July, 1988] © *1988 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***61***, *2287—2290 (1988)* 2287

Mixed Colloidal Dispersions of Silica and Hematite

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(Received November 4, 1987)

The colloidal behavior of mixed dispersions containing hematite (diameter=138.9 nm) and silica (diameter=7.0 nm) has been studied by measuring the stability ratio, zeta potential, and particle size. When various particle numbers of silica were added to a constant particle number of hematite, different colloidal behavior was observed, depending on the pH. In a pH region where the two solids were oppositely charged, hematite particles showed a dispersion-coagulation-redispersion process with increasing particle number of silica, resulting in a coating layer of silica particles on the hematite surface. On the other hand, in a region where both solids were negative, the addition of silica enhanced the stability of the hematite.

When an aqueous colloidal dispersion contains solid particles of more than one kind, it is expected that the various solids will have different surface charges in the solution and complicate interactions between their solids occur. Under these conditions, hetero coagulation due to the interaction of opposite charges can take place. The experimental testing of the theories of hetero coagulation proposed by Derjaguin,[1] Hogg et al.,[2] and Wiese and Healy[3] has been attempted by several workers.[4–6]

The phenomenon of hetero coagulation can be applied in the preparation of oxide supported metal catalysts. An oxide and an ultra fine particle of catalyst are mixed in aqueous solution. By adjusting the pH so that the oxide and the particle of catalyst are oppositely charged, it is possible to produce a well-spaced layer of catalyst particles on the oxide particle. However, many hetero coagulation studies have been limited to solid particles having similar particle size.

The aim of this work is to study the colloidal dispersion behavior of mixed silica and hematite spherical particles with narrow size distribution and a considerable difference in particle size. The mixed colloidal properties were characterized by measurement of the zeta potential, the stability ratio and the particle size.

Experimental

Materials. As solid particles, hematite, and silica were used.

Spherical hematite particles with a narrow size distribution were prepared by essentially the same procedure as Matijević and Scheiner[7] described. The 2×10^{-2} mol dm^{-3} of $FeCl_3$ aqueous solution was adjusted to pH 3.1 with HCl. The solution was then aged for 24 h at 100 °C. After cooling to room temperature, the collected particles were washed several times with aqueous $HClO_4$ solution (pH 3.1) to remove chloride and iron(III) ions. The particles were then redispersed in ion-exchanged water to be used as a stock sol. The final stock sol had a concentration of 3.20 mg cm^{-3}, as determined directly by dry-weight measurement. The particle diameter was determined to 138.9 nm by transmission electron microscopy.

Well monodispersed spherical silica was obtained from Japan Aerosil Co. The particle diameter was determined to 7.0 nm.

Procedure. Zeta potentials were measured using a Laser-Zee meter Model 500(Pen Kem Inc.).

The particle size of the mixed dispersion was measured using an Autosizer Model 700(Malvern Co., Ltd.).

Coagulation kinetics were followed using a standard turbidimetric technique,[8] in which the change of absorbance at 540 nm as a function of time was recorded continuously on a 220A Hitachi Spectrophotometer. As soon as the hematite sols had been mixed with the silica sols, the absorbance of the mixed dispersions was recorded and the initial slope of the absorbance vs. time curve was obtained. The stability ratio (W) was calculated from the ratio of the rapid-coagulation (k_0) to the slow-coagulation rate (k) of the sols:

$$W = k_0/k$$

The stability of the mixed dispersions was also evaluated from the magnitude of the absorbance after 12 h standing of the mixed dispersions, where the absorbance was also taken at 540 nm.

All measurements were carried out in 1×10^{-2} mol dm^{-3} sodium nitrate to keep the ionic strength constant. Nitric acid and sodium hydroxide were used to adjust the pH of these dispersions.

Results and Discussion

Figure 1 shows the zeta potentials of hematite and silica as a function of the pH and indicates that their isoelectric points are 7.9 for hematite and 3.1 for silica. To elucidate the behavior of colloidal mixed dispersions of hematite and silica, four different pH values were selected: pH 3.0, 4.0, 5.5, and 10.0. At pH 3.0, the zeta potential of the silica was almost zero, while that of the hematite was positive. At pH 4.0 and 5.5, the hematite and silica had opposite zeta potential values and at pH 10.0, they both showed negative zeta potentials. By using mixtures of these monodispersed particles with different isoelectric points, it is possible to study the interactions of dissimilar electrical double layers around spherical particles with different particle size.

