Available online at www.sciencedirect.com
ScienceDirect
Colloids and Surfaces A: Physicochem. Eng. Aspects 294 (2007) 236–246
COLLOIDS AND SURFACES A
www.elsevier.com/locate/colsurfa

Plate–sphere hybrid dispersions: Heterocoagulation kinetics and DLVO evaluation

D.J. Voorn [a,b,d], W. Ming [b,*], J. Laven [b], J. Meuldijk [c], G. de With [b], A.M. van Herk [a,**]

[a] *Laboratory of Polymer Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*
[b] *Laboratory of Materials and Interface Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*
[c] *Process Development Group, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*
[d] *Dutch Polymer Institute (DPI), Eindhoven University of Technology, P.O. Box 902, 5600 AX Eindhoven, The Netherlands*

Received 22 May 2006; received in revised form 7 August 2006; accepted 9 August 2006

Abstract

We have studied the formation of colloidal composite particles through the controlled heterocoagulation of anionically charged polystyrene (PS) and poly(isobutyl methacrylate) (PiBMA) latex spheres with positively charged gibbsite platelets. The latex particles, synthesized by emulsion polymerization, varied in size and surface charge density. The heterocoagulation was studied as a function of the number ratio between small latex particles and large gibbsite platelets (N_S/N_P), ionic strength and pH of the aqueous medium. The coagulation kinetics of latex spheres with inorganic platelets in aqueous dispersions were determined by time resolved dynamic light scattering (TR-DLS) experiments. The N_S/N_P values should be sufficiently high to prevent the formation of multilayer aggregates. It was shown that the heterocoagulated colloidal particles were stable up to an ionic strength of 2.5 mM for latex particles with a diameter of about 80 nm and ∼30 mM for those of 35 nm, respectively. The effect of pH on the colloidal dispersions was verified by the classical DLVO theory.

Keywords: Heterocoagulation; Latex; Platelet; Coagulation kinetics; DLVO

1. Introduction

Assemblies of smaller polymeric and larger inorganic colloidal particles can be formed by flocculation and coagulation [1–5] and are used in many industrial applications. Attachment of the polymeric colloidal particles onto the inorganic surface can produce typically two kinds of morphologies: random, multilayer aggregates with low dispersion stability and stable, isolated, composite particles with uniform deposition of particles on the inorganic surface. The stability of these heterocoagulates, which is very important for their potential applications, depends on several parameters such as surface charge, ionic strength, particle size difference, and mixing procedure.

Coagulation kinetics of two bodies were independently developed by Derjaguin, Landau, Verwey, and Overbeek and known as the classical DLVO theory [6–9] which readily explains the qualitative features of colloidal stability. Although several other theoretical prediction methods like the extended DLVO (XDLVO) theory describing the polar interactions [10] and the surface element integration (SEI) technique [11] have been reported, the DLVO theory is still widely used for the interaction between two colloidal bodies and predicts the stability reasonably well [12,13].

Over the past several decades the deposition of small latex particles onto larger, oppositely charged spherical latex particles has been reported extensively [14–25]. In this way, polymeric core-shell particles were prepared via the annealing of the low T_g polymer shell particles [26]. Furthermore, hybrid materials of inorganic core particles covered with smaller polymeric particles showed the feasibility of the heterocoagulation process for dissimilar particle adsorption [1,27,28]. Its extension to the heterocoagulation between platelets and spheres was only investigated scarcely [29–32]. Following the increasing interest in the process, several papers appeared reviewing the kinetics of the heterocoagulation processes [33,34] or presented theoretical simulations combined with experimental results [35,36]. These

---

[*] Corresponding author.
[**] Corresponding author.
E-mail addresses: w.ming@tue.nl (W. Ming), a.m.v.herk@tue.nl (A.M. van Herk).

0927-7757/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.colsurfa.2006.08.022

experiments often showed significant discrepancies between the calculated and measured heterocoagulation rates [28,37–39]. A factor that complicates the calculations is the difficulty to directly estimate the ratio between fast and slow coagulation as expressed in the so-called stability ratio (W), especially for non-spherical particle heterocoagulation.

