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A generalized model for the stability of polymer colloids

Zichen Jia [a], Cornelius Gauer [a], Hua Wu [a], Massimo Morbidelli [a,*], Alba Chittofrati [b], Marco Apostolo [b]

[a] *Institute for Chemical and Bioengineering, ETH Zurich, Hönggerberg HCI, 8093 Zurich, Switzerland*
[b] *Solvay Solexis SpA, Viale Lombardia 20, 20021 Bollate (MI), Italy*

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Abstract

A generalized model has been proposed to describe the stability of polymer colloids stabilized with ionic surfactants by accounting simultaneously for the interactions among three important physicochemical processes: colloidal interactions, surfactant adsorption equilibrium, and association equilibria of surface charge groups with counterions at the particle–liquid interface. A few Fuchs stability ratio values, determined experimentally for various salt types and concentrations through measurements of the doublet formation kinetics, are used to estimate the model parameters, such as the surfactant adsorption and counterion association parameters. With the estimated model parameters, the generalized model allows one to monitor the dynamics of surfactant partitioning between the particle surface and the disperse medium, to analyze the variation of surface charge density and potential as a function of the electrolyte type and concentration, and to predict the critical coagulant concentration for fast coagulation. Three fluorinated polymer colloids, stabilized by perfluoropolyether-based carboxylate surfactant, have been used to demonstrate the feasibility of the proposed colloidal stability model.

Keywords: Colloidal stability; Fuchs stability ratio; Surface charge; Surfactant adsorption; Counterion association; Hydration force

1. Introduction

Polymer latices produced by emulsion polymerization are typical colloidal suspensions with submicrometer particles. The kinetic stability of these systems is usually achieved through adsorption of ionic surfactants onto the particle surface, whose electrical charges create an electrical double layer (EDL), leading to electrostatic repulsive interactions between particles. The characterization and control of the stability of polymer colloids are of great industrial importance for both their manufacture and posttreatment (e.g., coagulation of the particles for separation of the polymer from the disperse medium). For this, it would be desirable to develop a model that can predict the effect of operating variables such as the type and concentration of electrolyte and the solution pH on the latex stability, i.e., on the Fuchs stability ratio, W.

The state of the art in describing the stability of colloidal systems has been centered on how to correctly describe the colloidal interactions. The centerpiece of modeling the colloidal interactions has been the DLVO (Deryaguin–Landau–Verwey–Overbeek) theory [1,2], which accounts for the competing effects between van der Waals attraction and EDL repulsion. Additional interaction forces such as long-range dispersion forces, short-range hydration forces, and capillary condensation are known to be important under certain conditions [3–6], and need to be considered specifically. However, unlike the DLVO interactions, such non-DLVO interactions are very difficult to either measure experimentally or predict theoretically, particularly in the case of complex colloidal systems, as industrial polymer latices often are.

Once a proper colloidal interaction model has been chosen, what one often proceeds to do in describing the stability of a colloidal system is as follows: first measure the surface charge or potential at properly defined conditions, and then use the measured surface charge or potential in the chosen colloidal interaction model, accounting for the ionic strength present in

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[*] Corresponding author. Fax: +41 44 6321082.
E-mail address: morbidelli@chem.ethz.ch (M. Morbidelli).

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the system, to compute the interaction energy barrier or use the Fuchs stability integral to calculate the Fuchs stability ratio W. Such an approach may correctly characterize the stability of the colloidal system under the exactly given conditions (i.e., at the given ionic strength, ion types, particle concentration, etc.). However, the problem is that due to the needs of practical applications, one often has to extend such obtained results to describe the stability of the same colloid at different ionic strengths, ion types, and particle concentrations by simply changing the ionic strength and ion type (valency) in the colloidal interaction model. Obviously, this often fails because this procedure has ignored the interactions among various physicochemical processes (e.g., colloidal interactions, association equilibria of surface charge groups with counterions, surfactant adsorption equilibrium). In fact, different ionic strengths and different ions have different association behavior with the surface charge groups, leading to changes in the surface charge and potential. This consequently leads to changes in the distributions of ions and surfactants in the system (the Boltzmann effect), which are then coupled back again with the changes in the counterion association of the surface charge groups. Such problems become even more severe in the case of industrial colloidal systems, where the surfactant systems are often very complex and the surface charge is difficult to measure correctly.

