

Deposition of Latex Particles: Theoretical and Experimental Aspects

P. Somasundaran, Sudhir Shrotri and K.P. Ananthapadmanabhan¹

Langmuir Center for Colloids and Interfaces, Columbia University, New York, NY 10027

145 River Road, Unilever Research US Inc., Edge Water, NJ, 07020

USA

ABSTRACT

Deposition of colloidal particles on surfaces is important in the processing of various products as minerals, cosmetics, detergents, and semiconductors. Several factors govern deposition making the phenomena rather complex. The main objective of this work is to elucidate the roles of the nature of the depositing particles and environmental conditions on deposition and to identify critical factors that govern deposition.

In the current study, deposition of anionic, cationic and zwitterionic latex particles on glass surface was done as a function of deposition time, pH, and particle concentration. The charge groups on latex particles are sulfate, carboxylic and amidine groups which are attached to the surface by hydrocarbon chains (referred to as "hairy groups" later). The data was subjected to theoretical treatment by considering forces involved in the deposition of different latex particles.

While amidine latex particles (IEP around pH 11) showed good deposition, sulfate latex particles did not show appreciable deposition. Since the glass surface is negatively charged in the pH range (3-12) of the deposition tests, the deposition of the oppositely charged particles was as expected and conforms to the theoretical calculations. In contrast to this, deposition in the presence of energy barrier was difficult. However the exception were zwitterionic latex particles, which showed considerable deposition on glass even when they were negatively charged. The deposition of zwitterionic latex particles with a negative zeta potential similar to that of sulfate latex was contrary to the theoretical predictions. We propose that the hairy groups on zwitterionic particles rearrange as they approach the surface to enable their attachment.

INTRODUCTION

Deposition plays a vital role in many technological and natural processes, such as, involving drugs,^{1,2} cosmetics, detergents,³ paper making,⁴ bacterial adhesion,⁵ carrier flotation, colloidal contaminants transport,⁶ filtration,⁷ and semiconductors.⁸ The study of particle deposition is also of intrinsic interest to the field of colloid science from a fundamental point of view.

There have been numerous studies encompassing different aspects of deposition, employing a wide array of colloidal particles and substrates. Researchers have studied deposition of latex particles,^{9,10,11}

Sulphur - grown cells and liquid ferrous iron grown cells exhibit different IEP values indicating differences in their surface chemistry. A proteinaceous cell surface appendage was formed on mineral grown cells, facilitating their adhesion. Adhesion of the bacterial cells on sulphide mineral surfaces promote bioleaching through the direct attack mechanism. Bacterial interaction with sphalerite and galena influenced their floatability. Through bacterial pretreatment, selective separation of sphalerite and galena could be achieved.

REFERENCES

1. H.L. Ehrlich : Geomicrobiology, Marcel Dekker, Newyork, 1990.
2. O.H. Tuovinen and I. J. Fry : Current opinion in Biotechnology, 1993, vol. 4; pp. 344-355.
3. E.R. Donati, S. Porro and P.H. Tedesco : Biotechnology Letters, 1988, vol. 10; pp. 889 - 894.
4. C. Polganni, G. Cruutchet, E. Donati and P.H. Tedesco : Biotechnology Letters, 1990, vol. 12; pp. 515-518.
5. K.S.N. Murthy and K. A. Natarajan: Miner. Metall. Process. 1992, vol. 9; pp. 20 - 24.
6. Srihari, R. Kumar, K.S. Gandhi and K.A. Natarajan : Appl. Microbiol. Biotechnol., 1991, vol. 36; pp. 278 - 282.
7. P. Devasia, K.A. Natarajan, D.N. Sathyanarayana and G. Ramananda Rao : Appl. Environ. Microbiol., 1993, vol. 59; pp. 4051-4055.
8. A.G. Kempton, N. Moneib, R.G.L. McCready and C.E. Capes: Hydrometallurgy, 1980, vol. 5; pp. 17 - 125.
9. R.G.L. McCready, B.P. LeGallais : Hydrometallurgy, 1984, vol. 12; pp. 281 - 288.
10. M.K. Yelloji Rao, K.A. Natarajan and P. Somasundaran : Miner. Metall. Process. 1992, vol. 9; pp. 95 - 100.
11. H.C. Van der mel, A.J. Leonard, A.H. Weerkamp, P.G. Roux and H.J. Busscher : J. Bacteriol, 1988, vol. 170; pp. 2462 - 2466.
12. M.P. Silverman and D.G. Lundgren : J. Bacteriol, 1959, vol. 77; pp. 642 - 647.
13. M. Rosenberg, D. Gutnik and E. Rosenberg : FEMS Microbiol. Lett., 1980, vol. 9; pp. 29 - 33.
14. A.J. Vogel : Text Book of Quantitative Inorganic Analysis, 2nd Edition, ELBS, London, 1951.
15. R.M. Bagdigian and A.S. Myerson : Biotech. Bioengg. 1986, vol. 28; pp. 467 - 479.

