FEATURES OF CASEIN INTERACTION WITH NONIONIC AND ANIONIC SURFACTANTS

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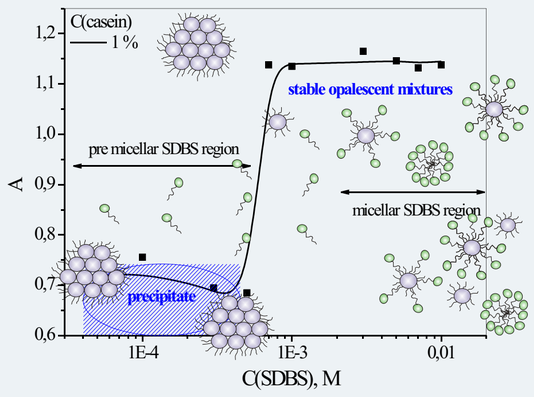
Introduction

Interaction in aqueous casein systems - surfactant is an extremely complex process, the mechanism of which depends significantly on many factors: the nature of the reactants, the nature of the protein (whether a mixture of different forms of casein or just one form), the ionic strength of the solution and pH, from the temperature at which the systems are examined and stored, from the storage time and others. In addition, the whole complex of physicochemical properties changes significantly and such changes often have extremal character.

Relevance of research

Protein-polymer mixtures can be used as emulsifiers, de-emulsifiers, wetting and foaming agents,functional food ingredients and as detergents in petroleum, petrochemicals, environmental management, agrochemicals, foods and beverages, cosmetics and pharmaceuticals, and in the mining and metallurgical industries. For medical applications, biosurfactants are useful as antimicrobial agents and immunomodulatory molecules.

Casein - SDBS system



In the region of domicellar concentrations of SDBS there is a macrophase separation of mixtures and white precipitate formation. During the transition to the region of micellar concentrations, stable opalescent systems are formed.

Fig.1. Absorbance value of 1%casein+SDBS mixtures as function of SDBS concentration.

Spectroscopically proved that the concentration of sodium ions in the solution above the precipitate coincides with the concentration of sodium ions formed as a result of dissociation of SDBS in the appropriate solution, so it can be argued that the precipitate formed is casein.

In the region of low concentrations of SDBS there is an increase in the surface tension of the systems with the addition of surfactants and a decrease in the effect of casein on the surface tension of the systems. During the transition to the region of micellar concentrations, there is an inflection on isotherm 2, and a slow decrease in the surface to the values ??characteristic of the corresponding solutions of SDBS. This concentration range coincides with the concentration range where the optical density of the systems has reached the limit level and has ceased to depend on the surfactant concentration, which may indicate the saturation of the polymer with a surfactant.

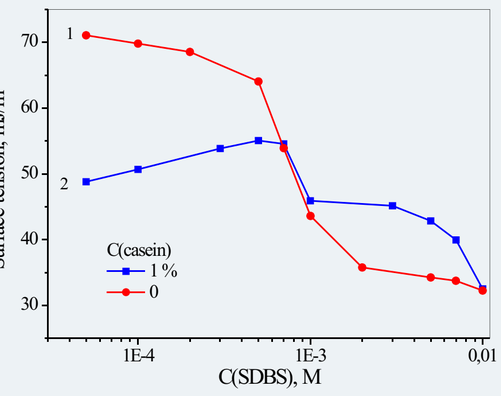


Fig.2. Isotherms of surface tension of DBSN solutions (1) and 1% casein-DBSN systems (2) depending on DBSN concentration.

Objects

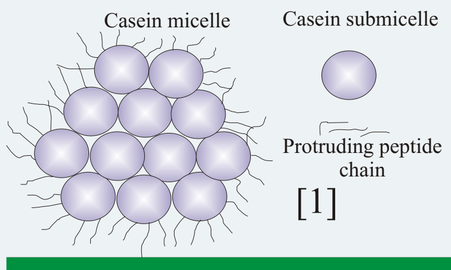
Aqueous systems protein-surfactant

- Protein - cow*s milk casein (mixture of a, ß, k)
- Non-ionic surfactant - Polysorbate 80 (Tween 80), $C_{64}H_{124}O_{26}$, Mw = 1310 g/mol
- Anionic surfactant - sodium dodecylbenzenesulfonate (SDBS) $CH_3(CH_2)_{11}C_6H_4SO_3Na$, Mw = 348 g/mol

Methods

- Surface tension measurements
- Photometry
- PH measurements
- Atomic-emission spectrometry