The stability ratio (W) and absorbance of the mixed dispersions are shown in Fig. 2 in which the various

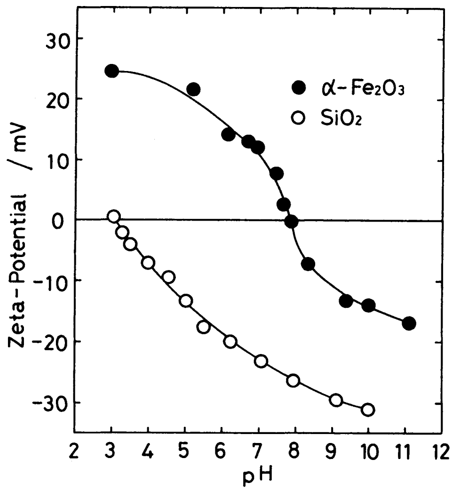

Fig. 1. Zeta potentials of hematite and silica as a function of pH.

particle numbers of silica are added to a constant particle number of hematite at four different pH. Here, the turbidity was mainly attributed to hematite particles because the particle size of the silica was too small to provide an appropriate turbidity value. Further, the silica particles were very stable over the entire pH region. In the case of hematite alone, the stability ratio was almost one at pH 3.0 and 10.0, whereas that at pH 4.0 and 5.5 was more than eight. When silica particles were added to the hematite dispersion system, the stability ratio varied, depending on the pH. At pH 3.0, the stability ratio was almost constant, i.e., one, against various particle numbers of silica. On the other hand, at pH 4.0 and 5.5, the stability ratio decreased upon addition of the silica particles. Further addition of silica considerably increased the stability ratio and a maximum stability ratio at pH 5.5 was greater than that at pH 4.0. At pH 10.0, the stability ratio upon addition of the silica increased gradually up to a certain amount of added silica (ca. 180). Thus, hematite particles exhibited the