mineral particles,^{12,13} carbon black,¹² bacteria and other biological colloids on various substrates such as glass,¹² polymers^{12,14} and minerals.^{11,14} The initial deposition process is generally described by set of transport equations, also known as Fokker Plank²⁵ equations which take into account particle - substrate surface interactions. During this stage a constant rate of particle deposition rate is generally observed.^{15,16} In contrast later stages of deposition are thought to be governed by desorption, surface heterogeneity,¹⁷ blocking of deposition sites and excluded area effects.¹⁸ Colloidal forces dominating deposition process¹⁹⁻²² and kinetic process^{23,24} involved have been widely reported and reviewed.²⁵

However there are some important issues such as, the importance of the discrete charges, and their rearrangement which have not been yet resolved. The present study was undertaken to elucidate these factors. The objective was to understand the influence of surface chemical features of particles and substrates; in this context the model system was chosen specifically to incorporate the effects such as discrete as well as rearrangeable charges. Deposition of three different type of latex particles on glass substrate was conducted and the results are discussed in terms of relevant colloidal forces present in the system.

MATERIALS AND METHODS

Materials

The latex particles were obtained from Interfacial Dynamics Corporation spheres (IDC) were used as received with out any further cleaning. Three different types of polymer lattices particles were employed, namely amidine, sulfate and zwitterionic lattices. These lattices are stabilized by the charge groups present on the surface (see Table I).

Table I: Latex Particle Specifications

<i>Latex Type</i>	<i>Diameter(μm)</i>	<i>Charge Group</i>	<i>Charge Behavior</i>
Amidine Latex	1.84	Amidine	Cationic
Sulfate latex	2.04	Sulfate	Anionic
Zwitterionic Latex	0.86	Amidine and Carboxyl	Mixed

A schematic of the latex is shown in Fig. 1. Microscopic, frosted glass slides purchased from Fisher Scientific company were used as substrates for the deposition of the particles.

Methods

Sample Preparation

Latex suspension preparation: In order to compare the extent of deposition, latex suspension of desired initial particle concentration was prepared by diluting known weights of latex suspension drops with triply distilled water with/without salt. HCl or NaOH, was added as required to adjust the pH and the weight was adjusted to 3.0 g. The suspension was then mixed for 4 minutes using a magnetic stirrer and desired quantity transferred onto the substrate using a micro pipette for the deposition test.

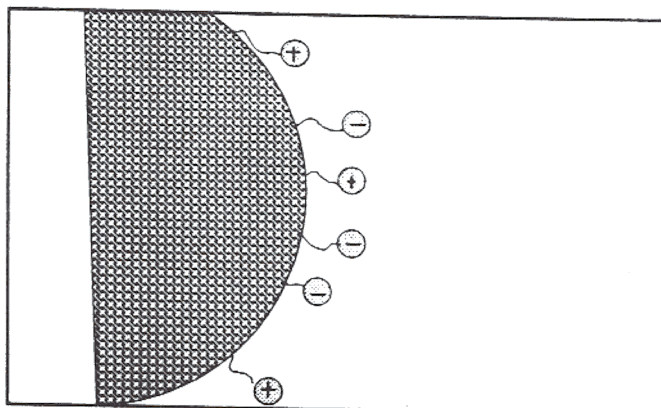


Figure A schematic of latex particles with charge groups present on the surface (figure not to scale).

Substrate preparation: As received slides were immersed in 1:1 Nitric acid solution for two minutes and washed with triple distilled water and air dried in an inverted slanted position to reduce deposition of dust particles.

Deposition

Deposition studies were carried out as a function of pH. A simple and reproducible deposition technique based on free settling adopted for the present study involved placing of , 50 μl of the latex suspension with the help of a micro pipette, on a precleaned glass slide. The slide was covered with a watch glass to prevent any dust contamination and left for free settling for desired interval. The slide was then washed with triple distilled water, air dried, and observed under a microscope.

