

Liquid-Liquid Polymorphous Transition VS. Micelle Formation of Surfactants

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Abstract Briefly introduced a new concept of micelle formation of surfactants. Explained smooth polymorphic transitions, oscillations, hysteresis properties, fluctuations in the size of the micelles.

Keywords: Liquid-liquid polymorphous transition, Aqueous solutions, Surfactants, Bistable micelles, Oscillations, Hysteresis properties, Fluctuations.

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1. INTRODUCTION

Liquid-liquid phase transitions (LL transitions) accompany phase separation of hydrocarbons, alcohols and water, surfactants micelle-formation, phase transitions of protein molecules [1]. Previously, the existence of phase transition in water was in doubt because different structures in single-component liquid were unknown. Using new physical methods, experimental data supporting our ideas in this area of knowledge formulated in 1985-1988 [2,3] were obtained. Polymorphic transition in the ensemble of small water systems of low and high density is possible in the water. Water clusters of ≈ 1 nm with low-density of LDL have a tetrahedral grid of H-bonds with caves. HDL clusters have H-bonds grid which is partially destroyed, densified [4, 5]. These achievements have intensified studying of water, but not LL transition in aqueous solutions of surfactants.

It is still believed that the spherical micelles occurs in the CMC₁ narrow concentrated area. Spherical micelles can be represented in the form of a hydrocarbon "drop" on the surface of which in adsorption and diffusion layer there are inorganic counter ions [6]. The established notions of the object are obsolete and, in our view, constrain the use of surfactants in the development of advanced technologies.

The theoretical basis for a new vision concerning micelles formation of surfactants lies in thermodynamics of small systems and the transition between two states [7]. The experimental data and formulated following conclusions will be presented in the paper.

2. RESULTS AND DISCUSSION

2.1 LL Transition Depending on the Concentration of the Surfactants.

Properties of water always vary smoothly in the area of LL transition depending on the concentration of the surfactants. The ensembles of molecules of water ejected from the cavities are considered as clusters. Cluster size is approximately equal to the volume of the amphiphile according our opinion. Polymorphic transition occurs in the ensemble of clusters of water (Fig. 1).

It begins on the first binodal (critical pre-micelle concentration) and ends at the second binodal CMC₂.

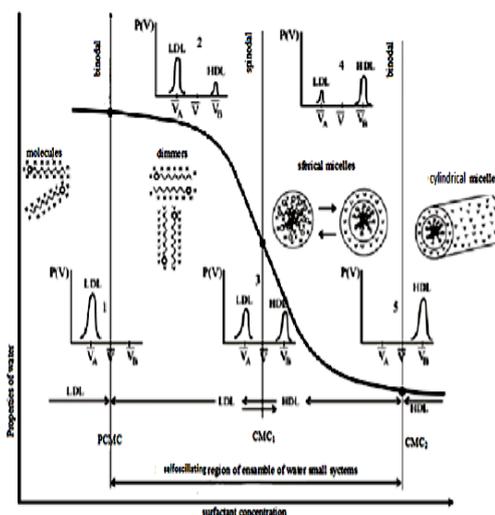


Fig. 1 – Processes accompanying the liquid-liquid polymorphous transition. The distribution function $P(V)$ volume of water in nano-ensemble

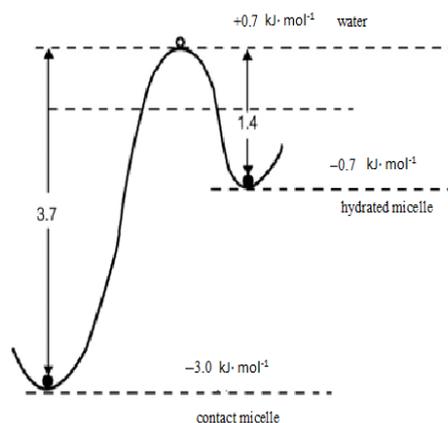


Fig. 2 – Increments Gibbs energy of micelle formation on methylene group bistable micelles in systems n -hydrocarbons - sodium alkylsulfates (250 °C)

