

Nucleation Kinetics in the Krafft Transition

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C16 ピリジニウム界面活性剤の Krafft 転移の動的過程が、過飽和溶液から結晶核が形成する過程と類似現象であること、結晶核形成誘導期間 t が、過飽和度 S の対数の-3 乗に比例すること、形成される水和固体が準安定の場合と安定状態の場合では、 t と S の上記関係の比例係数が異なることを見出した。

The surfactant molecules with alkyl chains in the solid state at a decreased temperature form the hydrated crystal in water, which is called as the Krafft transition. The hydrated solids or crystals usually form the multilamella structures consisting of bilayers. Recently we have found the long-lived metastable hydrated solid in the Krafft transition process of cetylpyridinium chloride (CPC) in water through the measurements of the small-angle X-ray scattering, the electric conductance and the calorimetry. [1] The multilamella structures in the metastable and stable solids, respectively, are composed of ordinary bilayers and interdigitated bilayers, which have been identified by their lattice spacings.[1] It has been found that a time lag between drops of an electric conductance, κ and a temperature, T exists in the Krafft transition process of CPC.[1] The time lag is the induction period of the formation of hydrated solid, during which the molecules overcome the activation barrier in order to form a critical nucleation cluster.[2]

A drop of κ of the bulk solution can be a good indication of the hydrated solid formation of surfactant. Just after decreasing the solution temperature, the κ of CPC solution slightly drops because of the increased viscosity of water, and it decreases very much at a later time because of the formation of the hydrated solid from the micelles and/or the monomers. The solubility curve as a function of temperature indicates that the Krafft point, T_K^* is about 9 °C. The metastable hydrated solids start melting at about 8 °C. This is indicated by the fact[1] that a lower temperature edge of the broad endothermic peak due to the melting metastable hydrated solid lies at about 8 °C. The metastable hydrated solid forms from the monomers in the solution phase and that it starts melting or is more destabilized at the surfactant concentrations higher than a critical micelle concentration (CMC =about 0.9 mM). The κ changes of 0.93, 5.3, 10.6, 20.6, 50.8 and 100 mM CPC solutions with times were measured after dropping T from 25 °C, which was much higher than the T_K^* , to the T lower than the T_K^* . The κ changes of 0.93 and 10.6 mM CPC solutions with times are shown in Figs. 1(a) and (b). It is noticeable that the

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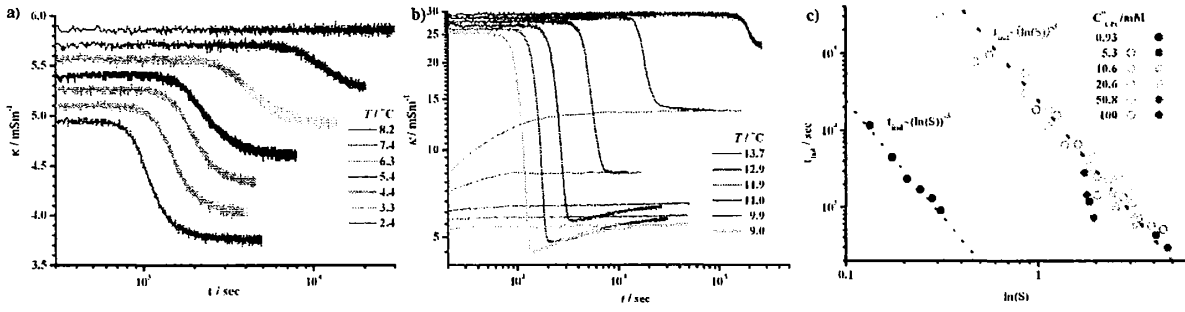


Figure 1: κ changes of 0.93 (a) and 10 (b) mM CPC solutions versus elapsing times after changing temperatures, and t_{ind} as a function of S (c). The solutions incubated at 25 °C for times longer than 12 h are cooled down to the target temperatures at $t=0$.

drop of κ lags long behind the T drop. Transparent solutions became cloudy with dropping κ because of the hydrated solid formation. The lag times are induction periods, t_{ind} for the nuclei formation of the hydrated solid. The t_{ind} increases with the T of solution. It is often observed in the crystallization of inorganic materials that the induction period for the crystal nucleation increases with a decrease in the relative super-solubility of solute, $S=C_s/C^*$, where C_s and C^* , respectively, are the solute concentration of supersaturated solution and the solubility. This is the case, since C^* increases and S decreases with an increase in the T . We plot t_{ind} against $\ln(S)$ and obtain the relation of $t_{ind}=A_k[\ln(S)]^{-3}$ as shown in Fig. 1(c). Here C_s is a prepared concentration of the CPC solution, which is in the supersaturated state before forming the hydrated solid. Obviously two regimes exist in the kinetics of hydrated solid formations, which are characterized by A_k values of 24 and 24000. It should be pointed out that the supersaturated CPC solution at a concentration lower than CMC and a temperature lower than the T_K^* gives the small A_k and that the solution at a concentration higher than CMC and a temperature higher than the T_K^* gives the large A_k . This fact also indicates that the former and the latter transitions, respectively, correspond to the solid formations from the monomers and the micelles. The physical meaning of A_k can be described on the basis of the simple theory for the nucleation driven by the successive bi-embryo collisions [2]. The obtained values of A_k indicate that the surface energy of the stable solid consisting of the interdigitated bilayers is much greater than that of the metastable solid consisting of the ordinary bilayers.

References

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