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ORIGINAL CONTRIBUTION

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Colloidal crystals of cationic spheres

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Abstract Colloidal single crystals of cationic polymer spheres (198–250 nm in diameter) in deionized aqueous dispersions were formed for the first time. The spheres used were poly(styrene-*co*-methacryloyloxyphenyldimethylsulfonium) cations. These cations are unstable in deionized suspensions with mixed beds of cation-exchange and anion-exchange resins. This was clarified by reflection spectroscopy, pH, conductance and ζ-potential measurements for 250 days after suspension preparation. Colloidal crystals formed over a period of 24 h for the deionized suspensions at sphere concentrations higher than 0.09 in volume fraction. The nearest-neighbor intersphere distances coincide satisfactorily with the calculated values using the diameter and the concentration of the spheres. Alloy crystals formed from binary mixtures of the cationic polymer spheres and the anionic silica spheres when the ratio of the volume fraction of cationic spheres against the sum of the both cationic and anionic spheres was smaller than 0.3.

Keywords Colloidal crystal · Cationic polymer colloids · Colloidal alloy of unlikely charged spheres · Reflection spectroscopy

Introduction

Recently, keen attention has been paid to the structural and dynamic properties of colloidal crystals [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13]. The colloidal crystals studied so far are grouped into "soft" crystals in dilute and deionized aqueous suspensions [14, 15, 16, 17, 18] and "hard" crystals in concentrated suspensions in refractive-index-matched organic solvents [19, 20, 21, 22, 23].

Generally speaking, most colloidal spheres in aqueous suspensions have negative charges on their surfaces. Furthermore, most of the colloidal crystals studied hitherto are composed of anionic colloids such as polystyrene and silica spheres. The colloidal crystallization of the cationic colloids has been investigated using spheres obtained by excess adsorption of multivalent simple cations on anionic polystyrene spheres [24]. However, no reports on the colloidal crystallization of typically cationic spheres have been published as far as the authors know. In this paper, crystallization of cationic colloidal spheres in deionized suspension is described.

The important role of the electrical double layers has been clarified for colloidal crystallization [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18]. A large number of simple ions distribute around the charged colloidal spheres, which are called "electrical double layers". In the deionized state, the double layers are very extended, and the electrostatic intersphere repulsive forces prevail to great distances on the order of micrometers. Thus, colloidal crystallization in deionized aqueous suspensions should take place quite easily at low sphere concentrations compared with systems without electrostatic intersphere repulsion. Quite recently, Itano et al. [25] reported that Coulomb crystals were formed for trapped spherical plasmas with positive charges in the gas phase. This observation supports strongly the important role of electrostatic repulsion forces for the crystallization. As clearly established, an essential part of the repulsion is caused by the translational Brownian (thermal) movement of the colloidal spheres themselves. Sizes of colloidal spheres ranging from 80 to 200 nm are appropriate for the formation of crystal-like distributions of spheres in water at room temperature. Spheres smaller than 50 nm move much more vigorously and do not form a crystal-like structure.

In this study, the stability and the structure of the cationic colloidal crystals are studied. It is established that colloidal crystallization takes place irrespective of the sign of the charges of the colloidal spheres.

Experimental

Materials

Four kinds of cationic polymer spheres, poly(styrene-*co*-methacryloyloxyphenyldimethyl-sulfonium methylsulfate) (CatA, CatB, CatC and CatD) were used. The preparation of the spheres was described in a previous paper [26]. The particle diameters were estimated from transmission electron micrographs (Hitachi-H8100). D1B28 consists of monodisperse polystyrene spheres from Dow Chemical Co. The charge density of the strongly acidic groups of D1B28 was $-1.29\ \mu C/cm^2$ [27]. The diameter and other characteristics of the spheres are compiled in Table 1. These stock suspensions were deionized with mixed beds of cation-exchange and anion-exchange resins [AG501-8 (D), 20–50 mesh, Bio-Rad., Hercules, CA] in Pyrex glass tubes (disposable culture tube, borosilicate glass, Corning Glass Works, Corning, NY, 11 and 13-mm inside and outside diameters) shielded tightly with Parafilm (American Can, Greenwich, CT) as completely as possible. The suspension was treated with a small amount of the Bio-Rad resins in the tube with gentle mixing several times a day.