Casein

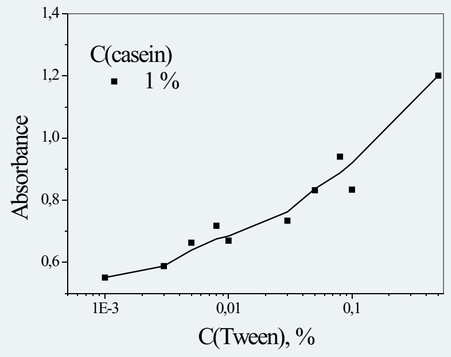


1 % casein solution

Acidity pH=4.3
Isoelectric point (IEP) 4.6
Optical density of 1% solution 0.38 (315 nm)
Surface tension 58 mJ/m^2
1% casein solution has a noticeable surface activity

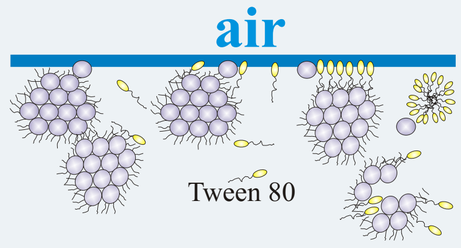
Casein - Tween 80 system

The association processes in casein-nonionic twin systems are much weaker than in ionic ones and occur at higher surfactant concentrations.



With increasing of surfactant concentration in the system, the optical density of the casein-Tween80 systems increases monotonically.

Fig 3. Absorbance value of 1%casein+Tween 80 mixtures as function of Tween concentration.



At low concentrations of nonionic surfactants, the surface tension of the systems is determined entirely by the adsorption of casein at the interface between the liquid-air phases.

With a further increase in the surfactant concentration, we observe a decrease in the surface tension and an increase in the effect of the surfactant on the surface properties of the systems. When C (Tween)> 0.008% begins a drop in surface tension of the systems, which coincides with the area of increaшiтп in the optical density of the systems, indicating the beginning of the association of casein-surfactant.

In the process of storage, the surface tension of the studied systems increases. This is due to the displacement of more active casein molecules from the surface layer by molecules of Tween 80, and this effect is most pronounced at concentrations of Tween 80 0.01-0.1 %.

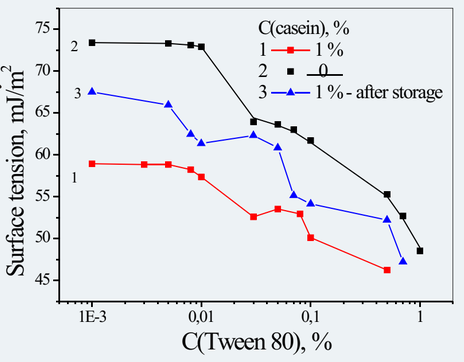


Fig.4. Isotherms of surface tension of 1% casein-twin 80 systems (*1* - one day after manufacturing, *3* - 7 days after manufacturing) and solutions of Twin 80 without casein additives (curve *2*).

Conclusions

1. The possibility of associative processes between like charged surfactant and protein was shown. It is possible because we were working in the area of the isoelectric point of the casein, where its charge is closer to neutral. At SDBS concentrations higher than CMC, casein micelles are destroyed by submicelles and submicelles are associated with SDBS molecules. In contrast to SDBS-PMAK systems [2], the dissolution of protein in surfactant solutions with the formation of stable opalescent systems is recorded visually.
2. There is a concentration interval within which the forces of hydrobiotic interaction become stronger than the electrostatic repulsion, which makes it possible to carry out the processes of association in mixtures of protein and surfactants of the same charge.
3. In contrast to ionic [3], in case of nonionic surfactants addition the greatest impact on the mixtures properties has the component whose concentration is higher. It is believed that the interaction of Tween 80 with casein is accompanied by the gradual displacement of protein molecules from the surface layer by surfactant molecules.This is indicated by a increase in the surface tension of casein-twin systems after storage.

[1] Pieter Walstra, Casein sub-micelles: do they exist?,International Dairy Journal,Volume 9,Issues 3–6,1999,Pages 189-192
[2]. Sachko, A.V., Zakordonskii, V.P., Voloshinovskii, A.S. et al. The mechanism of interaction of polymethacrylic acid with sodium dodecylbenzenesulfonate in aqueous solutions. Russ. J. Phys. Chem. 83, 1094-1101 (2009).
[3].Sachko A.V., Lukan Y.R., Zakordonskiy V.P. The association processes and physical-chemical properties of casein-benzethonium cloride aqueous systems // NANO-2018. Kyiv, 27-30.08.2018. - P.523.