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ORIGINAL CONTRIBUTION

S. Ottow
R. Zimehl

Polystyrene particles with proton-ionisable groups: pH-dependent stability of latices with weakly acidic groups

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S. Ottow · R. Zimehl (✉)
Institute of Inorganic Chemistry
University of Kiel
Olshausenstrasse 40
D-24098 Kiel
Germany
e-mail: r.zimehl@email.uni-kiel.de
Fax: +49-431-880 1520

Abstract Results of colloid chemical characterisation and stability measurements on electrostatically stabilised latex dispersions made from emulsions of styrene and 4,4′-azobis-(4-cyanovaleric acid) are reported. The deviant stability of the hydrophobic polystyrene particles at low pH and low ionic strength is related to a proton "tunable" hydration layer surrounding weakly charged particles. The idea implies the formation of a polymer-supported surface phase that does not have any clear boundary, either towards the polymer moiety or in the direction of the bulk solution. The formation of the surface phase is controlled by Coulombic, hydrophobic and van der Waals interactions and by the contribution from the water structure at the hydrophobic and hydrophilic domain of the polymer particles. Negative charges on the hydrophobic surface badly interfere with the water structure at the hydrophobic moiety of the particle, whereas positive or uncharged surface groups do not damage the balance of free and clustered water molecules at the interface. Because the hydrophobic nature of the surface changes with the degree of dissociation of the surface charges, the degree of hydrophobicity of the carboxylic latices can be adjusted by changing the pH; therefore, it may be concluded that the hydrated and discharged carboxylic particle is apparently more hydrophobic relative to the ionised one. Thus, our concept can also explain differences in the hydrophobicity of colloidal polymer particles.

Key words Latices · Electrostatic stabilization · Coagulation · Water structure · Tunable ionization

Introduction

Besides their technological importance, various kinds of latices have been widely used to investigate current theories of colloid stability. Most of the latex dispersions used as model colloids consist of smooth and almost spherical hydrophobic polymer particles immersed in an aqueous environment. The stability of these dispersions is achieved by a small number of charged and hydrophilic fragments of initiator molecules accumulated at the particle–water interface. According to this simple picture the stability of latex dispersions can be calculated by the Derjaguin–Landan–Verwey–Overbeek theory, which is based on pure electrostatic interactions [1, 2]. Pronounced deviations between theoretically predicted and experimentally derived stability have often been reported. The reason for the deviant stability of latex dispersions can be manifold. Firstly, one has to realise that, despite the fact that the polymer particles are charged, the stability of latex dispersions is not only determined by the number density of the surface charges and the degree of dissociation. The charged groups and their supporting polymer chains make the surface of the latex particles hydrophilic or even "hairy", which might provide additional stability even when the ionic strength in the dispersion is sufficiently high to screen the charges on the particle surface. In a number of contributions we have pointed out that the boundary region between the polymer particles and the dispersion medium can decisively influence dispersion stability [3–5]. We suggested that an appropriate model for the stability of colloids with hydrophilic groups at the particle surface should include strong solvation effects which contribute to stability. Secondly, one has to take into account the specific ion effects by which a certain number of the counterions may "condense" with surface groups by chemical interaction. Thus, a solvated layer of counterions close to the particle surface or even inside the hairy surface layer of the polymer particles is formed (cf. Stern layer adsorption). According to this clearer picture, the stability of these hydrophilic colloids should result from at least two effects, namely, electrostatical interaction and solvation.

Materials and methods

Chemicals

Carefully cleaned ion-exchanged water (Seradest) was used throughout all the experiments. The chemicals used were of AnalaR quality. The monomeric styrene (Fluka) and the radical initiator 4,4′-azobis(4-cyanovaleric acid), ACVS, (Sigma) were of high-purity grade: they were both used as received.

Latex preparation

The latex dispersions were prepared by emulsifier-free emulsion polymerisation of styrene with ACVS (Table 1). The polymerisation was performed in a 1-l round-bottomed three-necked flask according to the procedure given in Refs. [2–5]. Aliquots of the latex dispersions were purified by dialysis and centrifugation redispersion [2, 3, 5].