Zeta Potential Measurements

Electrokinetic characterization of glass slides was done by measuring streaming potential using a Brookhaven - AP Paar Electrokinetic analyzer. The samples to be measured were taken in the rectangular cell holder. Latex particles were characterized using Pen Kem Lazer Zee meter, model 500, that measures electrophoretic mobility. All experiments were performed at room temperature and ionic strength was maintained at 10^{-4} M using NaCl solution.

RESULTS AND DISCUSSIONS

The zeta potential behavior of the slide was measured using the streaming potential technique and is illustrated in Fig. 2 as a function of pH. The substrate is negatively charged throughout the pH range of 3–12.

The zeta potential of latex particles shown in Figs. 3 and 4 as a function of pH show the sulfate latex to be negatively charged under all pH conditions studied, and the zwitterionic latex particles and the amidine latex to possess an isoelectric points around pH 4 and 11 respectively.

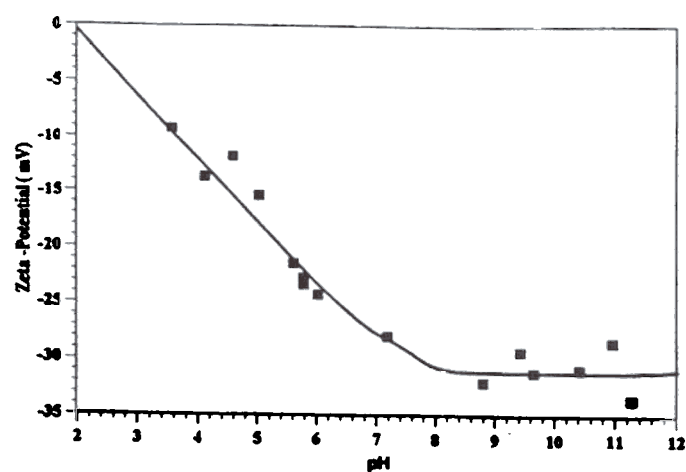


Figure 2: Zeta potential, converted from streaming potential values, as a function of suspension pH for the glass slides, ionic strength 10^{-4} M

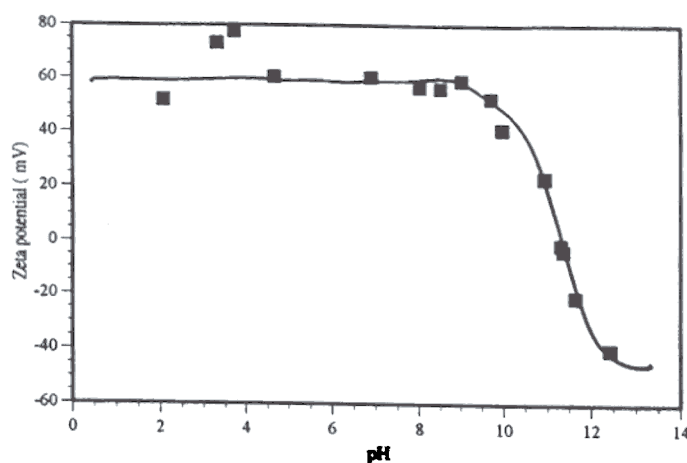


Figure 3: Zeta potential of amidine latex particles as a function of pH, ionic strength 10^{-4} M.

Deposition of Latex Suspension

Deposition study was done as a function of the pH and the micrographs for representative cases, are shown in Figs. 5 and 6. Glass surface is negatively charged under all test conditions and, the extent of deposition in the case of amidine latex, is governed by its zeta-potential. Around the IEP as expected the amidine latex particles had a tendency to aggregate and deposit on the slide as clumps. Above isoelectric point, the deposition is found to decrease drastically.

