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ORIGINAL CONTRIBUTION

R. Sprycha
H.T. Oyama
A. Zelenev
E. Matijević

Characterization of polymer-coated silica particles by microelectrophoresis

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R. Sprycha[1] · H.T. Oyama
A. Zelenev · Prof. Dr. E. Matijević (✉)
Center for Advanced Materials Processing
Clarkson University
Box 5814
Potsdam, New York 13699-5814, USA

[1]*Current address:*
Sun Chemical Corporation
631 Central Avenue
Carlstadt, New Jersey 07072, USA

Abstract Electrophoretic mobility measurements have been used to characterize monodispersed colloidal particles of silica, silica coated with alumina (cores), of these cores incorporating a dye (pigments), and finally of pigments coated with polymers. The latter consisted of poly(divinylbenzene), of poly(vinylbenzyl chloride), and of their copolymers, synthesized directly on the core or pigment particles, with and without subsequent sulfonation.

Key words Colloidal pigments – electrophoresis – pigments – polymer-coated particles – silica/alumina/dye particles

Introduction

Amorphous spherical monodispersed silica particles can be manufactured in a relatively simple manner and in large quantities. This material may be used directly or modified as needed for given applications. Due to their optical and morphological properties, such dispersions are particularly suitable for the preparation of high quality reproducible pigments [1–3]. The latter are obtained by the interaction of silica with anionic or cationic dyes, either by incorporation or adsorption of the latter, but the core materials may have to be properly chemically modified for this purpose.

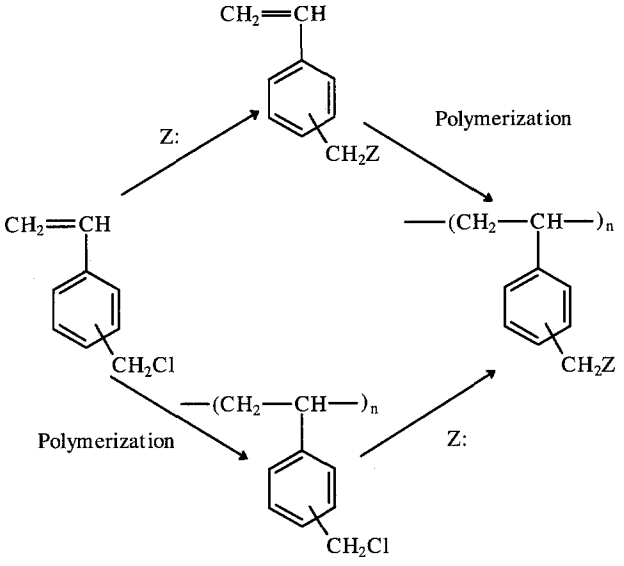
Some of the dyes bound to silica particles can leach out, when the pigments are dispersed in certain solvents. The extent of this effect depends both on the nature of the dye and on the dispersing medium. To prevent this undesirable behavior, the pigment particles so prepared can be coated with a protective polymer layer, such as cross-linked poly(divinylbenzene) (polyDVB). While the shell may be permeable to small inorganic ions, the dye molecules are too large to diffuse through the polymer [4].

It is well known that surface characteristics of silica and other oxides can be substantially altered by the adsorption of inorganic or organic (including polymer) species as evidenced by electrophoresis [5–8]. Indeed, in the case of high surface coverage, the mobility of such particles may be the same as observed for the pure adsorbate [5].

In a previous study, it was shown that spherical silica particles coated with an aluminum hydrous oxide layer can be encapsulated with polyDVB [4]. In order to produce the polymer coating, the inorganic cores were pretreated with a coupling agent, 4-vinylpyridine (4VP), then divinylbenzene (DVB) and a radical initiator were admixed in hot mineral spirits (MS). In the present work, this procedure was modified in order to prepare a functionalized particle surface by introducing a reactive co-monomer, vinylbenzyl chloride (VBC).