Latex characterisation

The polymer volume fraction of the crude and the cleaned latex dispersion was determined gravimetrically after drying several millilitres of the dispersion at about 70 °C overnight in an air-conditioned oven. The surface charge density of the latex particles was estimated by polyelectrolyte titration of the cleaned and the uncleaned samples using a streaming current detector (particle charge detector, PCD 02, Mütek). In this instrument the amount of polyelectrolyte required to reach the point of zero charge was determined. From these data, the latex diameter and the volume fraction the surface charge of the particles were calculated (Table 2). The particle size was measured by sedimentation of the dispersions in a disc photocentrifuge (BI-DCP particle sizer, Brookhaven Instruments). Before measuring the particle diameter, the dispersions were diluted with water to a particle volume fraction of about 2×10^{-4} and were then equilibrated for at least 3 h. These equilibrated latex dispersions were used without further purification. The results were verified by measuring the diameters at different acceleration rates with sedimentation times between 30 and 60 min (Table 2).

Table 1 Preparation recipes of carboxylic polystyrene latices. Polymerisation was performed at 90 °C in 250 ml deionised water

Latex	Styrene (ml)	4,4′-azobis (4-cyanovaleric acid) (mg)	KOH (mg)	Reaction time (h)
A/2/2	5	280	112	6
A/3/1	7.5	280	112	6
A/4/5	10	371	149	12

Table 2 Colloid chemical characteristics of the carboxylic polystyrene latices

Latex	Particle diameter (nm)	Specific charge (C g^{-1})	Charge density (μC cm^{-2})	Packing density (A^2/CO_2^-)
A/2/2	187	4.3	13.4	120
A/3/1	262	3.4	15.8	100
A/4/5	287	3.3	17.0	94

Stability measurements

The stability of the latex dispersions at fixed pH values was determined by the kinetic approach [2]. The critical coagulation concentration was determined from the initial slope of the turbidity versus time plots of very dilute latex samples in the presence of different amounts of electrolyte. Prior to the coagulation experiments, the latices were diluted with deionised water to a volume fraction of exactly 2×10^{-4} and were equilibrated in tightly closed vessels for at least 4 days. Amounts (1 ml) of the pretreated dispersions were transferred to 3-ml disposable cuvettes and were further diluted with 1 ml electrolyte solution of the desired concentration. To adjust the pH during the coagulation experiments, the electrolyte solutions were prepared in 10^{-4} M hydrochloric acid, deionised water or 10^{-3} M potassium hydroxide solution to give a final pH of 4, 6–7 or 11, respectively.

Mobility measurements

Electrophoretic mobility was measured using a photon-correlation spectrometer (BI-ZetaPlus, Brookhaven Instruments) at 20 °C. Before measuring the particle mobility, the dispersions were diluted with HCl, KOH or KCl solutions to a final weight fraction of approximately 1 g l^{-1}. These dispersions were then checked for the desired pH and equilibrated. The results were verified by measuring the diameter and mobility after different equilibration times (several minutes to 4 days).

Results

The stability of the polystyrene latices carrying carboxylic groups at their particle surface strongly depends on the pH of the dispersion medium. The values of the critical coagulation concentration (c_k) for $MgCl_2$ and $CaCl_2$ at three different pH values are presented in Table 3. The dispersions of the anionic particles have a maximum stability at $pH < 5$. The critical coagulation concentration at high pH values is always lower. The change in c_k of the 2:1 electrolytes for carboxylic

Table 3 Critical coagulation concentration of inorganic 2:1 electrolytes $MgCl_2$ and $CaCl_2$ at different pH values for carboxylic polystyrene latices

Latex	Electrolyte	Coagulation concentration (mmol l^{-1})		
		pH ≈ 4	pH ≈ 6–7	pH ≈ 11
A/2/2	$CaCl_2$	26	13	13
A/2/2	$MgCl_2$	29	17	15
A/3/1	$CaCl_2$	21	16	13
A/3/1	$MgCl_2$	31	23	18

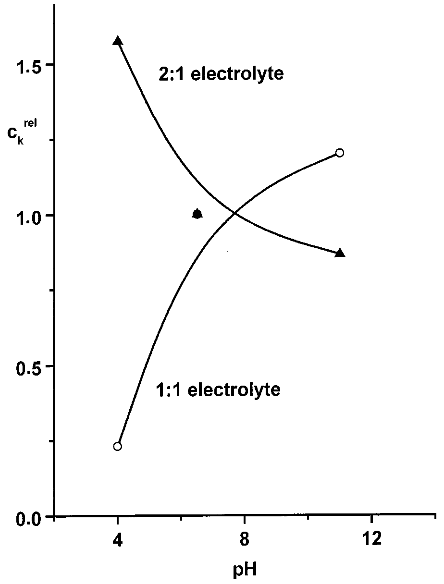

Fig. 1 Relative critical coagulation concentration ($c_k^{rel} = c_k/c_k^{pH=7}$) of inorganic electrolytes at different pH values for carboxylic polystyrene latices

polystyrene particles at different pH values is illustrated in Fig. 1. Furthermore, Fig. 1 depicts the relative change in the critical coagulation concentration for simple inorganic 1:1 electrolytes and comparable carboxylic polystyrene particles. The c_k value is largest for the alkaline dispersion (pH ≈ 11) and decreases at lower pH values (pH ≈ 4).