Deposition on glass surface as a function of pH was also done with sulfate latex and zwitterionic latex. In the pH range where the zwitterionic is positively charged, as expected good deposition was found. Interestingly, above IEP under conditions when both the zwitterionic and sulfate latex particles had same

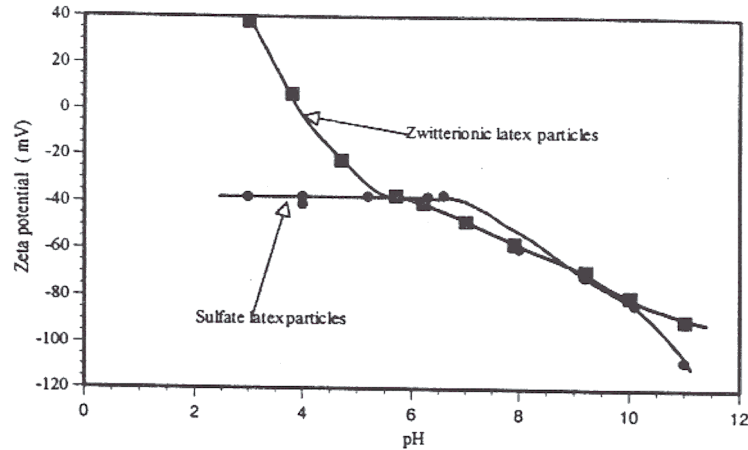


Figure 4: Zeta potential measurement of sulfate (●) and zwitterionic (■) latex as a function of suspension pH, ionic strength $10^{-4}M$.

zeta potential the former deposited well while the latter did not (see Fig. 6). It is to be noted that deposition of zwitterionic latex particle took place even though it is similarly charged to the glass substrate.

THEORY

The deposition was done here under free settling conditions. Assuming that there is no convective transfer and quiescent conditions prevail throughout the deposition process. Forces associated with the attachment of latex particles on to glass arise from the overlap of the electrical double layers of the particle and substrate (F_{el}), van der Waals forces (F_{vdw}) and the gravitational force (F_g): Hence, the total interaction force can be expressed as a sum of:

$$F_T = F_{el} + F_{vdw} + F_g \quad (1)$$

The hydrodynamic force between the particle and substrate is negligible under these conditions. Expressions developed to estimate the magnitude of these interactions are discussed below.

Electrical Double Layer Interactions

Various expressions have been developed for electrical double layer overlaps in the past and differ essentially in the choice of boundary conditions, namely, constant charge or constant potential of the interacting surfaces during their mutual approach.²⁶⁻²⁹ The constant potential condition is suitable for cases where electrochemical equilibrium of the potential determining ions and adsorbed species is maintained during the interaction. Under constant charge conditions, the adsorbed or chemically bound species that are responsible for the charge development at the interface are not regulated rapidly enough during the approach of surfaces. These conditions are however the two extremes and in real systems,

both charge and potential can undergo regulation. For the purpose of this study, nonetheless, constant charge expressions are utilized, as the charges are chemically bound to the surface.