Water for the sample preparation was purified by a Milli-Q reagent grade system (Milli-RO5 plus and Milli-Q plus, Millipore, Bedford, MA).

Reflection spectroscopy

The reflection spectra at an incident angle of 90° were recorded using a multichannel photodetector (MCPD-7000G3, Otsuka Electronics, Hirakata, Osaka) connected to a Y-type optical fiber cable at 25 ± 0.05 °C.

ζ-potential measurements

Electrophoretic light-scattering measurements were made to observe ζ-potential values using an electrophoretic spectrophotometer (ELS8000, Otsuka Electronics, Osaka) at 25 ± 0.02 °C.

Table 1 Characteristics of cationic and anionic spheres used

Sphere	d_0 (nm)	δ (nm)	δ/d_0
CatA	244	10	0.041
CatB	250	8.5	0.034
CatC	226	8.4	0.037
CatD	198	6.9	0.035
D1B28	212	2.9	0.014

pH and conductance measurements

The pH values of the sample suspensions were measured using a model ϕ34 pH meter (Beckman, Tokyo) with a glass electrode (model 6378-10D, Horiba, Kyoto) at 25 ± 0.05 °C. The conductivity of the suspensions was measured using a model DS-14 conductivity meter (Horiba, Kyoto) with an electrode (3552, Horiba) at 25 ± 0.05 °C.

Results and discussion

Stability of the cationic spheres in the deionized suspensions

The chemical structure of the cationic colloidal spheres used in this work is shown in Fig. 1. The sulfonium cations were not too stable, especially in the deionized state in coexistence with the mixed beds of cation-exchange and anion-exchange resins. The reflection spectra of a CatD suspension in the presence of the ion-exchange resins are shown in Fig. 2. Colloidal crystals formed in a suspension of 0.238 in volume fraction 30 h after suspension preparation. The single crystals were very small owing to the high sphere concentration. At high sphere concentrations, the nucleation is so fast and a huge number of nuclei are formed. From our series of the experiments on the phase diagram, the critical

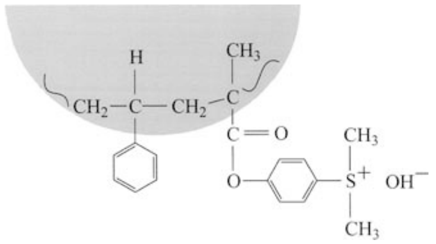


Fig. 1 Chemical structure of the cationic spheres

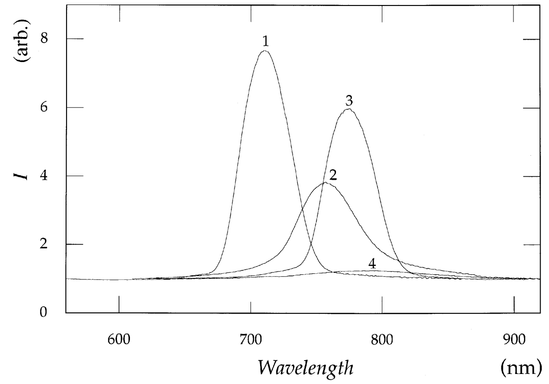
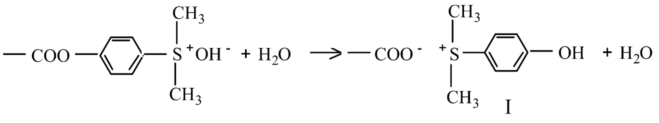


Fig. 2 Reflection spectra of colloidal crystals of CatD spheres at 25 °C. $\phi = 0.238$, with resins. 0 h (*curve 1*), 16 h (*curve 2*), 24 h (*curve 3*), 40 h (*curve 4*) after suspension preparation

concentrations of melting, ϕ_c, are 0.00015 and 0.0002–0.0004 for deionized suspensions of polystyrene and silica spheres (100–200 nm in diameter), respectively [16, 17, 18]. The giant single crystals (2–8 mm) form at sphere concentrations somewhat higher than the critical concentration of melting. The size of the single crystals decreased sharply as the sphere concentration increased.

