Macromol. Symp. ***151,*** *427–434 (2000)*

Colloidal Stabilization and Destabilization of a Carboxyl Latex by Adsorption of Triton X-100.

M.S. Romero-Cano[1], A. Martín-Rodríguez[2] and F.J. de las Nieves[1*]

[1]Complex Fluids Physics Group, Department of Applied Physics, Faculty of Experimental Sciences, University of Almería, 04120 Almería (Spain);

[2]Biocolloid and Fluids Physics Group, Faculty of Sciences, University of Granada, 18071 Granada, Spain.

SUMMARY: The stability behaviour of a carboxyl latex after adsorption of Triton X-100 has been studied with respect to the surfactant coverage, being the pH an important variable due to the weak character of the surface groups. Three different types of stabilization can be distinguished as a consequence of the relation between the van der Waals attraction energy (V_A) and the steric interaction energy (V_S): electrostatic ($V_S = 0$), electrosteric ($V_S < |V_A|$) and steric ($V_S > |V_A|$) stabilizations. Most of the cases may be explained using the extended DLVO theory. However, at acid pH and low coverage a destabilization phenomena, non-predicted by colloidal stability theories, was found. This encountered fact may be explained by the consideration of a specific interaction between the carboxyl groups and the ethylene oxide chains through hydrogen bonding.

Introduction

In the present time, there are few remarkable methods by which colloid stability can be imparted in a controlled fashion. Electrostatic and steric stabilization are two general and currently employed tools imparting stability to a colloidal system.

According to the DLVO theory[1-2)], the stability of electrostatic stabilized colloidal dispersion is determined by two particle interaction energies, repulsive (V_R) and attractive (V_A). The net interaction energy (V) is given by the algebraic sum of the two (V_R+V_A). V_R is due to the overlap between the diffuse double layers of the particles and is usually considered to decay exponentially with the distance of separation between them. V_A is due to the London van der Waals (dispersion) energy, decaying in accordance to a power law. While V_A is not sensitive

CCC 1022-1360/00/$ 17.50+.50/0

to the electrolyte concentration, V_R is, and thus, the stability of colloidal dispersions can be controlled by changing the ionic strength of the solution.

Additionally, non-ionic surfactants adsorbed onto colloidal particles can act as steric stabilizers$^{3)}$. In this case the colloidal stability is imparted by a combination of electrostatic and steric effects. Electrolyte insensitivity is one clear advantage of the steric stabilization as indicated by steric interaction potentials proposed by Vincent et al.$^{4-5)}$. The colloidal stability theory including steric repulsion is usually refereed as extended DLVO theory, which gives the net interaction energy by the sum of all three potential energies: $V = V_R+V_A+V_S$.

As a consequence, we can introduce a classification for colloidal dispersions, based in their electrolyte sensitivity which is directly related with the magnitude of the steric interaction energy (V_S).

i. Sensitive to electrolyte: electrostatic ($V_S=0$) and electrosteric ($V_S<|V_A|$) stabilized.
ii. Insensitive to electrolyte: steric ($V_S>|V_A|$) stabilized.

In this work the attention is focused on the influence of the surfactant coverage over the colloidal stability of the latex-surfactant complexes. In particular we have studied the influence of the surfactant desorption on the colloidal stability of the latex-surfactant complexes and we have found that, at acid pH, the complex with lower coverage displays a colloidal stability lower than the bare latex. The pH of the medium is also an interesting variable that can modify the colloidal stability of the complexes due to the change in the surface charge density of the carboxyl latex. Controlling both variables we are able to observe the above mentioned three kind of colloidal stabilizations.

Experimental

A. Chemicals

All Chemicals were of analytical grade and were used without further purification. The water in all experiments was ultrapure with specific electrical conductivity lower than 1 μS/cm (ATAPA S.A. Spain).

B. Latex characterization

The latex used in this work was synthesized in our laboratories. Styrene (Merk) was previously distilled under low pressure (10 mm Hg and 40 ºC). Negatively-charged polystyrene latex (PS-C) was prepared using the emulsifier-free method, with 4,4'-Azobis (4 cianopentanoic acid) (ACPA) as initiator, in a discontinuous reaction, according to recipes of other authors[6-7)]. The maximum surface charge density and the electron microscopy diameter were $-(21\pm3)$ $\mu C/cm^2$ and (303 ± 9) nm, respectively, with a polydispersity index of 1.0029.