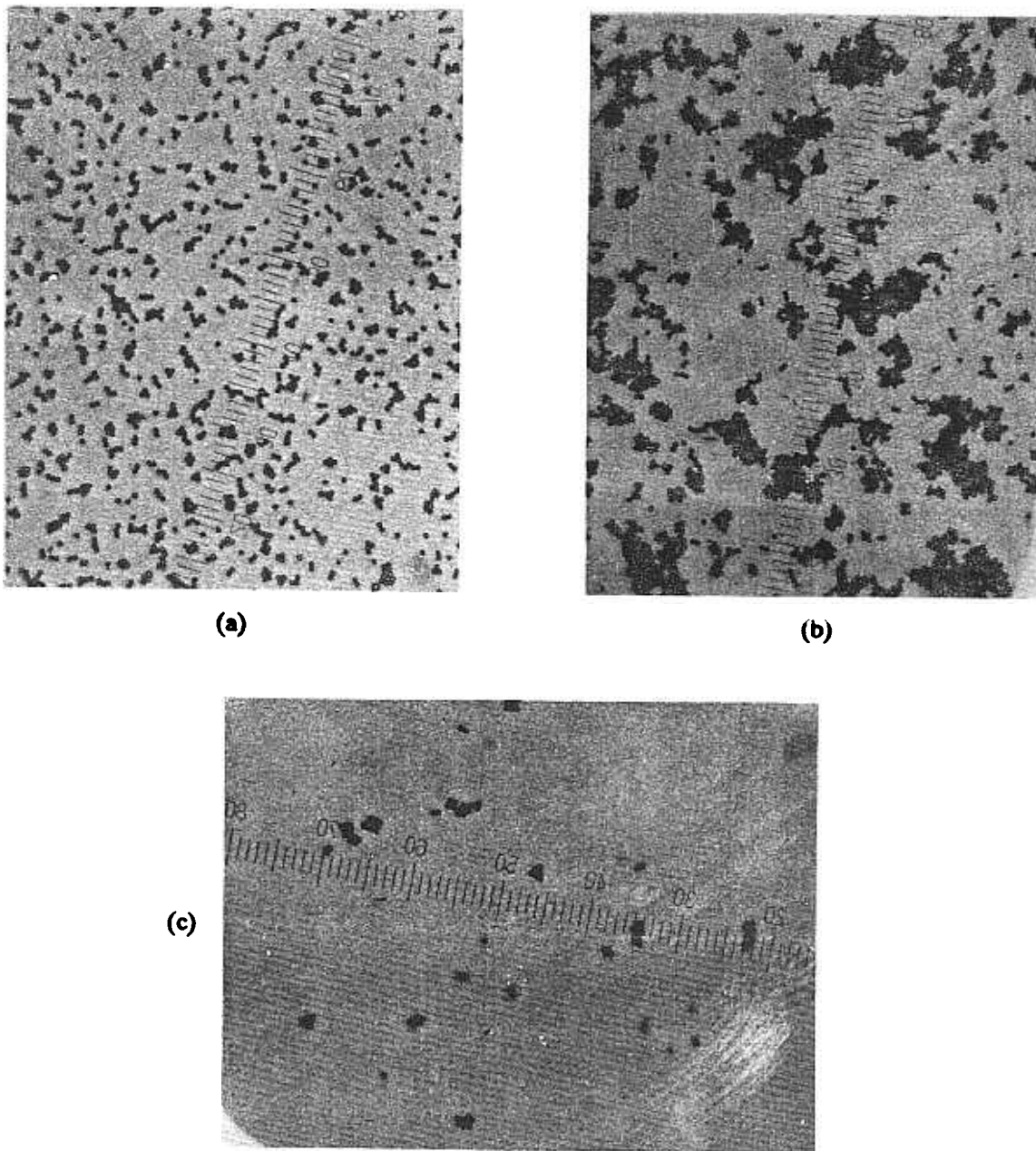


Figure 5: Representative deposition micrographs of amidine latex particles on glass when they are (a) positively charged (b) near isoelectric point (c) negatively charged.

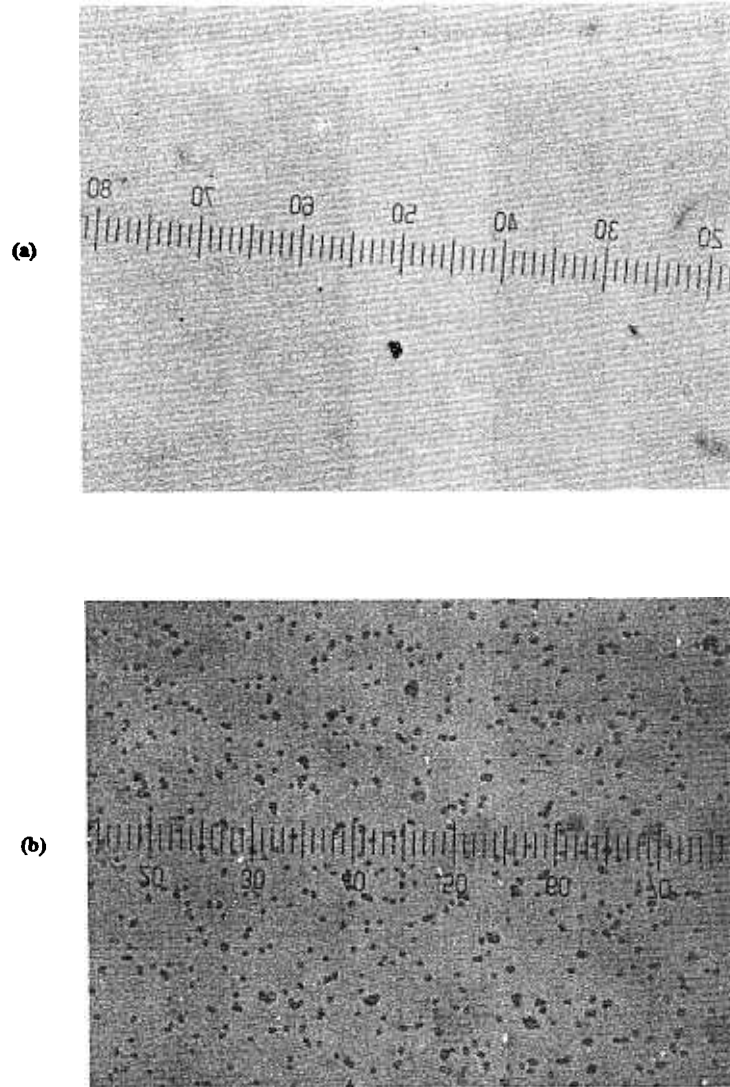


Figure 6: Representative deposition micrographs of (a) sulfate latex particles and (b) zwitterionic latex particles on glass when both particles were similarly charged to the glass.

