

Aggregation in Charge-Stabilized Colloidal Suspensions Revisited

S. H. Behrens

*Department of Chemistry, Clarkson University, Potsdam, New York 13699-5814, and
Swiss Federal Institute of Technology, ETHZ-ITO, Grabenstrasse 3,
8952 Schlieren, Switzerland*

M. Borkovec*

Department of Chemistry, Clarkson University, Potsdam, New York 13699-5814

P. Schurtenberger

Swiss Federal Institute of Technology, Institut für Polymere, 8092 Zürich, Switzerland

Received November 14, 1997. In Final Form: February 10, 1998

The Derjaguin–Landau–Verwey–Overbeek (DLVO) theory commonly used to describe interactions of charged surfaces across liquids has traditionally been reported to fail when used for quantitative predictions of deposition and aggregation in aqueous colloidal suspensions. Yet direct force measurements have recently confirmed the theory down to surface separations of a few nanometers. Aggregation studies on latex and hematite colloids now reconcile these contrasting findings. Well-known discrepancies between theory and experiment with respect to the dependence of aggregation rates on pH (or electrolyte concentration) and particle size are shown to disappear when charge densities are reduced.

Aggregation and deposition studies of colloid particles not only have had a great impact on numerous branches of applied sciences such as materials engineering, biochemistry or environmental chemistry but also have been recognized as an important tool to test our general understanding of interactions between charged surfaces across a liquid.

For 5 decades, since the pioneering work of Derjaguin, Landau, Verwey, and Overbeek (DLVO),¹ such interactions have been modeled by simply superposing van der Waals attractions and electrostatic double layer forces calculated on the basis of the Poisson–Boltzmann equation.² This explained the main qualitative feature of aggregation and deposition, namely, the existence of a regime where charges are fully screened by electrolyte ions and processes are driven purely by diffusion (fast regime) and a regime where the suspension is kinetically stabilized to some degree by a barrier in the net interaction energy (slow regime). These two regimes determine the growth dynamics and structure of the clusters in the late stages of aggregation.³

For the early stages of aggregation, rate constants in the fast regime could be quantified reasonably well by including hydrodynamic interactions.^{2,4,5} It seemed impossible, however, to understand quantitatively the very gradual stabilization observed with decreasing electrolyte

concentration; whenever the right onset of stabilization was recovered (as commonly achieved by adjusting the Hamaker constant), predicted aggregation and deposition rates in the slow regime were too small by many orders of magnitude.^{2,6,7}

Another striking discrepancy concerned the influence of the particle size and has been stressed by Overbeek himself.⁸ For large particles, the theory predicts a much stronger variation of stability with electrolyte concentration than for small particles.⁹ Increasing the primary particle size should lead to a visible steepening of the measured stability curves; yet in none of the previous experiments could this trend ever be confirmed.¹⁰

Many reasons for these disagreements between theory and experiments have been suggested.¹¹ Some authors argued that pure diffusion represents too poor an approximation of particle dynamics and discussed additional dynamic processes.¹² Others claimed that supplementary non-DLVO forces result in a significant additional attraction.¹³ Further efforts were made to incorporate in

* To whom correspondence should be addressed. E-mail: borkovec@polaris.clarkson.edu.

(1) Derjaguin, B. V.; Landau, L. *Acta Physicochim. U.S.S.R.* **1941**, *14*, 633. Verwey, E. J. W.; Overbeek, J. Th. G. *Theory of the Stability of Lyophobic Colloids*; Elsevier: Amsterdam, 1948.

(2) Russel, W. B.; Saville, D. A.; Schowalter, W. R. *Colloidal Dispersions*; Cambridge University Press: New York, 1989.

(3) Weitz, D. A.; Huang, J. S.; Lin, M. Y.; Sung, J. *Phys. Rev. Lett.* **1985**, *54*, 1416. Lin, M. Y.; et al. *Nature* **1989**, *339*, 360.

(4) van Zanten, J. H.; Elimelech, M. *J. Colloid Interface Sci.* **1992**, *154*, 1.

(5) Lichtenfeld, H.; Knapschinsky, L.; Sonntag, H.; Shilov, V. *Colloids Surf.* **1995**, *104*, 313.

(6) Lips, A.; Willis, E. *Trans. Faraday Soc.* **1973**, *69*, 1226. Zeichner, G. R.; Schowalter, W. R. *J. Colloid Interface Sci.* **1979**, *71*, 237. Table 3: in Bowen, B. D.; Epstein, N. *J. Colloid Interface Sci.* **1979**, *72*, 81. Elimelech, M.; Gregory, J.; Jia, X.; Williams, R. *Particle Deposition & Aggregation*; Butterworth-Heinemann: Oxford, 1995 and references therein.