Forty hours after suspension preparation colloidal crystals were not recognized with the naked eye: this was also supported by the very weak peak intensity in the reflection spectroscopy (Fig. 2). This observation suggests that the sulfonium cations are unstable in the deionized suspension. Thus, several measurements were made in order to clarify the stability of the cationic spheres. The change in the pH values of the suspensions for 250 days is shown in Fig. 3. The pH values were about 9 when the resins were present and about 4 otherwise. These results strongly suggest that the sulfonyl cations are hydrolyzed and that the suspensions become acidic:



(1)

With the resins, the sulfonyl cations released (I), i.e., the product of the hydrolysis, are exchanged with hydronium ions. The latter are neutralized and then water is produced. The deionized suspension is still basic because of the hydroxide anions, i.e., counterions of the dissociated sulfonium cations remaining on the colloidal surfaces. The pH values of the suspensions with and without the resins should decrease slightly in the course of the hydrolysis; however, these tendencies are not clearly observed in Fig. 3 owing to the rather large experimental errors.

The conductance of the colloidal suspensions is shown in Fig. 4. When ion-exchange resins were present the conductance values were fairly low and decreased further with time. These results strongly suggest that the hydrolyzed and desorbed ions are ion-exchanged with the resins and that the concentration of the cationic groups on the spheres decreases with time. The decrease was surprisingly high, i.e., the conductance decreased from one half to one seventh over 250 days. This indicates that a significant part of the sulfonium cations on the colloidal surface disappears because of hydrolysis. On the other hand, the conductance of the suspensions without resins was high and even increased slightly with time. In this case, the suspensions were stable but the slightly hydrolyzed ions were desorbed into the water phase.

The ζ potential of the spheres is shown in Fig. 5 as a function of time after suspension preparation. In the

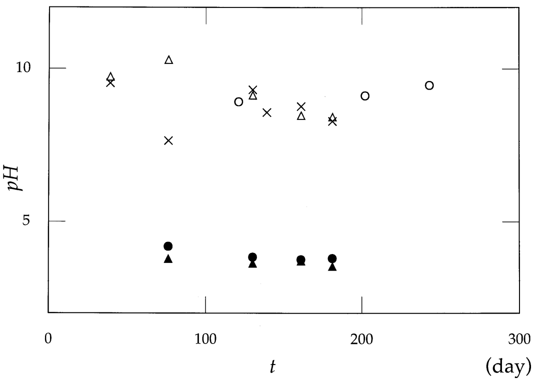


Fig. 3 pH changes of the suspensions of cationic spheres with time at 25 °C. CatA, $\phi = 0.096$, with resins (*open circles*), CatB, $\phi = 0.041$, with resins (*crosses*), CatB, $\phi = 0.058$, without resins (*closed circles*), CatC, $\phi = 0.126$, with resins (*open triangles*), CatC, $\phi = 0.209$, without resins (*closed triangles*)

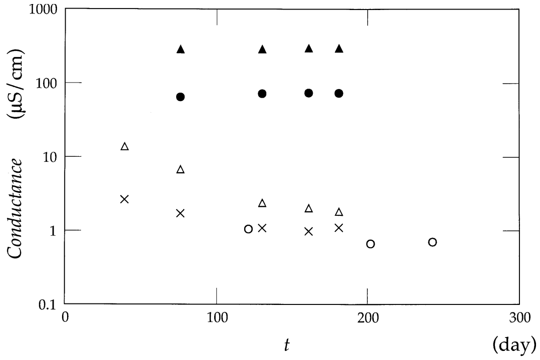


Fig. 4 Conductivity changes of suspensions of cationic spheres with time at 25 °C. CatA, $\phi = 0.096$, with resins (*open circles*), CatB, $\phi = 0.041$, with resins (*crosses*), CatB, $\phi = 0.058$, without resins (*closed circles*), CatC, $\phi = 0.126$, with resins (*open triangles*), CatC, $\phi = 0.209$, without resins (*closed triangles*)