For the case when the radius of particle, r_p , is much smaller than the radius of curvature of the substrate, r_s , F_{el} , based on the model by Hogg et al.²⁹ can be expressed as:³⁰

$$F_d = 4\pi \varepsilon r_p \kappa \zeta_p \zeta_s \frac{\exp(-\kappa r_p H)}{\{1 + \exp(-\kappa r_p H)\}} \quad (2)$$

where ζ_p is the electrokinetic potential of particle, ζ_s is the electrokinetic potential of substrate, κ is the debye parameter, ϵ is the permittivity ($= 78.54 \times 8.8542 \times 10^{-12}$ at 25°C) F/m and H is the approach distance.

van der Waal's Interactions

For the case of a flat plate (1) and a sphere with radius r_p (2) that interact across a medium (3) the following equation is a satisfactory approximation:³⁰

$$F_{vdw} = - \frac{A_{132}}{6 r_p H^2} \quad (3)$$

where A_{132} is the effective Hamaker constant for two materials (1 and 2) in a medium (3) and can be expressed as:³¹

$$A_{132} = (\sqrt{A_{11}} - \sqrt{A_{33}}) (\sqrt{A_{22}} - \sqrt{A_{33}}) \quad (4)$$

where A_{11} , A_{22} , A_{33} are the Hamaker constants for the materials (1 and 2) and the medium (3) respectively.

Gravitational Force

The gravity force acting on the particle, neglecting the resistive force by the medium is:³²

$$F_g = -\frac{4}{3} \pi r_p^3 (\rho_p - \rho_1) g \quad (5)$$

Where ρ_p is the particle density, ρ_1 is the density of medium and g is the gravitational force

THEORETICAL CALCULATIONS

The calculated forces for the amidine, zwitterionic and sulfate latex are shown Figs. 7, 8 and 9. Typical values used for the calculation are also shown in Table II.

Table II: Typical Parameters used for the Calculation of Interaction Forces for the Latex Particles

Type of Latex	Hamaker constant, A_{132} (in J)	Zeta - potential Particles (in mV)	Zeta potential Substrate (in mV)	Debye length in nm
Amidine	4.5×10^{-21}	+40.0	-20.0	
Sulfate	4.5×10^{-21}	-40.0	-20.0	30
Zwitterionic	4.5×10^{-21}	-40.0	-20.0	30

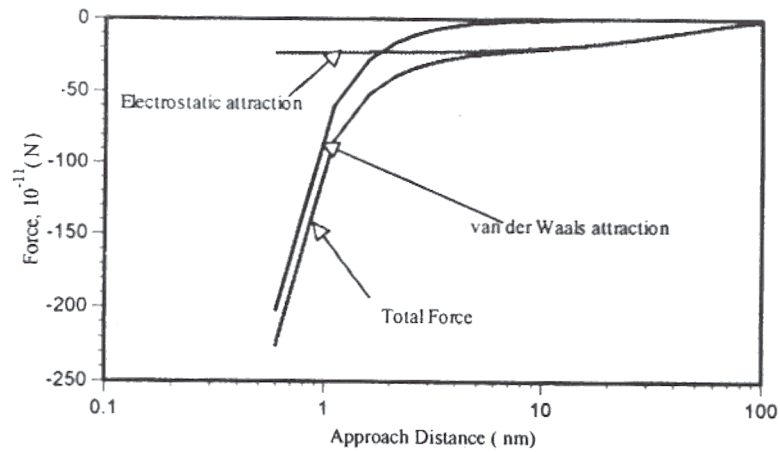


Figure 7: Interaction force between amidine latex particles and glass surface as a function of approach distance.