(7) Kihira, H.; Ryde, N.; Matijevic, E. *Chem. Soc., Faraday Trans.* **1992**, *88*, 2379.

(8) Overbeek, J. Th. G. *Adv. Colloid Interface Sci.* **1982**, *16*, 17.

(9) Reerink, H.; Overbeek, J. Th. G. *Discuss. Faraday Soc.* **1954**, *18*, 74.

(10) Ottewill, R. H.; Shaw, J. N. *Discuss. Faraday Soc.* **1966**, *42*, 154. Matthews, B. A.; Rhodes, C. T. *J. Colloid Interface Sci.* **1968**, *28*, 71. Kotera, A.; Furusawa, K.; Kudo, K. *Kolloid Z. Z. Polym.* **1970**, *240*, 837. Joseph-Petit, A. M.; Dumont, F.; Watillon, A. *J. Colloid Interface Sci.* **1973**, *43*, 649. Penners, N. H. G.; Koopal, L. K. *Colloids Surf.* **1987**, *28*, 67. Elimelech, M.; O'Melia, C. R. *Langmuir* **1990**, *6*, 1153. Tsuruta, L. R.; Lessa, M. M.; Carmona-Ribeiro, A. M. *J. Colloid Interface Sci.* **1995**, *175*, 470.

(11) An overview is given in: Swanton, S. W. *Adv. Colloid Interface Sci.* **1995**, *54*, 129.

the framework of DLVO theory the effect of surface roughness¹⁴ or of heterogeneity in the surface potential of the particles.⁷ One may also question the basis of the DLVO approach altogether by pointing at the effect of ion-ion correlations that are neglected in the Poisson-Boltzmann equation and are expected to have a particularly strong influence on solutions of polyvalent electrolytes.¹⁵

Quite surprisingly and in a seeming contradiction to observations of colloid stability, recent force and potential measurements have essentially confirmed the classical, unextended DLVO theory down to surface separations of typically 1–3 nm.^{16,17} Unfortunately, under the conditions corresponding to slow aggregation, the exact force profile at the position of the maximum in the interaction energy (separation of zero force) is difficult to access. In direct force measurements,¹⁶ the approaching surfaces usually jump into contact near this point, while optical tweezer techniques are reliable at larger separations only.¹⁷ Still, it was unclear why the theory should be confirmed by probing colloidal forces directly and proved false when looking at the resulting aggregation behavior.

Here, we report that the theory does work properly for aggregation, too, and that a criterion for its applicability seems to be given by the distance of the DLVO energy barrier from the surface. As long as this distance is at least a few nanometers, we find that the DLVO approach gives a perfectly satisfactory description of colloid stability; only for situations in which the barrier lies at very small surface separations (where the theory is not confirmed by force measurements either) do we recover the typical pattern of deviations.

The condition of validity of the DLVO theory is obtained at moderately low ionic strength but still in the high salt regime (typically 0.1–10 mM). Then, correspondingly low charge densities of just a few mC/m² are required to allow aggregation—much less than in the model systems commonly used. Polystyrene latex spheres with carboxylic surface headgroups represent an ideal system for this kind of investigation, because their surface charge, resulting from partial deprotonation of the carboxyl groups, can easily be tuned by adjusting the solution pH. For the same reason, well-characterized amphoteric oxide particles close to their point of zero charge may be suitable as well.

We used two types of monodisperse carboxyl latex spheres with similar headgroup density but different particle size and also investigated hematite colloids synthesized in our laboratory from an alkaline iron chloride gel (Table 1). The absolute rate constant k_{fast} of

Table 1. Characterization of the Samples

particle type	size ^a (nm)	CV ^b	site density ^c (nm ⁻²)	exptl rate ^d (10 ⁻¹⁸ m ³ /s)	theor rate ^e (10 ⁻¹⁸ m ³ /s)
latex	309	0.028	0.57	2.4	7.7
latex	104	0.10	0.46	3.0	7.7
hematite ^f	122	0.24	8.0	3.5	9.2