In this paper we study the heterocoagulation kinetics by using time resolved dynamic light scattering (TR-DLS) and determine the stability ratio (W) of different latex particles that were coagulated with gibbsite platelets. Previously, we reported the controlled heterocoagulation of latex particles with inorganic platelets, leading to the formation of colloidally stable, anisotropic hybrid particles [40]. To the best of our knowledge only a few articles were published up till now on the heterocoagulation of particles (inorganic, in particular) onto the surface of platelets [30–32,41,42] and none of these deal with heterocoagulation kinetics. The interaction of platelets and spheres is currently investigated for their significance for several colloidal processes [43,44]. This investigation aims at elucidating the formation of stable plate–sphere heterocomponent colloids. We used the classical DLVO theory to quantify the influence of latex particle size and pH on the heterocoagulation behavior. Furthermore, we succeeded in showing the influence of ionic strength and pH on the rate of coagulation and colloidal stability of the heterocoagulated structures.

2. Modeling

2.1. DLVO calculation of plate–sphere interaction

Theoretical understanding of colloidal dispersion stabilities provides significant information about the interaction of similarly and oppositely charged particles and the formation or prevention of aggregated particles [37,45,46]. The encounters between particles are frequent and the result of such encounters is determined by the interactions between the particles. The total interaction energy between colloid particles in an aqueous medium can be described according to the classical DLVO theory as the sum of the van der Waals (vdW) attraction and the electrostatic double layer interaction and can be written as:

$$V_\mathrm{T} = V_\mathrm{A} + V_\mathrm{R} \tag{1}$$

where V_T is the total interaction energy, V_A the vdW attraction, and V_R the electrostatic double layer interaction. For certain applications additional acid base interaction, hydrophobic interaction, depletion interaction and Born repulsion terms should be added [10,47–50].

2.2. Electrostatic interaction

The electrostatic interaction of approaching particles is due to the overlap of their double layers. Overlapping of diffuse double layers has been analyzed by several authors [51–54]. Hogg, Healy, and Fuerstenau (HHF) [52] were the first to relate the interaction of dissimilar double layers of binary particle mixtures to the surface characteristics of the particles. Furthermore, they provided an expression for the repulsive force between a spherical particle and a plate, derived from the constant surface potential expression for two infinite flat plates, the linear superposition principle [54] and the Derjaguin approximation for scaling the interaction energy. Although some doubts have been raised about the lower experimentally obtained energies [55,56] the HHF expressions are still widely accepted. According to Hogg et al. [52], the potential energy of interaction between two flat double layers (V_I) is equal to the change in Gibbs free energy of the double layer system when two plates are brought together from infinity:

$$V_\mathrm{I} = \Delta G = G_d - G_\infty \tag{2}$$

where G_d and G_∞ are the Gibbs free energies of the double layer system when two plates are separated by a distance of d and infinity, respectively. With the application of the Debye–Hückel approximation, the potential energy of interaction can be written as:

$$V_\mathrm{I} = \frac{\varepsilon_0 \varepsilon_\mathrm{r} \kappa}{2}\left[(\psi_1^2 + \psi_2^2)(1 - \coth(2\kappa d)) + 2\psi_1\psi_2 \cos\mathrm{ech}(2\kappa d)\right] \tag{3}$$

where ε_0 is the permittivity in vacuum, ε_r is the relative dielectric permittivity of the solvent, ψ_1 and ψ_2 are the surface potentials of the interacting platelets, and d is the distance between the platelets. The Debye–Hückel parameter κ is the reciprocal of the effective “thickness” of the diffuse double layer and known as the Debye length:

$$\kappa^{-1} = \left(\frac{\varepsilon_0 \varepsilon_\mathrm{r} RT}{F^2} \sum c_i z_i^2\right)^{1/2} \tag{4}$$

with R the gas constant, F Faraday’s constant, T the absolute temperature, c_i and z_i the concentration ($\mathrm{mol\,m^{-3}}$) and charge number of the ions of type i in the dispersion medium.

Derjaguin and Landau [6] derived the interaction between the double layers of dissimilar spherical particles from the interaction of two infinite plates, provided that the thickness of the double layer is small compared to the particle size. A particle is supposed to be composed as a collection of small parallel rims from which the interaction with its counterpart on the other particle can be deduced from the infinite flat plate. This results in the energy of electrostatic interaction (V_R) between double layers of spherical particles:

$$V_\mathrm{R} = \int_0^\infty 2\pi h V_\mathrm{I} \,\mathrm{d}h \tag{5}$$

where V_I is defined by Eq. (3) and h is the height of the ring segment (Fig. 1). In a similar manner the energy of interaction of the plate–plate situation can be converted into the plate–sphere situation by reducing the term $h\,\mathrm{d}h$:

$$\begin{aligned} H - H_0 &= a - \sqrt{a^2 - h^2} \\ \mathrm{d}H &= \frac{h}{a\sqrt{1 - (h/a)^2}}\mathrm{d}h \end{aligned} \tag{6}$$