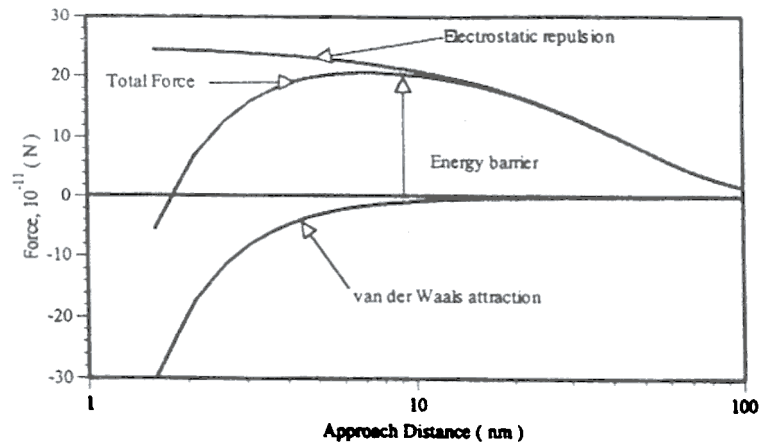


Figure 8: Interaction force between sulfate latex particles and glass surface as a function of approach distance.

As expected for the Amidine latex deposition, an attractive force prevails at all distances of approaches when the latex is positively charged. Gravitational force, though negligible compared to the double layer and van der Waals forces, also assists the deposition. The sulfate latex particles and the substrate are similarly charged and thus an energy barrier is encountered due to electrostatic repulsion when they approach the substrate. The energy barrier is also substantially more than kT , preventing any thermal or diffusional escape of the particles. Under the present deposition scheme the only external force is the gravitational one and thus is negligible compared to the barrier and hence deposition is not feasible.

For zwitterionic latex, the conditions are very much the same as that for the sulfate latex and once again an energy barrier is encountered. This barrier is also substantially more than kT and again the gravitational pull is negligible compared to the barrier.

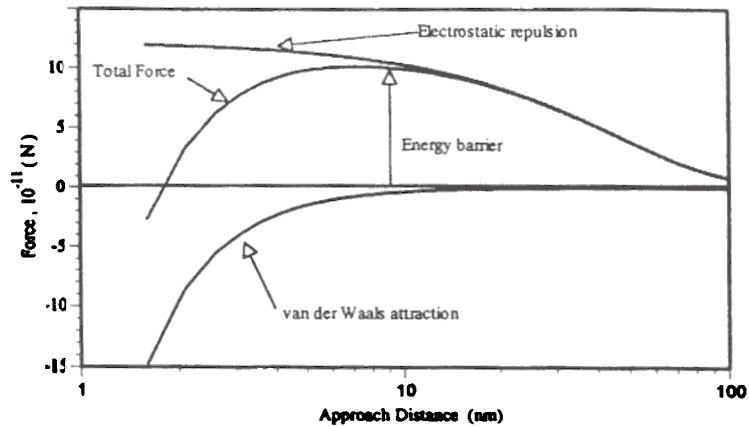


Figure 9: Interaction force between zwitterionic latex particles and glass surface as a function of approach distance.

Based on these calculations, it is expected that zwitterionic particles should behave similar to the sulfate latex and deposition should not be feasible under the present deposition scheme. Quite contrary to this, a good amount of deposition was observed in this study.

UNCONVENTIONAL DEPOSITION OF ZWITTERIONIC LATEX PARTICLES

As seen from both the experimental and the theoretical calculations, zwitterionic particles deposit in an unexpected fashion. Deposition of colloids on similarly charged substrates is not new particularly in the biological field. There are several examples where negatively charged bacteria would deposit on a negatively charged surface. Similar behavior by the mixed charge latex is interesting since it can indicate possible mechanisms for such natural processes. We propose that the mixed charge groups present on the latex surface rearrange in such a manner such that the positive charge sites are extended and the negative ones retracted. Thus even though the over all average zeta potential is negative, the hairy charges are proposed to rearrange when the two surfaces can feel each other; the schematic of this is shown in Fig. 10.

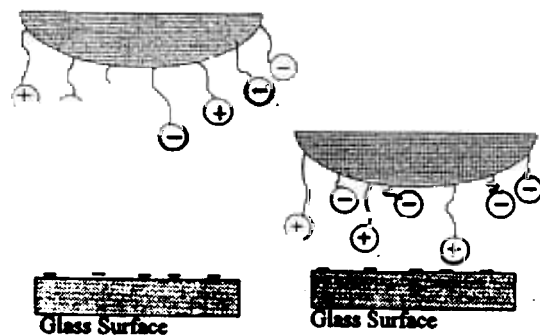


Figure 10: Schematic of proposed rearrangement of mixed charges on a zwitterionic latex particle as it approaches a similarly charged surface.