^a Number averaged mean diameter obtained from transmission electron microscopy. ^b Corresponding coefficient of variation. ^c Density of chargeable headgroups obtained from conductometric titration of carboxyl latex and estimated from a crystallographic analysis for hematite. ^d Absolute fast aggregation rate constant measured by simultaneous static and dynamic light scattering under different angles; values are similar to previously reported ones.⁴ ^e Absolute fast rate constant as predicted by eq 2. It is not clear why these calculated values are substantially larger than the measured ones, but in contrast to the stability ratio in the slow aggregation regime, they depend strongly on the details of the dispersion, of hydrophobic and hydrodynamic interaction at all distances, which are not sufficiently well-known. A crude but common way of accounting for retardation in the van der Waals contribution would lower the predicted rate constants by only 10–20%. ^f Further characterization is given in ref 27, where this sample is denoted by Hm-2.

dimer formation in the fast aggregation regime was measured by simultaneous static and dynamic light scattering under different scattering angles on a home-built experimental setup described elsewhere.¹⁸ Colloid stability, commonly expressed by the ratio

$$W = k_{\text{fast}}/k \quad (1)$$

of the aggregation rate in the fast regime and the rate in the actual conditions under consideration, was then monitored by conventional dynamic light scattering.

The pH was adjusted with hydrochloric acid or potassium hydroxide, while the desired ionic strength was obtained by adding potassium chloride. For experimental convenience, we measured stability as a function of pH with the ionic strength held constant, rather than varying the ionic strength for a given pH (or charge). The latex batches were extensively dialyzed against deionized water (Nanopure quality) prior to experiment; this kind of investigation is extremely sensitive to impurities. Theoretical aggregation rate constants were calculated from the modified Fuchs expression²

$$k = 4\pi \left\{ \int_{2a}^{\infty} \frac{\exp[\beta V(r)]}{r^2 D(r)} dr \right\}^{-1} \quad (2)$$

where $D(r)$ is the relative diffusion coefficient for two spheres of radius a and center-to-center-distance r incorporating the effect of hydrodynamic interaction according to Honig,¹⁹ $\beta^{-1} = k_{\text{B}}T$ is the thermal energy, and $V(r)$ stands for the net interaction energy of a pair of colloid particles^{1,2}

$$V(r) = V_{\text{vdW}}(r) + V_{\text{dl}}(r) \quad (3)$$

composed of a (nonretarded) van der Waals attraction and a repulsive double layer contribution. The latter has been calculated from the nonlinear Poisson-Boltzmann equation and can be expressed in terms of Jacobi elliptic functions.^{20,21} Throughout this work, we used the Derjaguin approximation to generate the interaction energy

(18) Holthoff, H.; Egelhaaf, S. U.; Borkovec, M.; Schurtenberger, P.; Sticher, H. *Langmuir* **1996**, *12*, 5541. Holthoff, H.; et al. *J. Colloid Interface Sci.* **1997**, *192*, 463.

(19) Honig, E. P.; Roeberson, G. J.; Wiersema, P. H. *J. Colloid Interface Sci.* **1971**, *36*, 97.

(12) Frens, G.; Engel, D. J.; Overbeek, J. Th. G. *Trans. Faraday Soc.* **1967**, *63*, 418. Lyklema, J. *Pure Appl. Chem.* **1980**, *52*, 1221. Dukhin, S. S.; Lyklema, J. *Faraday Discuss. Chem. Soc.* **1990**, *90*, 261. Shulepov, S. Yu.; Dukhin, S. S.; Lyklema, J. *J. Colloid Interface Sci.* **1995**, *171*, 340. Shulepov, S. Yu. *J. Colloid Interface Sci.* **1997**, *189*, 199.

(13) Kékicheff, P.; Spalla, O. *Phys. Rev. Lett.* **1995**, *75*, 1851. Israelachvili, J.; Wennerström, H. *Nature* **1996**, *379*, 219. Larsen, A. E.; Grier, D. G. *Nature* **1997**, *385*, 230.

(14) Shulepov, S. Yu.; Frens, G. *J. Colloid Interface Sci.* **1995**, *170*, 44. Shulepov, S. Yu.; Frens, G. *J. Colloid Interface Sci.* **1996**, *182*, 388.

(15) Kjellander, R.; Marcelja, S. *Chem. Phys. Lett.* **1986**, *127*, 402. Kjellander, R.; Marcelja, S. *J. Phys. Chem.* **1986**, *90*, 1230. Kjellander, R.; Akesson, T.; Jönsson, B.; Marcelja, S. *J. Chem. Phys.* **1992**, *97*, 1424.