C. Surfactant characterization

Triton X-100 (p-(1,1,3,3-tetramethylbutyl) phenyl polyethyleneglycol), a gas chromatography grade material from Merk was used without further purification. Surfactant concentrations during adsorption and desorption experiments were determined by UV spectrophotometry at 275 nm[8)] using a Spectronic Genesys 5 spectrophotometer (Milton Roy, USA). The extinction coefficient obtained was equal to $1.33\cdot10^3$ $M^{-1}cm^{-1}$. The critical micelle concentrations (CMC) were determined by measuring the absorbance at different concentrations due to the change in slope of the absorbance versus concentration curve that appears during the micellization process. The value of this characteristic magnitude was of $(5.1\pm0.1)\cdot10^{-4}$ M. In order to gain more information about the purity of the surfactant sample, a mass spectroscopy spectrum was done (University of Granada). The result showed that the surfactant is of a good purity with a polydispersity index ($\langle M_w\rangle/\langle M_n\rangle$) of 1.031.

D. Preparation of complexes

Latex-surfactant complexes were obtained by surfactant adsorption[9-10)] in batteries, for 24 h at (25.0 ± 0.1) ºC with various added contents of surfactant onto 0.25 m^2 of latex surface. The surfactant-latex mixtures were gently shaken during the adsorption experiment.

E. Colloidal stability

The stability of the dispersions was evaluated with a Spectronic Genesys 5 spectrophotometer (Milton Roy, USA) by measuring the absorbance (λ_0 = 900 nm) as a function of time for different electrolyte concentrations. In a typical coagulation experiment, 2.4 ml of a buffered latex solution was put into the spectrophotometer cell and the optical absorbance was measured. Then, 0.6 ml of a sodium chloride solution at a given concentration was quickly added and mixed automatically11). The final particle concentration in the cell was $1.2 \cdot 10^{16}$ p/m^3. The optical absorbance was measured immediately and recorded continuously via computer for a period of 30 s. The initial slope of these curves, $(dAb/dt)_0$, is directly proportional to the initial coagulation rate (see Fig. 1).

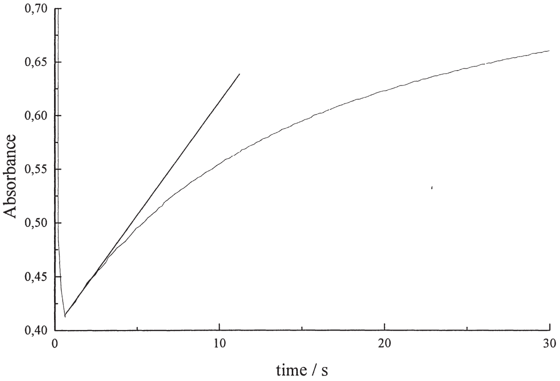

Fig. 1: Optical absorbance variation versus time in an aggregation reaction.

Results and discussion

The colloidal stability experiments of latex-surfactant complexes were done at two extreme pHs and different surfactant coverages. The control of these variables enables the introduction of the colloidal system into region characterized by a different combination of electrostatic and steric repulsive interaction energies.

Figures 2 and 3 show the absorbance change $(dAb/dt)_0$ versus the NaCl concentration for different PS-C-TX100 complexes, with different amounts of surfactant adsorbed, at pHs 5 and 10. The weak character of the carboxyl groups yields an electrostatic repulsion that will be maximum at pH 10, where the carboxyl groups are ionized, and much lower at pH 5, where most of the weak acid groups are protoned.

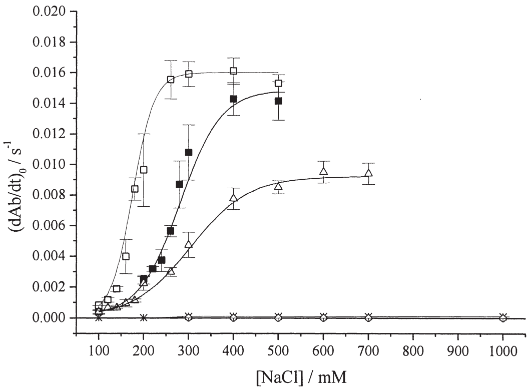

Fig. 2: Aggregation kinetics of PS-C-TX100 system at pH 5 with different coverages: ■ = bare, □ = 1.0 μmol/m^2, △ = 1.5 μmol/m^2, ∗ = 2.0 μmol/m^2, ◇ = 2.5-3.0 μmol/m^2.