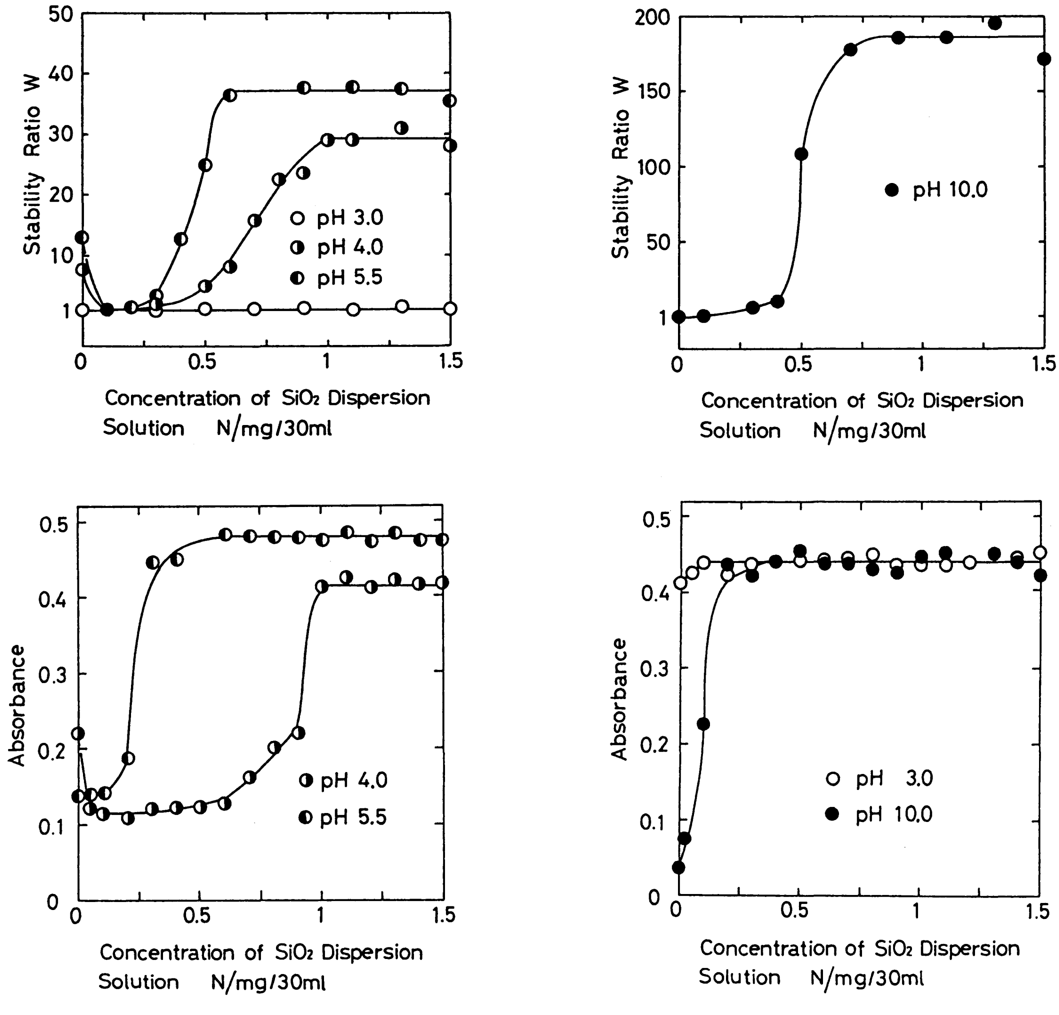

Fig. 2. Variations of stability ratio and optical density in mixed dispersion of hematite and silica with increasing amounts of silica: amount of hematite, 0.64 mg/30 ml.

dispersion–coagulation–redispersion process on addition of silica at pH 4.0 and 5.5. The optical density of the mixed dispersion after 12 h standing was also measured to evaluate the colloidal stability of mixed dispersion. The result is also shown in Fig. 2 which indicates that the behavior of the optical density upon addition of silica almost coincides with the stability ratio except at pH 3.0. At pH 3.0, the optical density of the mixed dispersions was high upon addition of silica although the stability ratio was almost unity. In order to clarify the relationship between the pH and the zeta potential in the mixed dispersion, the zeta potential of the mixed dispersion was plotted as a function of pH (Fig. 3). It can be seen that the zeta potential is significantly altered upon addition of silica at different pH. Further, it is noteworthy that the zeta potential values of the mixed dispersion upon addition of more than 0.5 mg/30 ml of silica at each pH coincide with that of silica alone at the corresponding pH. This implies that a coating layer of silica particles is formed on the hematite particle.

The change in mean particle size of the mixed dispersions is shown in Fig. 4. Here, the mean particle size is mainly considered to be due to hematite or silica coated hematite. At pH 4.0, 5.5, and 10.0, the behaviors in mean particle size of mixed dispersions are in fair agreement with the stability ratio and optical density. However, at pH 3.0, the mean particle size hardly changed upon addition of silica. This can be interpreted as follows: since the silica particles form a three-dimentional chain structure throughout the volume of the aqueous solution, this structure can generate a well dispersion state of hematite. The rate of structure formation will be remarkedly influenced by the time which the silica particles exist in aqueous solution. That is, during the measurement of the

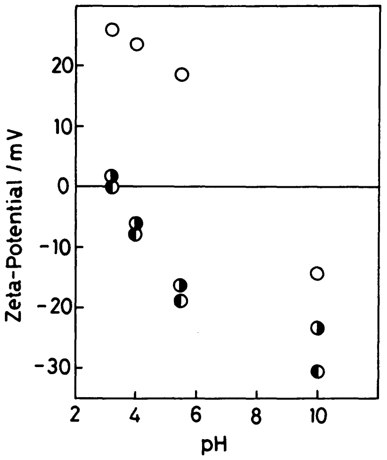

Fig. 3. Variation of zeta potential of mixed dispersion of hematite and silica with different additive amounts of silica at pH 3.0, 4.0, 5.5, and 10.0: concentration of silica; (○) 0, (◑) 0.1, (◐) 0.5 mg/30 ml.

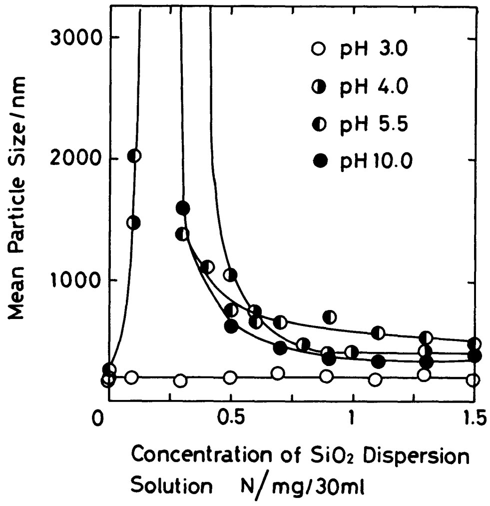

Fig. 4. Mean particle size of mixed dispersion of hematite and silica as a function of the concentration of silica: amount of hematite, 0.64 mg/30 ml.