(16) Israelachvili, J. N.; Adams, G. E. *Nature* **1976**, *262*, 774. Pashley, R. M. *J. Colloid Interface Sci.* **1980**, *80*, 153. Pashley, R. M. *J. Colloid Interface Sci.* **1981**, *83*, 531. Pashley, R. M.; Israelachvili, J. N. *Colloids Surf.* **1981**, *2*, 169. Israelachvili, J. N.; Pashley, R. M. *Nature* **1983**, *306*, 249. Christenson, H. K.; Horn, R. G. *Chem. Phys. Lett.* **1983**, *98*, 45; Horn, R. G.; Clarke, D. R.; Clarkson, M. T. *J. Mater. Res.* **1988**, *3*, 413.

(17) Crocker, D.; Grier, D. G. *Phys. Rev. Lett.* **1994**, *73*, 352. Crocker, D.; Grier, D. G. *Phys. Rev. Lett.* **1996**, *77*, 1897. Sugimoto, T.; Takahashi, T.; Itoh, H.; Sato, S. I.; Muramatsu A. *Langmuir* **1997**, *13*, 5528.

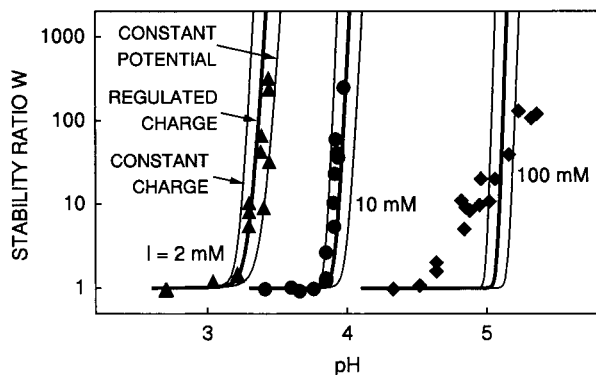


Figure 1. Comparison of dynamic light scattering data for carboxyl latex (309 nm) with DLVO theory at three different ionic strengths. Experimental stability ratios W were obtained from the measured increase in hydrodynamic radius r_h as $W = [(dr_h/dt)_{\text{fast}} / (dr_h/dt)_{t \rightarrow 0}]$, while theoretical values were calculated according to eqs 1–3. The chosen Hamaker constant of 1.8×10^{-20} J gives the best simultaneous fit to the measurements at ionic strengths of 2 and 10 mM.

for two equal spheres from the corresponding energy density of two half spaces. This approximation should be rather accurate for all situations considered, since the Debye length is still much smaller than the radius of our particles.²²

In Figure 1 measured stability ratios are compared with calculated curves for the limiting boundary conditions of constant charge and constant potential, as well as for full charge regulation in the framework of the simple diffuse layer model (DLM).^{20,23} This model assumes the diffuse part of the electric double layer to be in direct contact with the particle surface, where all of the charge from the dissociated headgroups is localized. With a dissociation pK of 4.9 for the carboxyl surface groups, the DLM describes reasonably well the charging behavior of our latex particles, as was inferred from results of potentiometric acid–base titrations and electrophoretic mobility measurements to be published in a forthcoming paper. While the charging behavior determines the slope of the predicted stability curves in the slow regime, a change in the Hamaker constant essentially results in a parallel shift of the curves (when plotted logarithmically).²⁴ By adjusting the Hamaker constant to the experimentally observed onset of stabilization, we found the value of 1.8×10^{-20} J, which compares nicely with the expected theoretical value of 1.3×10^{-20} J from Lifshitz theory for polystyrene across water.²⁵ The remaining difference may be due to hydrophobicity of the particle surfaces, also manifested by a contact angle of more than 90° for a water droplet on a dried layer of our latex.²⁶ Clearly, the quality of the theoretical prediction is rather insensitive to the details of charge regulation but closely linked to the