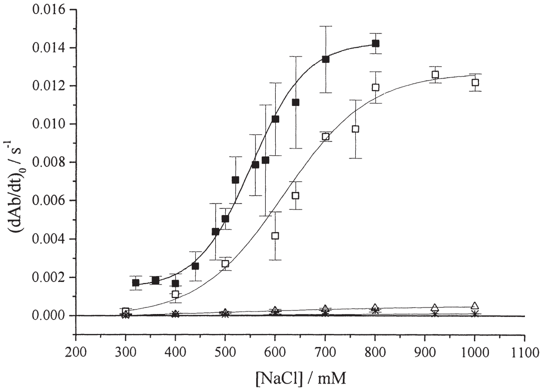

Fig. 3: Aggregation kinetics of PS-C-TX100 system at pH 10 with different coverages: ■ = bare, □ = 1.0 μmol/m^2, △ = 1.5 μmol/m^2, ∗ 2.0-3.0 μmol/m^2.

The observation of the curves permits the distinction between electrostatic stabilized particles (without surfactant), electrosteric stabilized particles (intermedium coverage) and steric stabilized particles (maximum coverage). At pH 5, however, and for a low surfactant coverage the colloidal stability of the complex is lower (significant change in dAb/dt) than that of the bare particles. This result can not be explained within the frame of the actual colloidal stability theories, and may be accounted for when looking at the chemical nature of the molecules present on the particles surface. A well-known interaction between the ethylene oxide chains (EO) and the carboxyl surface groups (COOH) is probably taking places through hydrogen bonding[12)]. This interaction will rarely occur in complexes with a highly packed monolayer of Triton X-100, while at low coverages and because of the great flexibility of the hydrophilic moieties the interaction could be favoured. A direct consequence of this interaction will be the change in the surfactant layer configuration which is worth of passing from extended to flat. Experimental evidence of an enhanced steric stabilization was found by Dobbie et al.[13)] However, this change will only explain the decrease in the steric repulsive interaction energy, and thus will not succeed in explaining the observe destabilization. In addition to this, the electrokinetic behaviour of the complexes[14-15)] indicate a relative decrease of surface charge at low pH pointing to the possible excess of positive charge (H^+ ions), as a consequence of the mentioned interaction. The explanation for the unexpected results may then be attributed to a decrease of electrostatic repulsive interaction energy, due to a screening of the charge by the H^+ ions that arise because of the EO-COOH interaction.

Another interesting result is related to the coagulation kinetics. The observed decrease in the coagulation velocity of electrosteric and steric stabilized particles with respect to that of bare particles, can be explained considering that the steric repulsive interaction energy is not affected for the electrolyte concentration, at least at the maximum concentration (1M NaCl) employed in this work. This constant barrier causes a decrease in the collision efficiency and on lowering the diffusion velocity of the particles. The increase in the coagulation velocity of the complexes with low coverage at pH 5 compared to that of bare particles might be explained as a consequence of an increase in the secondary minimum due to dehydration of ethylene oxide chains which will manifest by increasing the collision effectivity during the aggregation process[16)].

Figures 4 and 5 show the colloidal stability results for the same system after centrifugation. As found in others works[14,17)], an important desorption phenomena occurs when a precipitated complex is redispersed in a new medium. If we take into account this fact the results showed in these figures are self explained with the above arguments. At pH 5 the complexes after centrifugation have a low coverage (1.0-1.5 $\mu mol/m^2$), and the EO-COOH interaction causes the observed destabilization. However, in the absence of this effect (pH 10) the centrifuged complexes have a relatively higher colloidal stability than the bare particles but lower than non-centrifugated ones because of the non-appearance of a steric stabilization.