SUMMARY

Conventional deposition was found for amidine and sulfate latex particles. The electrostatic forces play a dominant role in the deposition in these systems. The presence of an attractive electrostatic force leads to a favorable deposition of amidine latex particles whereas that of a repulsive electrostatic force, deposition was difficult for sulfate latex.

Zwitterionic particles behaved in an unconventional fashion and in spite of the presence of an apparent electrostatic repulsion, good deposition was observed. Modification and rearrangement of the mixed hairy charge groups are proposed to bring about this effect.

ACKNOWLEDGMENTS

Financial support from Unilever Research US Inc. and National Science Foundation for this study is acknowledged.

REFERENCES

1. W.J. Gallin and D. L. Paul(eds): Cell-cell interactions, A practical approach, Oxford university press, New York, 1992.
2. S.D. Bruck : J. Biomed. Mater. Res, 1972, 6, 173.
3. A. Kithara and A. Watanabe (eds): Electrical phenomena at interfaces; Fundamentals, measurements and applications, Marcel Dekker, Inc., New York, 1984
4. S.Varenes and T.G.M. van de Ven: Colloids Surf., 1988,33, 63.
5. W. Norde and J. Lyklema: Colloids Surf., 1989, 38,1.
6. L.M. McDowell-Boyer, J.R. Hunt and N. Sitar: N. Water Resour. Res., 1986, 22, 1901.
7. C. Tien: Granular Filtration of Aerosols and Hydrosols, Butterworths: M.A. Stoneham, 1989.
8. K.L. Mittal ed.: Particles on surfaces I: Detection adhesion and removal, Plenum press, New -York, 1988.
9. M. Hull, and J.A Kitchner: Trans. Faraday society. 1969, 65, 3093.
10. M. Elimelech and C.R. O'Melia: Langmuir, 1990, 6, 1153.
11. V. Graneir and A Sarte: Langmuir, 1995, 11, 2179
12. J.K. Marshall and J.A. kitchner: J. Colloid Interface Sci, 1966, 22, 342.
13. G. Onoda and P. Somasundaran: J. Colloid Interface Sci, 1987,1,169.
14. J. Sjollema and H.J. Busscher: Colloids and Surf., 1990,47,337.
15. J.K. Marshall, J.A. Kitchner: J. Colloid Interface Sci. 1966,22, 342.
16. T. Dabros and T.G.M. Van de Ven: J. Colloid Interface Sci. 1982, 89,232.
17. J. Sjollema and H.J. Busscher: Colloids and Surfaces, 1990,47, 337.
18. P. R. Johnson and M. Elimelech: Langmuir, 1995, 11, 801.
19. S.S Dukhin: Adv. Colloid and Interf. Sci., 1993,44,1.
20. L.A. Speilman and S.K. Friedlander: J. Colloid Interface Sci, 1974,46,22.
21. L.A. Speilman and J.A. Fitzpatrick: J. Colloid Interface Sci, 1973,42,607.
22. L.A. Speilman and P.M. Cukor: J. Colloid Interface Sci,1973,43,51.
23. L. Song, P.R. Johnson and M. Eilmelech: Env. Sci and Techn., 1994, 28, 1164.
24. P. R. Johnson and M. Elimelech: Langmuir, 1995, 11.
25. Z. Adamczyk, T. Dabros, J. Czarniecki and T.G.M. Van de Ven: Adv. Colloid Interface Sci., 1983, 19, 183.
26. B.V. Derajquin: Disc. Faraday Soc., 1954,18,85 .
27. G.R. Weise and T.W. Healy: Trans. Faraday Soc., 1970,66,490.
28. P. Somasundaran, P. Chandar and K. Chari: Colloids and Surfaces, 1983, 8, 121.

29. R. Hogg, T.W. Healy and D.W. Fuerstenau: *J. Chem. Soc., Faraday Trans.* 1966, 1, 62, 1638.
30. K. Okada, Y Akagi, M Kogure and N. Yoshioka: *The Canadian Journal of Chemical Engineering*, 1990, 69, 614.
31. J. N. Israelachvili: *Intermolecular and Surface Forces*, Academic press. London, 1985.
32. K. Okada, Y Akagi, M Kogure and N. Yoshioka: *The Canadian Journal of Chemical Engineering*, 1990, 68, 393.