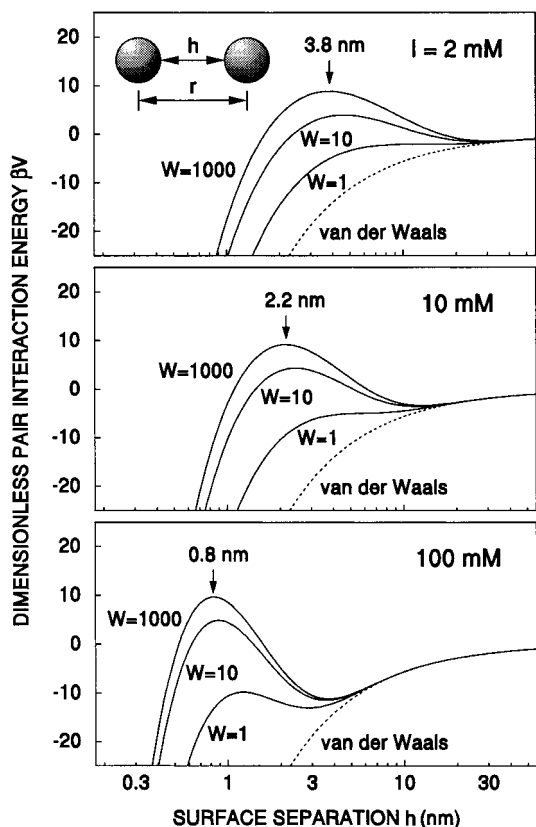


Figure 2. Pair interaction energy corresponding to points on the (charge regulated) curves of Figure 1. The shift of the energy barrier toward smaller separations with increasing ionic strength is accompanied by the build-up of a deep secondary minimum.

position of the barrier in the interaction energy (Figure 2). We find excellent agreement between DLVO theory and experiment at moderately low ionic strengths, where the maximum of the energy lies at a surface separation of more than 2 nm. For high ionic strength, where this distance is a few Å only, measured stability changes much more gradually with pH, although the predicted slope of the stability curve in the slow regime is even higher. This feature is equivalent to the well-known overestimation of stability dependence on ionic strength for a given charge.^{2,6,7}

To show that at moderately low ionic strength the correct particle size dependence can be recovered as well, we compare the results for our two latex samples in 10 mM solution (Figure 3). A reduced slope of the experimental stability curve is observed for the smaller particles, indeed. In a long history of experiments designed to check that aspect of the prediction,^{8,10} to our knowledge, this is the first confirmatory one. Also note that the same value of the Hamaker constant, fitted to the data of the larger particles only (Figure 1), was used for both samples.

Together, our findings suggest that the DLVO theory of colloid stability may be applicable to suspensions of weakly charged particles quite generally. This conjecture is also supported by data for a colloidal system of completely different composition and surface characteristics.²⁷ We applied the same modeling strategy to analyze

(20) Ninham, B. W.; Parsegian, V. A. *J. Theor. Biol.* **1971**, *31*, 405.

(21) For the presently considered system, we expect that the Poisson–Boltzmann approach is accurate and effects of ion–ion correlations are negligible.

(22) Carnie, S. L.; Chan, D. Y. C.; Stankovich, J. *J. Colloid Interface Sci.* **1994**, *165*, 116. Sader, J. E.; Carnie, S. L.; Chan, D. Y. C. *J. Colloid Interface Sci.* **1995**, *171*, 46.

(23) Healy, T. W.; White, L. R. *Adv. Colloid Interface Sci.* **1978**, *9*, 303. For a comparison of this model with other electrostatic models in the case of oxide surfaces, see also: Westall, J.; Hohl, H. *Adv. Colloid Interface Sci.* **1980**, *12*, 265.

(24) A parallel shift in the $\log W$ vs $\log I$ (or $\log W$ vs pH) plots would also be caused by accounting for hydrodynamic retardation or for the hydrophobic effect, as discussed in ref 7.

(25) Parsegian, V. A.; Weiss, G. H. *J. Colloid Interface Sci.* **1981**, *81*, 285. Prieve, D. C.; Russel, W. R. *J. Colloid Interface Sci.* **1988**, *125*, 1. For a review, see also: Bowen, W. R.; Jenner, F. *Adv. Colloid Interface Sci.* **1995**, *56*, 201.

(26) Hydrophobic interactions can be assumed to decay with distance in very much the same way as the dispersion forces and can thus be lumped into an effective Hamaker constant, see: Yoon, R.-H.; Flinn, D. H.; Rabinovich, Y. I. *J. Colloid Interface Sci.* **1997**, *185*, 363. From their findings, an even stronger modification of the theoretical Hamaker constant due to hydrophobicity could be expected.

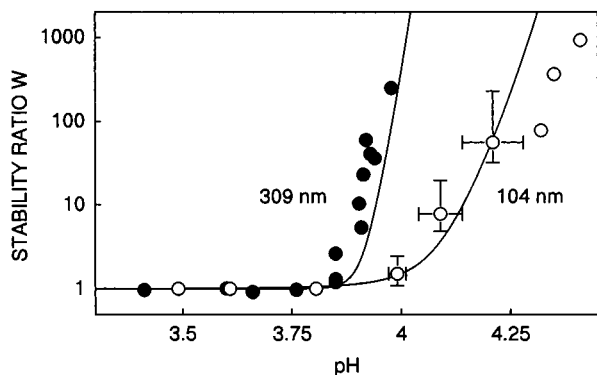


Figure 3. Influence of particle size. Measured stability and DLVO prediction for carboxyl latex spheres of different diameter. For better legibility, some measured values for very similar addition of acid have been averaged; error bars denote the corresponding standard deviations. Their asymmetry is due to the logarithmic representation.