Based on the practical problems mentioned above in describing the stability of colloidal systems, we have in this work proposed to describe the colloidal stability by putting together all the important physicochemical processes (such as surfactant adsorption equilibrium, association equilibria of the surface charge groups with counterions, colloidal interaction model) in a single model so that their coupling interactions can be simultaneously accounted for and correctly described. Such a model is referred here to as a generalized model for describing the colloidal stability.

It is evident that including so many physicochemical processes in one model leads to many model parameters such as surface charge or potential, surfactant adsorption parameters, and association equilibrium parameters of surface charge groups with counterions. To estimate these parameters, we have considered two aspects. First, if values of any parameters are reported in the literature and applicable, we use directly these values in our model. Second, for those parameters that cannot be found in the literature and also are difficult to measure experimentally, we estimate their values using a few Fuchs stability ratio values W, determined experimentally for various salt types and concentrations through measurement of the doublet formation kinetics. The estimated parameters are then compared with those reported in the literature for systems that are close to ours in order to assess their reliability.

The paper is organized as follows. In Section 2 we describe all necessary details of each process, based on the literature sources, in order for the reader to understand how we treat each process and where the parameters come from. In the following two sections, as an illustrative example, we demonstrate the application of the model to three fluorinated latices for which limited information is available (for example, the surfactant adsorption isotherm is not known). It will be seen that with the estimated parameters, the developed model is able to predict the colloidal stability behavior of the latices, which includes, for example, the stability ratio in the presence of different types and amounts of electrolytes, the extent of the double-layer compression under different operating conditions, and the critical coagulant concentration (ccc).

2. Model development

As mentioned above, strong interactions exist between the charged colloidal particles and the electrolytes in solution, which lead to a distribution of the ionic species around the particle that is governed by the Poisson–Boltzmann equation. The change of the ionic strength in the bulk liquid phase causes the redistribution of the ionic species, which in turn changes the association and dissociation equilibria between the ionic surfactant adsorbed on the particle surface and the counterions in the liquid phase, and consequently also the surface charge density and then the colloidal stability. In the following, we briefly formulate a model for describing the equilibrium between the interface electrochemistry and the distribution of the ionic species in the liquid phase, accounting for the specifics of the polymer colloids, based on the theories and relevant treatments available in the literature [2,7–9].

2.1. Sources of charges on the particle surface

In polymer colloids produced by emulsion polymerization, ionic surfactants (denoted by E in the following) are often adsorbed on the particles, and their dissociation leads to the formation of negative charges on the surface. Since the surfactant adsorption is typically reversible, the charges deriving from the surfactant molecules are referred to as mobile charges. The amount of the surfactant molecules adsorbed on the particle surface depends on the adsorption equilibrium between the particle surface and the liquid dispersion. In this work, a Langmuir-type adsorption isotherm is used to describe the surfactant adsorption equilibrium, which may be written as [10]

$$bC_\mathrm{t}^\mathrm{i} = \frac{\Gamma/\Gamma_\infty}{1-\Gamma/\Gamma_\infty}, \tag{1}$$

where Γ is the surface coverage of the surfactant, Γ_∞ the surface coverage at saturation, and b the adsorption constant. Note that in the above adsorption isotherm (1) the total surfactant concentration at the particle–liquid interface, C_t^i, is used, instead of the concentration in the bulk liquid phase, C_t^b.

Furthermore, ionically dissociable polymer end-groups may exist on the particle surface, and these also contribute to the colloidal stability. A typical example is given by polymers produced using KPS (potassium persulfate) as initiator for the polymerization, which may result in sulfate head groups ($-\mathrm{SO}_4^-$) on the polymer chains, exposed on the particle surface. Since these charges (denoted by L) are covalently bound to the surface, they are referred to as fixed charges in the following.