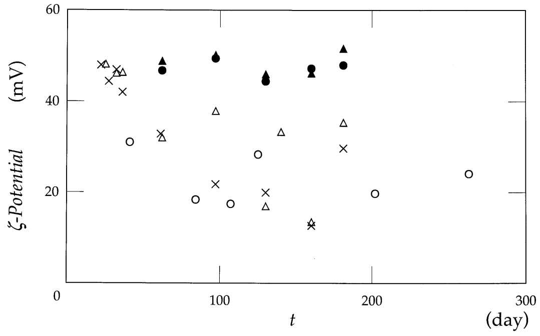


Fig. 5 Change in the ζ potential of cationic spheres with time at 25 °C. CatA, $\phi = 4.8\times10^{-6}$, with resins (*open circles*), CatB, $\phi = 5.2\times10^{-6}$, with resins (*crosses*), CatB, $\phi = 3.6\times10^{-6}$, without resins (*closed circles*), CatC, $\phi = 3.2\times10^{-6}$, with resins (*open triangles*), CatC, $\phi = 2.6\times10^{-6}$, without resins (*closed triangles*)

deionized suspensions, the ζ potential decreased with time, but retained positive values. Thus a significant part of the sulfonium cations on the colloidal spheres disappears because of hydrolysis. On the other hand, the ζ potentials without resins were around 50 mV for a long time, which suggests the suspensions are fairly stable without resins.

Reflection spectroscopy of cationic colloidal crystals

The reflection spectra of CatA ($\phi = 0.096$) and CatD ($\phi = 0.094$, 0.142, 0.236 and 0.321) spheres in the deionized suspensions are shown in Fig. 6. The measurements were made within 3 h of suspension preparation with the ion-exchange resins. In the reflection measurements the incident white light hits the surface of the sample cell at right angles. When the cell contains an "ordered" colloidal suspension, the light is turned back by Bragg diffraction (Fig. 6). Generally, the profile of the reflection spectrum consists of a single peak, a double peak or a single peak with a shoulder. The doublet peaks were always close together, with a wavelength ratio of 1.03. This difference supports the idea that the peak appearing at the longer wavelength is ascribed to the face-centered cubic (fcc) lattice, while the shorter-wavelength peak corresponds to the body-centered cubic (bcc) lattice. Using a simple theoretical calculation, the ratio of the nearest-neighbor intersphere distance for fcc lattices to that for bcc is found to be 1.028 at the same sphere concentration. However, only single peaks appear in Fig. 6. Thus, it is impossible to determine the lattice structure from Fig. 6 only. The intersphere spacing observed, l_{obs}, was determined from the peak wavelength [28]. For both fcc and bcc lattices the distance ($l_{\mathrm{obs,fcc}}$ or $l_{\mathrm{obs,bcc}}$) at a scattering angle of 90° is given by

$$l_{\mathrm{obs,fcc}} = l_{\mathrm{obs,bcc}} = 0.6124(\lambda_{\mathrm{m}}/n_{\mathrm{s}}) \tag{2}$$

where n_{s} is the refractive index of the sphere suspension (taken as that of water) and λ_{m} is the peak wavelength. The fcc structure was stabler at higher sphere concentrations than the bcc structure. The reflection peaks in the figure arose primarily from the Bragg reflection, which was clarified by comparison of the primary peak wavelengths calculated from the initial sphere concentration and the observed peak wavelengths.

A comparison of l_{obs} with the intersphere distance, l_{calc}, calculated using the diameter and concentration of the spheres is given in Table 2. The agreement between l_{obs} and l_{calc} is good when the experimental errors are taken into account.