For further investigation of the differing stability of the carboxylic latices, we performed some electrophoresis experiments with our polystyrene dispersions at pH values of about 4, 6 and 11 at different equilibration times (Fig. 2). The electrophoretic mobility of most of the latex dispersions is highest at a pH of about 6 and lowest at a pH of about 4. The magnitude of the mobility strongly depends on the time gap between the adjustment of the pH and the ionic strength and the mobility measurement. In other words, the relaxation of the particle–solution boundary plays a decisive role in the stability of the latex dispersion. Similar behaviour was observed for the stability measurements with 2:1 electrolytes. If the latex dispersions are equilibrated for 4 days with HCl prior to the coagulation experiments, the curve for the 2:1 electrolytes in Fig. 1 shows a smaller difference in the c_k values between pH 4 and pH 6. In general, the critical coagulation concentration is somewhat larger for the nonequilibrated dispersions and 2:1 electrolytes, and the difference is more pronounced for crude dispersions than for dialysed ones.

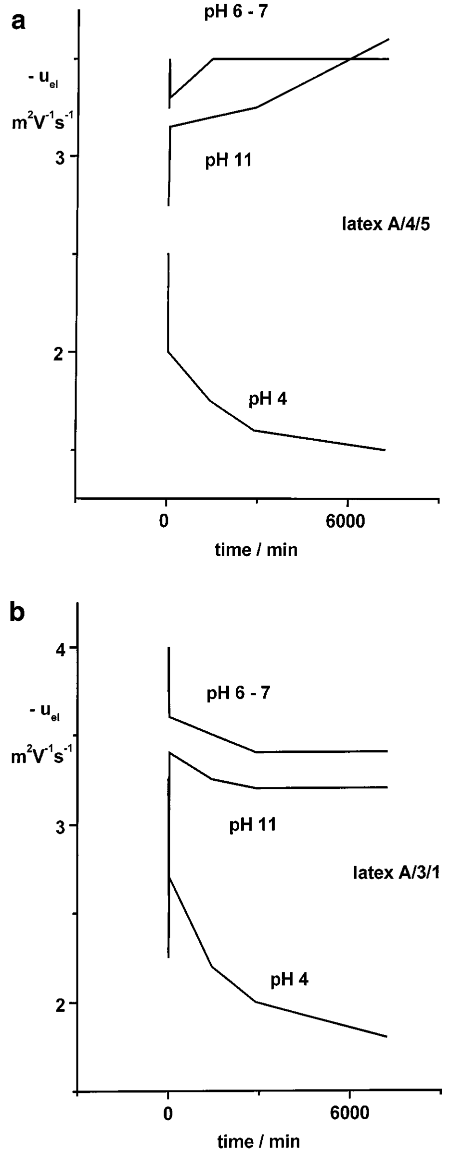

Fig. 2a, b Electrophoretic mobility of carboxylic polystyrene latices at different pH values. The time scale represents the time elapsed between mixing the latex dispersion with electrolyte solutions of 10^{-3} M KCl (pH ~ 6–7), 10^{-3} M KOH (pH ~ 11) and 10^{-4} M HCl (pH ~ 4). **a** Latex A/4/5 and **b** Latex A/3/1

