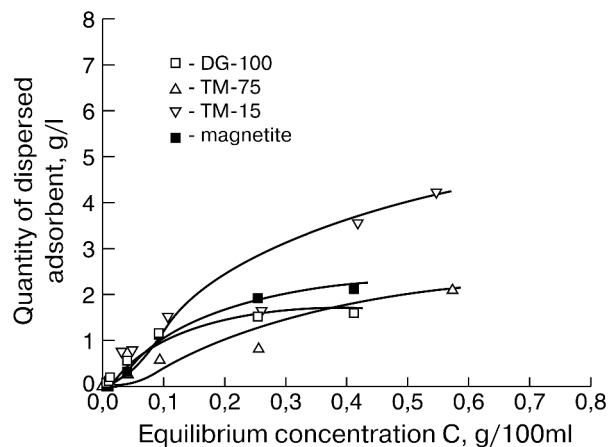


Figure 1. Quantity of colloidal-dispersed highdispersed adsorbent in the equilibrium oleate of natrium solutions

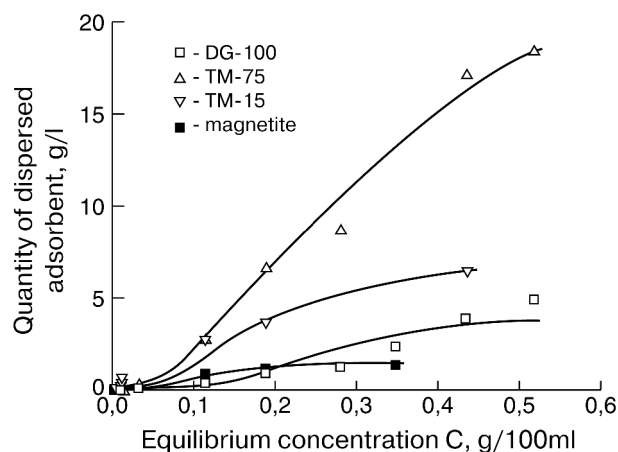


Figure 2. Quantity of colloidal-dispersed highdispersed adsorbent in the equilibrium syntanol solutions

If it is assumed, that in each micelle of CSAS is only one fragment of a highly dispersive adsorbent, then after an adsorption of an oleate of natrium on magnetite, according to calculations there is 0.07 g/l of colloiddally dispersed matter in equilibrium solution (it is assumed micellar weight for an oleate of natrium is equal 20000).

In dependence on the size of a micelle and fragments of used adsorbents in micelles of emulsifier different quantities of fragments can be colloiddally dispersed. So for example, at the adsorption on miscellaneous samples of technical carbon from 1.8 g/l up to 14.2 g/l can be dispersed. If at the adsorption on technical carbon one or the smaller number of fragments of the adsorbent have to each micelle of

emulsifier then at the adsorption on magnetite it can have to 25 fragments on each micelle.

At research of the syntanol adsorption on magnetite it is revealed, that still lot of fragments of magnetite can be dispersed in micelles of syntanol. In this case according to calculations 0.0068 g/l can be dispersed.

Thus, at the development of composite materials it is necessary to take into account the phenomena of the colloidal dispersion. If in micelles of CSAS the most highly dispersive fraction is colloidally dispersed, then purely quantity of colloidally dispersed fragments will be augmented.

## **Biography**

Iryna Opaynych received her M.S. in Physical Chemistry from the University of L'viv in 1965, and her Ph.D. in Chemistry from the University of L'viv in 1983. Dr. Opaynych is current an associate professor of chemistry at the chemical faculty of the L'viv University. She has published over one hundred papers, including inventions, one of inventions has been patented in USA, France, UK, Japan and others countries. Iryna Opaynych works in the area of polymeric composite materials chemistry.