Reflection spectroscopy of colloidal alloys of cationic spheres with cationic or anionic spheres

Let us discuss whether colloidal crystals (colloidal alloys, strictly speaking) form or do not from binary mixtures of cationic and anionic spheres in deionized suspensions. The mixture is composed of cationic spheres, anionic spheres, hydronium ions (H^+) and hydroxide ions. Colloidal crystals of CatD were mixed with colloidal crystals of CS83 spheres, keeping the concentration of the latter constant, 0.033 in volume fraction (Fig. 7).

Table 2 Observed and calculated intersphere distances

Sphere	ϕ	l_{obs} (nm)	l_{calc} (nm)		
			Face-centered cubic	Body-centered cubic	Simple cubic
CatA	0.096	420	485	470	430
CatD	0.094	400	400	380	355
CatD	0.142	380	350	335	310
CatD	0.236	325	290	280	260
CatD	0.321	310	260	255	235

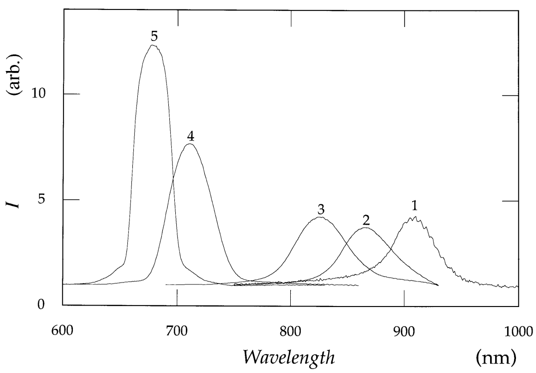


Fig. 6 Reflection spectra of cationic colloidal crystals at 25 °C. CatA, $\phi = 0.096$ (*curve 1*), CatD, $\phi = 0.094$ (*curve 2*), CatD, $\phi = 0.142$ (*curve 3*), CatD, $\phi = 0.236$ (*curve 4*), CatD, $\phi = 0.321$ (*curve 5*)

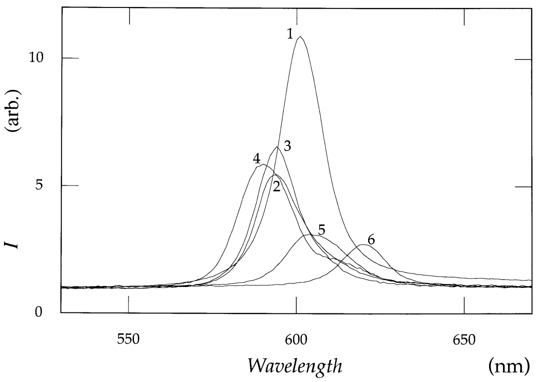


Fig. 7 Reflection spectra of colloidal alloys of CatD and CS83 at 25 °C. $\phi_{\mathrm{CS83}} = 0.033$. $\phi_{\mathrm{CatD}} = 0$ (*curve 1*), $\phi_{\mathrm{CatD}} = 0.00017$ (*curve 2*), $\phi_{\mathrm{CatD}} = 0.00055$ (*curve 3*), $\phi_{\mathrm{CatD}} = 0.0017$ (*curve 4*), $\phi_{\mathrm{CatD}} = 0.0055$ (*curve 5*), $\phi_{\mathrm{CatD}} = 0.011$ (*curve 6*)

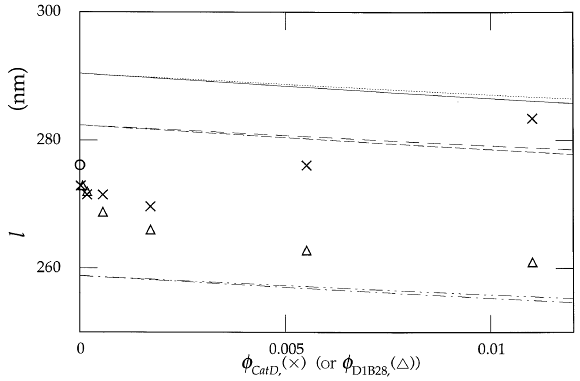


Fig. 8 Intersphere distance of colloidal alloys of CatD and CS83 (*crosses*) and D1B28 and CS83 (*triangles*) as a function of CatD or D1B28 concentration at 25 °C. $\phi_{CS83} = 0.033$, CS83 only (*circles*). CatD + CS83: ____ calculated, face-centered cubic; ----- body-centered cubic; – · – · – simple cubic. D1B28 + CS83 ..... calculated, face-centered cubic; - - - - body-centered cubic; – ·· – ·· – simple cubic