Discussion

The stability of the pH behaviour of carboxylic latices in different electrolyte solutions has been reported in several studies [6, 7]. Our results for polystyrene latices stabilised solely by surface carboxylic groups agree with the results of these studies. The results may be explained by assuming a hydrophobic hydrated surface layer [8]. In a simple model (Fig. 3a), hydrophobic hydration entails the formation of a water structure around the particles (several water molecules thick) in which the O-H bonds point away from the hydrophobic surface [8]. Flexible polymer segments at the particle solution interface, especially the polymer segments with carboxylic acid groupings, can take up a large number of water molecules and contribute to a hydrated surface phase (Fig. 3b, c). This will of course induce changes in the water structure at the interface and in the neighbouring solution. At a low pH of the immobilised solvent layer at the particle interface, some of the carboxylate groups become protonated. The water molecules around the protonated charges adopt a similar orientation as the water molecules at the hydrophobic surface (Fig. 3b). In contrast, the negatively charged carboxyl groups force the water molecules into the opposite orientation (Fig. 3c). To induce rapid coagulation of the latex particles, the swollen polymer brushes of the extended boundary must be dehydrated. The dehydration of this interphase is achieved when a sufficient amount of salt is added. The salt ions compete for water molecules, and the balance of free and clustered water is changed. At a low pH the coagulation of the latex dispersion can only be achieved by a surplus of the electrolyte, which is sufficient to eliminate the water clustering around the protonated carboxylate groups. The reverse behaviour of crude negatively (and highly hydrated) charged polymer particles in acidic 2:1 electrolyte solutions (i.e. when the CO_2^- groups are protonated) is explained by the adsorption of specific water clusters which causes swelling of the particle–solution interface. For this reason the critical coagulation value of the 2:1 salts (e.g. $CaCl_2$ or $MgCl_2$) is distinctly larger in acidic solution then in neutral or even alkaline salt solution and an unusual pH dependence of the c_k values is observed. In contrast, the addition of simple 1:1 electrolytes (e.g. NaCl or KCl) causes the latex dispersion to coagulate at almost any pH i.e. c_k in acidic electrolyte solution is remarkably smaller than that in alkaline solution. In the case of simple 1:1 electrolytes, high electrolyte concentrations (greater than several hundred mmol l^{-1}) are required for the compression of the diffuse double layer and so too many ions are present in solution to compete for water molecules. In this case, deswelling of the surface layers occurs clearly below the critical coagulation concentration at any pH. The behaviour of the negatively charged polystyrene particles is then apparently similar at all pH values, and the differences in c_k are determined by the degree of dissociation of the carboxylic groups at the particle surface.

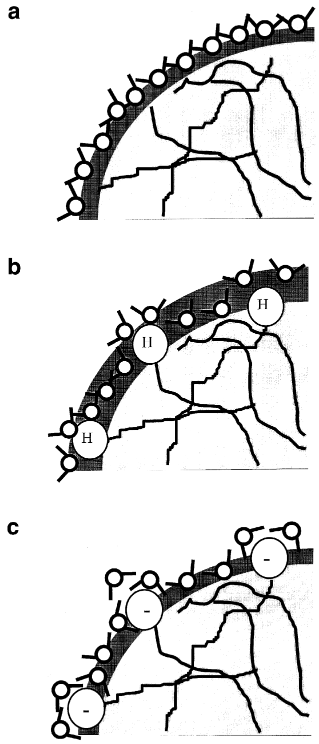

Fig. 3 a Model of the orientation of water molecules on the surface of hydrophobic polymer particles. **b** Carboxylic groups with associated protons fit in the molecular arrangement and will possibly expand the hydration layer while **c** the negative charges of dissociated carboxylic acid groups force the water molecules to adopt a different orientation

Conclusions

Polystyrene particles of low surface charge which are dispersed in aqueous surroundings (electrostatically stabilised hydrophobic latices) exhibit a relatively complex and somewhat contradictory colloidal stability. We propose a simple explanation for the deviant stability of hydrophobic polystyrene particles with carboxylic acid groups at low pH and low ionic strength. The model implies the formation of a polymer-supported surface phase that does not have any clear boundary, either towards the polymer moiety or in the direction of the bulk solution. Such a dynamic and diffuse solvation shell could account for additional stability by hydration effects. The formation of the surface phase, which may also determine the stability of more hydrophilic latices and the aggregation of dispersions of hydrophobic particles in the presence of organic counterions [9] and long-chain alcohols [10], is controlled by a subtle balance of different surface forces. These forces include Coulombic, hydrophobic and van der Waals interactions and a contribution from the water structure at the hydrophobic and hydrophilic domain of the particle. Negative charges on a hydrophobic surface badly interfere with the water structure at the hydrophobic moiety of the interface, whereas positive or uncharged surface groups do not damage the balance of free and clustered water molecules [11, 12] at the interface.

Our idea is a proton "tunable" hydration layer surrounding the weakly charged particles. Because the hydrophobic nature of the surface changes with the degree of dissociation of the surface charges, the level of hydrophobicity of the carboxylic latices [and several other polymer colloids, e.g. poly(2-vinylpyridine) latices [13]] can be adjusted by changing the pH. Therefore, it is concluded that the hydrated and discharged carboxylic particles are apparently more hydrophobic relative to particles with ionised surface groups. Thus, our concept explains the differences in the hydrophobicity of colloidal polymer particles.

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