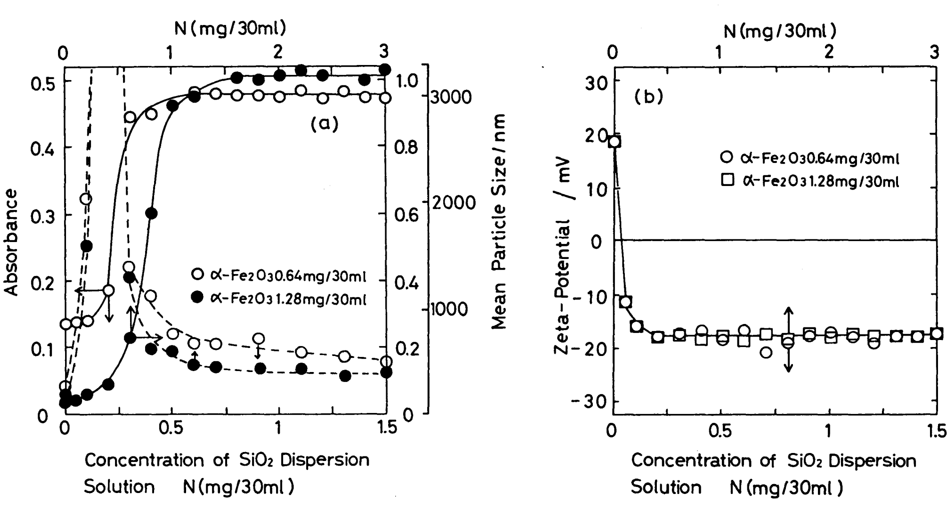

Fig. 5. Effect of amount of hematite on mixed dispersion of hematite and silica: (a) absorbance; solid line, mean particle size; dotted line (b) zeta potential.

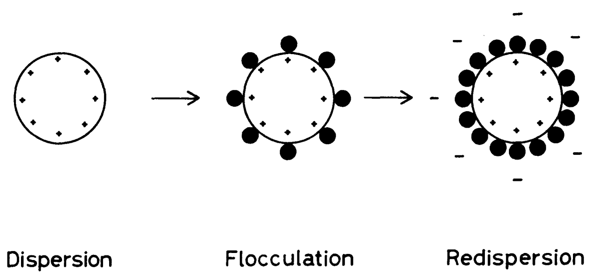

Fig. 6. A model for mechanism of coagulation and dispersion of mixed hematite and silica.

stability ratio, the structure formation is not fully established so that the stability ratio remains unity. On the other hand, during the measurement of the mean particle size and absorbance, sufficient time will be provided for the structure formation to stabilize the hematite particles.

Further, the amounts of hematite was varied and its effect on the mixed dispersion was studied. The result is shown at pH 5.5 in Fig. 5. Even using different amounts of hematite, the behavior in zeta potential, particle size and absorbance at pH 5.5 was similar to the result described before. Similar trends were observed for the other pH.

From the above results, the following mechanisms of mixed dispersions are proposed: at pH 4.0 and 5.5, silica particles are adsorbed on hematite particle due to electrical attraction forces since silica and hematite particles are oppositely charged. In the region where the zeta potential of the mixed dispersion becomes zero and the mean particle size becomes significantly large, the mixed dispersion leads to a coagulated state. On further addition of silica, a significant amount of silica particles are adsorbed on to the hematite particle and both the zeta potential and the mean particle size decrease appreciably, resulting in redispersion of the mixed coagulate. This model is presented in Fig. 6. Similar behavior was reported with latex and silica mixtures where the much smaller silica particles also adsorbed on the latex to form a monolayer and caused the latex to behave like a silica sol.[9)]

In conclusion, when hematite and silica are oppositely charged, silica particles with a small particle size are adsorbed on hematite particles, resulting in coagulation of the hematite particles. Upon further addition of silica the coagulated hematite particles are redispersed due to considerable adsorption of silica particles on hematite. This mechanism is demonstrated by measurements of the stability ratio, the zeta potential and the particle size.

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