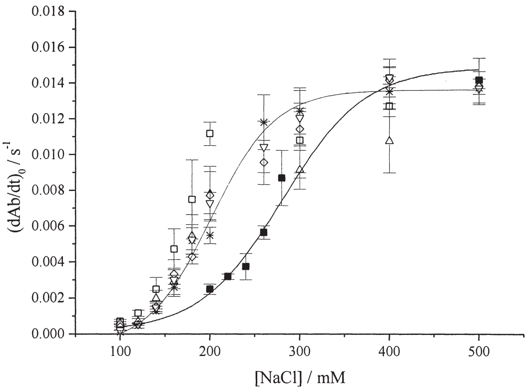

Fig. 4: Aggregation kinetics of PS-C-TX100 system at pH 5 with different coverages after centrifugation: ■ = bare, □ = 1.0 μmol/m^2, △ = 1.5 μmol/m^2, ∗ = 2.0 μmol/m^2, ◇ = 2.5 μmol/m^2, ▽ 3.0 μmol/m.

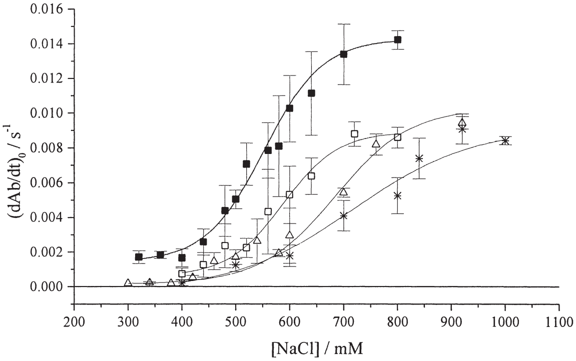

Fig. 5: Aggregation kinetics of PS-C-TX100 system at pH 5 with different coverages after centrifugation: ■ = bare, □ = 1.0 μmol/m^2, △ = 1.5 μmol/m^2, ∗ = 2.0-3.0 μmol/m^2.

Conclusions

Non-ionic surfactants are known to be excellent tools for controlling the stability of a colloidal system. This stability is improved with an adequate surface coverage. Additionally, its adsorption at low coverage may surprisingly yield the destabilization of the colloidal system, when the particles have the lower surface charge.

Acknowledgements

The financial support provided by the CICYT (under Project MAT 96-1035-C03-03) is greatly appreciated.

References

1. B.V. Derjaguin, L.D. Landau, Acta Physicochim. URSS **14**, 633 (1941)
2. E.J.W. Verwey, J.Th.G. Overbeek, in: *Theory of Stability of Lyophobic Colloids*, Elsevier, Amsterdam 1948
3. D.H. Napper, in: *Polymeric Stabilization of Colloidal Dispersion*, Academic Press Inc., London 1983
4. B. Vincent, P.F. Luckham, F.A. Waite, J. Colloid Interface Sci., **73**, 508 (1980)
5. B. Vincent, J. Edwards, S. Emmett, A. Jones, Colloids Surfaces, **18**, 261 (1986)
6. W.H. Guthrie, PhD Thesis, Lehigh University 1985
7. D. Bastos-González, J.L. Ortega-Vinuesa, F.J. de las Nieves, R. Hidalgo-Álvarez, J. Colloid Interface Sci., **176**, 232 (1995)
8. Ma Chiming, Colloids Surfaces , **28**, 1 (1987)
9. A. Martín-Rodríguez, M.A. Cabrerizo-Vílchez, R. Hidalgo-Álvarez, Colloids Surfaces A., **92**, 113 (1994)
10. M.S. Romero-Cano, A. Martín-Rodríguez, G. Chauveteau, F.J. de las Nieves, J. Colloid Interface Sci., **198**, 266 (1998)
11. F.J. Rubio-Hernández, F.J. de las Nieves, R. Hidalgo-Álvarez, B.H. Bijsterbosch, J. Dispersion Sci. Technol. **15**, 1 (1994)
12. G.C. Pimentel, A.L. McClellan, in: *The Hidrogen Bond*, Freeman, San Francisco 1960
13. J.W. Dobbie, R. Evans, D.V. Gibson, J.B. Smitham, D.H. Napper, J. Colloid Interface Sci., **45**, 557 (1973)
14. M.S. Romero-Cano, PhD Thesis, University of Granada 1998
15. M.S. Romero-Cano, A. Martín-Rodríguez, F.J. de las Nieves, in preparation.
16. L. Thompson. J. Chem. Soc. Faraday Trans., I **80**, 1673 (1984)
17. M.S. Romero-Cano, A. Martín-Rodríguez, F.J. de las Nieves, sent to publish in J. Colloid Interface Sci.