The average concentration of the transition corresponds to the concentration of spherical micelles formation CCM₁ or spinodal. The equilibrium in the ensemble of water clusters on the first binodal is maximum shifted to the LDL. On the second binodal the equilibrium is maximum shift-

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ed to HDL. When LL transition occurs, the ensemble of water nanosystems oscillates between two states A and B. Therefore, the micelles are bistable (Fig. 2) and have self-oscillatory properties. They exist 10^{-3} sec in state A, and 10^{-5} sec in state B. Two Gibbs energies of activation during the transition between two states of a self-oscillating system correspond to two rate constants, obtained in the experiments [8].

For sodium dodecyl sulfate micelles of fast and slow processes ΔG are respectively -19.4 and -29.8 kJ·mol $^{-1}$. The difference between them is -10.4 kJ·mol $^{-1}$, and is less than ΔG of hydrogen bond in the water $-2(-5)$ kJ·mol $^{-1}$. The extensive thermodynamic parameters of the nanosystem ensemble fluctuate significantly up to 40 %.

2.2 LL Transition Depending on the Size of Surfactants Molecules

Depending on the size of surfactants molecules and their concentration at the binodal, different by their nature small systems of water molecules of polymorphic phase transition in the metastable area are formed. Their chemical potentials are equal to the chemical potentials of small systems of surfactants, i.e. molecules consisting of several methylene groups. A kind of “discrete phase transition” of changing the density of small water systems, depending on the size of the molecules of surfactants from a loose LDL through an unstable LDL to a denser LDL with hydrophobization of hydrophilic group is observed on first binodal (Fig. 3).

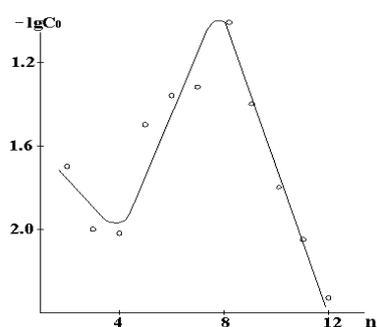


Fig. 3 – The negative logarithm of the concentration dependence of s-alkylisothiuronium chlorides lying on the binodal versus amount of carbon atoms in the alkyl group

Small water systems formed on the first binodal determine the type of LL transition by concentration. We observe “melting” of clathrate-like structures of amphiphiles with $n = 2-4$ with increasing concentration, which leads to the microseparation with concentration fluctuations. Surfactants with $n = 8-12$ have a denser LDL structure which gradually turns into HDL to form bistable spherical micelles. Cooperative self-organization is accompanied by surface, volumetric and thermodynamic instability. Amphiphiles with $n = 7$ has a critical volume. At the critical point the structure of LDL and HDL do not differ from each other and critical line $CMC_1(n)$ goes out from the point.

3. CONCLUSIONS

A new concept of micelle formation does not contradict the experimental data which are already recognized. In the equation $\Delta G_M^0 + (1 + K_d)RT \ln CMC_1$ the bistability of micelle formation is taken into account: the first term of the equation corresponds to the contribution to the Gibbs energy of pseudo phase A, and the second one corresponds to the associate B. Already well-known theories of kinetics of micelle formation are unable to accurately interpret the correspondence of the relaxation processes and structures in the process of micelle formation [9], therefore, a new interpretation of experimental kinetic parameters is possible. Using experimental data of the enthalpy of dissolution of sodium dodecylsulfate in the area of LL transition, the enthalpy of «melting» of the ensemble of water clusters 4.9 kJ·mol $^{-1}$ was calculated. It is roughly equal to the enthalpy of ice melting and the enthalpy of hydrocarbons clusters «melting».

A new concept explains synthesis of the nanoparticles of metals from their ions in aqueous micellar solutions of surfactants [10], transmission of information through a semipermeable membrane and water between them [11], hysteresis of micelles properties, stochastic resonance in micelles [12], optical activity of the micellar solution [13], the effect electromagnetic field on CMC, oscillation induced by ionic surfactant molecules at a water / nitrobenzene interface [14].

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