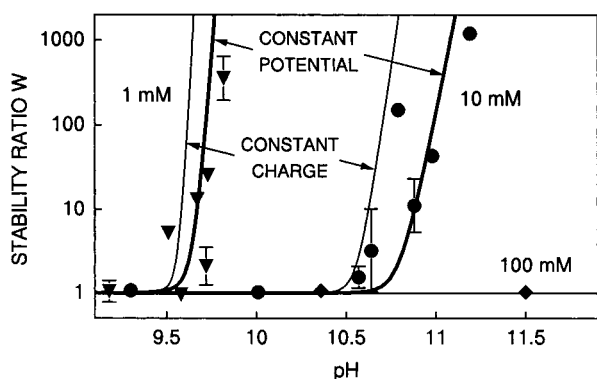


Figure 4. Measured and calculated stability ratios for colloidal hematite in alkaline sodium nitrate solution. Experimental points correspond to the rate constants reported in ref 27. A point of zero charge at pH 9.2, a value of 0.3 for the logarithm of the ion pair formation constants—both inferred from titration and electrophoresis data—and a Hamaker constant of 6×10^{-20} J previously used in a linear theory²⁷ were now adopted in the (nonlinear) treatment already discussed for the latex. For all points on the calculated constant potential curve, the distance corresponding to maximum interaction energy is larger than 2.6 nm.

stability data for negatively charged hematite (Figure 4). Here, the charging properties are more readily described by a 1-pK-Basic Stern model allowing for ion pair

formation on the surface.²⁸ Because of the more involved coupling between surface and bulk properties of this system, we had to restrict our solution of the nonlinear Poisson–Boltzmann equation to the limiting cases of constant charge and constant potential. On theoretical grounds, the true, charge-regulated solution for these particles is expected to lie rather close to the constant potential limit.²⁹ In fact, either of these two limits already gives a surprisingly good description of the observed aggregation behavior.³⁰

The mentioned results clearly indicate that for colloid particles of low surface charge density (roughly <3 mC/m²) and moderately low ionic strength in the slow aggregation regime (typically 0.1–10 mM) the classical DLVO theory of colloid stability works quantitatively.³¹ Under these conditions, the pair interaction energy has its maximum at distances of more than 2 nm, which is precisely the regime where DLVO theory has been confirmed by direct force measurements. We believe that the present findings might eventually promote a better understanding of typical, highly charged colloids, too; they certainly shed new light on one of the oldest and most prominent problems of colloid science.

Acknowledgment. We thank H. Holthoff, M. Schudel, and H. Sticher for various kinds of support. Helpful discussions with J. Israelachvili are gratefully acknowledged. This work was financed by the Swiss National Science Foundation.

LA971237K

(27) Schudel, M.; Behrens, S. H.; Holthoff, H.; Kretzschmar, R.; Borkovec, M. *J. Colloid Interface Sci.*, in press.

(28) Hiemstra, T.; van Riemsdijk, W. H. *J. Colloid Interface Sci.* **1996**, *179*, 488.

(29) It is the large slope of the charge density vs pH (surface potential) curves for these particles²⁷ that suggests a regulation behavior close to the constant potential limit. A quantitative criterion within a linearized model is derived in: Carnie, S. L.; Chan, D. Y. C. *J. Colloid Interface Sci.* **1993**, *161*, 260. Based on: Chan, D. Y. C.; Mitchell, D. J. *J. Colloid Interface Sci.* **1983**, *95*, 193.

(30) It must be mentioned that the same sort of description fails to describe correctly the low pH regime where the hematite is positively charged. However, we doubt that for this situation the requirements of cleanliness and surface homogeneity are fulfilled to the same degree as for the system of negatively charged hematite (Figure 4), because of the different role of negatively charged residual impurities. Experimental data for the whole pH range and the corresponding discussion are given in ref 27.

(31) This conclusion is also strongly supported by a recent study on sulfate latex: Behrens, S. H.; Semmler, M.; Borkovec, M. *Prog. Colloid Polym. Sci.*, in press.