

NOTE

The Density of Aggregated Polystyrene Spheres

We show that density measurements can provide an alternative method for determining the number and species of ions adsorbed onto colloidal particles. We cause charge-stabilized colloidal dispersions of polystyrene spheres to aggregate by adding various salts. The solvents are mixtures of H₂O and D₂O in which the colloids are neutrally buoyant after aggregation, which we verify by centrifugation of the samples. By this method we are able to determine the density of the aggregated colloids. We find that the density depends on the species of salt added to initiate the aggregation and can be calculated on the assumption that a cation of the added salt binds with each ionizable group on the surface of the colloidal particles. © 1995 Academic Press, Inc.

Polystyrene latex colloids formed by emulsion polymerization are widely used as model colloidal systems; they also find a variety of technological uses. These colloidal particles are typically stabilized by coulombic forces due to the presence of ionizable end groups on their surfaces. There are usually a large number of ionizable groups on each particle. In solution, most groups become associated with a counterion and remain neutral; the coulombic stabilization originates from only a small fraction of dissociated groups. Thus, the number of ionizable groups is often determined by titration. Similarly, the type of adsorbed counterions is also usually determined by chemical means. The nature of these counterions can be quite important; the chemical properties of these colloids can be adjusted by varying the molecules adsorbed onto their surfaces, thereby affecting the ultimate use of the colloids. Thus, obtaining information about the type and number of adsorbed species can be quite useful. While this can be done by a variety of chemical means, in this Note we suggest an alternative, very simple, physical means. We use mixtures of H₂O and D₂O to buoyancy-match the colloidal particles and thus determine their densities. This allows us to effectively "weigh" the particles in solution and thus to determine the amount and type of adsorbed species.

Charge-stabilized polystyrene spheres suspended in water can be caused to aggregate by the addition of a salt (1). In recent years there has been considerable interest in the kinetics of the aggregation and the structure of the aggregates. Given enough time, the aggregates that form even in quite dilute colloids may eventually link up, so that the entire sample volume is filled with a diffuse, typically fractal network. We study such colloidal gels with volume fractions of colloids ϕ on the order of 10^{-4} . They are so fragile that they cannot bear their weight unless the density match of the aggregates to the solvent is quite close. Polystyrene, with density $\rho \approx 1.05 \text{ g/cm}^3$, is density-matched by an H₂O/D₂O mixture whose D₂O fraction is about 0.6 by mass. We find, however, that the required solvent density for a close match to the density of the colloidal aggregates is higher and depends on the salt added to cause the aggregation. This observation indicates that an exchange of associated cations takes place when the salt is added, with the result that the density of the colloid becomes shifted from that of bulk polystyrene by a new amount.

We use 19-nm sulfated polystyrene latex spheres obtained as an aqueous suspension from a commercial supplier. The surface density of ionizable

groups is $\sigma_s = 0.315 \text{ nm}^{-2}$, as stated by the manufacturer. We dilute the concentrated suspension in an H₂O/D₂O solution. To induce aggregation, we add an equal volume of an H₂O/D₂O/salt solution with the same composition of H₂O and D₂O. The final volume fraction of colloids is $\phi = 2.9 \times 10^{-4}$. The salts are NaCl, KCl, CaCl₂, MgCl₂, and BaCl₂; we also use HCl. The sample attains a time-independent gelled state after about an hour. We determine whether the gel is more or less dense than the solvent by centrifuging the sample and noting whether the gel collapses to the top or the bottom of the sample cell. The density of the solvent is then measured directly with a pycnometer. In this way we obtain a pair of values that bracket the density of the aggregated colloid. We estimate that the error is less than $\pm 0.005 \text{ g/cm}^3$.

We choose a concentration for each added salt that is the minimum one sufficient to induce rapid, diffusion-limited aggregation (1). In this way we ensure that the structure of the aggregates is the same for all salts. That is, in all cases the aggregates have a very open structure characterized by a fractal dimension of 1.8, which we verify with light-scattering measurements. Noteworthy is the fact that the concentrations required for the divalent salts are lower than those required for the monovalent salts by a factor of about 100. Thus the valence dependence of the minimum salt concentration sufficient for diffusion-limited aggregation appears to follow the same sixth-power law (Schulze-Hardy rule) that governs the salt's much lower critical flocculation concentration for slow aggregation (2). Typical salt concentrations used in the experiments are 10 and 1000 mM, respectively, for di- and monovalent salts.

Figure 1 shows the measured density of aggregated polystyrene colloids as a function of the molar mass M of the cations of the added salt. For the divalent ions this mass includes the mass of a chloride ion. Thus in the case of MgCl₂, for example, we take the "new" cation to be $[\text{Mg}^{2+}\text{Cl}^-]^+$. Association with the complex is necessary for a group to remain neutral; a small number of dissociated groups remain and carry one unit of negative charge. To calculate the density ρ of the aggregate, we assume that the mass of a colloidal monomer is increased by M for each ionizable group and that the

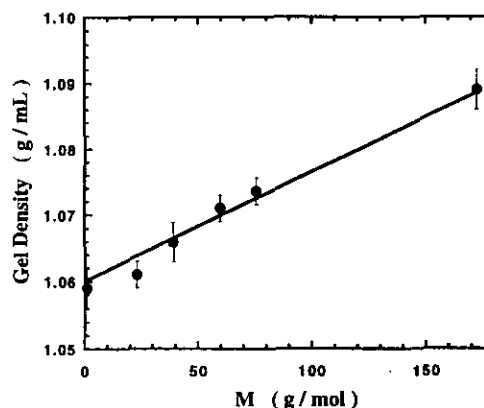


FIG. 1. The density of aggregated polystyrene spheres as a function of the molar mass M of the cations of the aggregating agent.

change in the volume is negligible. The neglect of the ion's volume is justified because of its high density compared to that of polystyrene. For example, taking the radius of a sodium ion as 0.97 Å, we estimate 10.0 g/cm³ for the density of Na⁺. These assumptions lead to

$$\rho = \rho_0 + 3M\sigma_s/N_0R, \quad [1]$$

where ρ_0 is the density of polystyrene, $R = 9.5$ nm is the radius of the colloidal monomers, and N_0 is Avagadro's number. We allow ρ_0 to float and find a value of 1.060 g/cm³, which is somewhat higher than the value of 1.055 g/cm³ supplied by the manufacturer. The higher value is possibly due to the sulfate coating. The curve calculated from Eq. [1] agrees well with the data. The good agreement shows that quantitative information about the surface characteristics of colloidal particles can be directly obtained by density measurements.

According to our interpretation, an appreciable density shift occurs because the new cations bind with all the ionizable groups on the colloid, not just the dissociated ones. We thus suppose that when the salt is added the original Na⁺ cations associated with the neutral groups are replaced by new cations as a consequence of chemical equilibrium with the new cations which are present in high concentration in solution. Actually, as was also the case before the new salt was added, a small fraction of the groups remains dissociated, and the colloid therefore carries a charge. This charge may differ from the original one; indeed, it seems likely that the rapid aggregation is due to the lowering of the effective charge on the colloidal particles.

We undertook this study because we need closely density-matched samples in order to study the tenuous colloidal gels. The significant effect of the adsorbed counterions on the mass of small colloidal particles may prove to

be useful for other purposes as well. For example, it might be the basis of a separation process. Furthermore, the measurement of the density shift can provide an alternative to conventional chemical methods for the determination of the amount and type of adsorbed counterions.

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REFERENCES

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