Interactions of Colloidal Particles With Complex Ions and Polymers[1]

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ABSTRACT

The lecture represented a review of the work done in the author's laboratory dealing with the behavior of a variety of submicronic particles in the presence of simple and complex ions, surface active agents, polyelectrolytes and polymers. Experimentally, the stability of colloidal sols, which can be readily followed by optical methods, was investigated as a function of the composition of the electrolyte environments. This approach offers a number of advantages when the evaluation of solid-solute interactions is attempted. By selecting various colloidal sols one can study the interactions of counterions with particles of different surface properties, such as the charge density, type and concentration of stabilizing ions, degree of solvation, surface ionization, etc.

INTRODUCTION

In order to better understand the problems of detergency, it is essential to elucidate the interactions of various solute species with solid substrates of different surface characteristics.

The concentrations of counterions necessary to destabilize a sol (due to particle aggregation) or to restabilize it (due to charge reversal or steric protection) may vary over a range of about eight orders of magnitude. For a given sol this will depend on the nature of the counterions (their charge, size, configuration, ligand composition, exchangeability, etc).

The most important single aspect of the interactions of solute species with solid interfaces, which will determine the sol stability in an electrolyte environment, is the counterion adsorptivity. The latter will depend both on the nature of the sol particles (particularly their surface characteristics) and on the composition of the counterions. Because of their large specific surface areas, colloidal sols lend themselves well for the study of the adsorption of solute species. In this regard, the monodispersed sols, which are now available for a large variety of suspended materials, are of special interest. Several techniques can be used for the detection or for a direct evaluation of the ion adsorption. Restabilization of sols, readily detected by optical measurements or by electrophoretic mobility, especially when charge reversal takes place, can act as excellent indicators for the adsorption of charged counterions. Furthermore, radioactive tracers or various other analytical techniques (spectroscopy, interferometry, etc.) may be employed for a quantitative determination of the adsorbed amounts.

The reasons for the adsorption of counterions, other than constituent ions, are not always well understood. They will vary in different solid-solution combinations. It was shown, for example, that hydration of the particles hinders the adsorption of ions which otherwise adsorb strongly on lyophobic surfaces (1). However, interactions between strongly hydrated sols and solutes will occur if special mechanisms are possible. For example, hydrated silica particles may adsorb cations by ion exchange with surface protons (2) or, in the case of hydrolyzed metal ions, by oxygen-bridging (3) involving surface silanol groups.

Of particular interest are the interactions of various complex ions with lyophobic interfaces. In general, strongly hydrated solute species do not adsorb on such surfaces regardless of their ionic charge. If the coordinated water is substituted by some other ligands, the adsorptivity can be significantly increased. This is especially so when specific bonds are formed between a given ligand of the complex solute and a constituent or stabilizing species at the particle interface. Thus, studies of adsorption of various selected complexes with particles of well characterized surfaces should eventually lead to a better insight into the interfacial reactions responsible for various phenomena, such as adhesion, detergency, corrosion, flotation, etc.

Systematic investigations of interactions of various metal ion complexes with lyophobic colloids, carried out in our laboratory, illustrate some of the effects.

Probably the most important ligand to be considered is the hydroxyl group, OH^-. It has been established beyond any doubt that substituting at least one coordinated water molecule by the hydroxyl group dramatically enhances the adsorption of metal ions on lyophobic surfaces of various chemical composition (4-13). It could be shown that even the neutral soluble hydrolyzed species, such as $Hf(OH)_4$, adsorb strongly on glass, latex or silver halides (14,15). This stresses the predominant role of the hydroxyl group and the negligible effect of other factors, such as the counterion charge, size, shape, etc., in determining the adsorptivity of the hydrolyzed ions. As yet the reason why the hydroxyl group is producing this rather enormous adsorption effect is not clear. Whereas a partial or complete dehydration of the counterions, which underwent hydrolysis, may contribute to its better adsorptivity on lyophobic surfaces, this certainly cannot be the entire explanation of the observed effects. A substitution of the coordinated water of the hydrated aluminum ion by other inorganic ligands, such as sulfate or fluoride ions, does not improve its poor adsorptivity. The only consequence of such complexing is a reduced coagulation ability due to the lowering or reversing the charge of the counterion (16,17). In any event, the hydrolysis of metal ions must be carefully considered in every system consisting of lyophobic surfaces and polyvalent metal cations, which makes the pH of such systems a significant variable.

To investigate the effects of other ligands upon the solid-solute interactions, metal chelates seem to be particularly well suited. With the use of the same central atom and different ligands, it is possible to prepare complex ions of the same charge but of various sizes having different active groups. By replacing the central atom and using the same ligands, one can change the ionic charge keeping all other parameters essentially constant.

Rather dramatic effects had been observed when various metal chelates were added to silver halide sols. For example, the coagulation concentration of Ni^{2+} for a negatively charged silver bromide sol was reduced by more than four orders of magnitude when this ion was complexed with 1,10-phenanthroline. The $Ni(phen)_3{}^{2+}$ chelate also acted as an exceedingly efficient charge reversal agent indicating its strong adsorptivity. In contrast, $Ni(aq)^{2+}$

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cannot reverse the charge of the same sol which means that its adsorption on silver halide particles at low pH must be negligible (18). It could be shown that the phenanthroline ligand coordinates with the constituent silver ions of the colloidal particles, which explains the nature of the specific interaction in this case (19). The coordination is so strong that 1,10-phenanthroline alone (in the absence of the chelated nickel ion) can replace the bromide ion and eventually reverse the charge of silver halide particles from negative to positive even when pH is high enough for the phenanthroline to exist in neutral (unprotonated) form.

When such coordination is not possible, as is, for example, the case with polyvinyl chloride latex, the same chelate shows much less pronounced effects (20).

Recently, various polymers and polyelectrolytes have been used in many applications in which interfacial phenomena are involved. There is no doubt that the adsorption of macromolecular species is responsible for a variety of effects such as flocculation, sensitization, protection, charge reversal and interactions with surfaces of the same sign of charge caused by these solutes. Again, the reasons for the adsorption of individual segments on specific adsorbent sites are not well understood. It is believed that the work with selected chelates will assist in the elucidation of the solid-macromolecular solution interactions.

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