Surprisingly, sharp reflection peaks, which demonstrate the existence of the crystalline order, were observed when the ratio, x, of the volume fraction of the cationic spheres against the sum of both the cationic and the anionic spheres was smaller than about 0.3. We first expected that the strong association by the electrostatic attraction between cationic and anionic spheres leads to aggregation and that crystal ordering never occurs in the presence of even small amounts of cationic spheres.

For comparison, the reflection spectra were taken for a mixture of CS83 (anionic silica spheres) and anionic polystyrene spheres, D1B28 (212 nm in diameter). Surprisingly, a crystalline structure was formed only when x was smaller than 0.3. In other words, there was no difference in the stability of the crystal for the mixtures between spheres of like and unlike charge. The nearest-neighbor intersphere distance, l, is shown in Fig. 8 as a function of the concentration of cationic CatD spheres and the corresponding anionic spheres, D1B28. l first decreased slightly as the concentration of CatD or D1B28 increased in the range of sphere concentrations below 0.002 in volume fraction. This is explained by the fact that the total number of spheres in the cell increases with the concentration of the added spheres. The calculated l values for the binary mixtures are given by

$$l_{\mathrm{calc,fcc}} = \left\{ \left[\phi_1 / \left(0.74 d_1^3 \right) \right] + \left[\phi_2 / \left(0.74 d_2^3 \right) \right] \right\}^{-1/3} \quad (3)$$

for the fcc lattice,

$$l_{\mathrm{calc,bcc}} = \left\{ \left[\phi_1 / \left(0.68 d_1^3 \right) \right] + \left[\phi_2 / \left(0.68 d_2^3 \right) \right] \right\}^{-1/3} \quad (4)$$

for the bcc lattice and

$$l_{\mathrm{calc,sc}} = \left\{ \left[\phi_1 / \left(0.52 d_1^3 \right) \right] + \left[\phi_2 / \left(0.52 d_2^3 \right) \right] \right\}^{-1/3} \quad (5)$$

for the simple cubic lattice. Here, subscripts 1 and 2 indicate the two kinds of spheres in the mixtures. Interestingly, at higher amounts of CatD added, the intersphere distance increased, whereas the distance decreased on the addition of D1B28 (Fig. 8). When the cationic spheres are mixed with CS83 spheres, weak association (or aggregation) takes place between cationic and anionic spheres. It should be noted here that a peak shift toward longer wavelengths was often observed for colloidal crystals of polydispersed colloidal spheres.

On the other hand, when spheres of like charge are mixed, l_{obs} decreased further as the concentration of the added spheres increased. This is due to the fact that no aggregation took place when the spheres of like charge were mixed and the intersphere distance decreased as the concentration of the other type of spheres increased.

The reason why the colloidal alloys form from mixtures of spheres of unlike charge is not clear yet. However, it is plausible that the "segregation" effect took place between the spheres of unlike charge, since the size of the cationic CatD spheres is about twice that of the anionic CS83 spheres [28, 29, 30, 31]. Owing to segregation effects, regions of colloidal crystals of small and large spheres coexist separately.

Conclusions

It is established that cationic colloidal spheres form colloidal crystals. Intersphere repulsion forces which arise from the electrostatic repulsion of the electrical double layers especially in the deionized system and also from the thermal fluctuation of the colloidal spheres are essential for colloidal crystallization. The repulsion forces are long-ranged and there is no difference between the cationic or anionic spheres. Formation of the colloidal alloys for mixtures of cationic spheres and anionic colloidal silica spheres was observed for the first time.

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