The benzylic chloride group is easily displaced by many nucleophilic reagents (Z:) under mild conditions, either prior to polymerization [9], or even as a post-

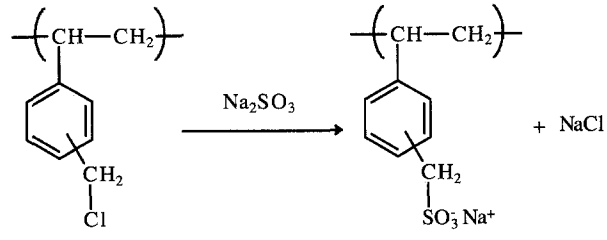
treatment of polymerized materials [10], according to



This procedure should keep the core materials, such as composite pigment particles, unchanged during the process of polymerization on their surfaces.

There are many methods available to transform the CH_2Cl group to other forms, such as $-CH_2CN$, $-CH_2N{=}C{=}S$, $-CH_2COOH$, $-CH_2OH$, $-CH_2OR$, $-CH_2NH_2$, and $-CH_2N^+(CH_3)_3Cl^-$. Therefore, once the method to include VBC as comonomer in the encapsulating procedure is established, the surface of polymer coated particles may be easily modified to achieve desirable characteristics due to these functional groups.

The aim of this study is to establish the properties of polymer coatings on silica through their electrophoretic behavior. For this purpose, the monodispersed silica particles were first covered with aluminum hydrous oxide, and then with a polymer shell which was synthesized from DVB and VBC using two kinds of coupling agents, i.e., 4-vinyl-pyridine (4VP) and 1-vinyl-2-pyrrolidone (VPo). After the completion of the encapsulation reaction, the polymer coated particles were sulfonated in a sodium sulfite (Na_2SO_3) solution as follows [10]:



Polymer coated particles prepared under different conditions were characterized by electrophoresis, microscopic observation, and thermogravimetry.

Experimental

Reagents

4-Vinylpyridine (4VP), divinylbenzene (DVB), benzoyl peroxide (BP), mineral spirits (MS), 1-vinyl-2-pyrrolidone (VPo), 3-vinylbenzyl chloride (VBC), and sodium sulfite (Na_2SO_3) were obtained from Aldrich. The hydroquinone derivatives and p-tert-butylcatechol inhibitors in vinyl monomers were removed using an ion exchange resin prior to the polymerization reaction. Commercial DVB consisted of a mixture of isomers (55%), while the remainder was mainly 3- and 4-ethylvinylbenzene. The VBC was also composed of an isomer mixture of (70%) 3- and (30%) 4-vinylbenzyl chloride.

Core and pigment particles

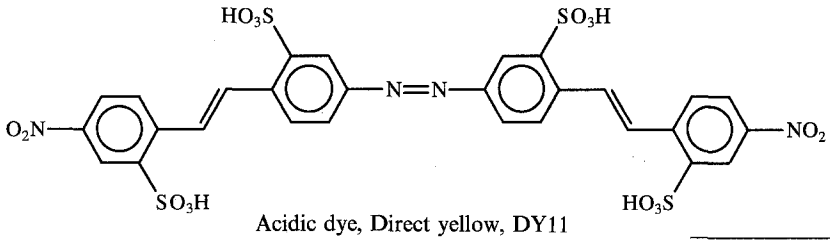
Silica coated with aluminum hydroxide [$SiO_2/Al(OH)_3$]

The monodispersed silica particles of 650 nm in diameter were obtained by hydrolysis of tetraethylorthosilicate (TEOS) in ethanol-ammonia solution, as described elsewhere [11,12]. To prepare core materials, these particles were coated with aluminum hydroxide by treating the silica suspension with an aqueous solution containing $AlK(SO_4)_2$ and $Al(NO_3)_3$ in the presence of urea at elevated temperature by the procedure given in ref [4]. Once the process was completed, the solids were rinsed repeatedly with distilled water and then dried in the oven.

Pigmented form of inorganic particles with Direct Yellow 11, DY11 (Dye Pigment)

An acidic dye, Direct Yellow 11 (DY11) was chosen to prepare the pigmented form of inorganic particles (see structure on the next page).

To incorporate this dye into the core particles (silica coated with aluminum hydroxide, $SiO_2/Al(OH)_3$), 5 g of these solids were dispersed in an aqueous solution containing $\sim 10^{-3}$ mol dm^{-3} DY11 in an ultrasonic bath. The resulting colored pigment particles were then separated by centrifugation at 3000 rpm for 20 min and washed several times with distilled water.



Acidic dye, Direct yellow, DY11

Encapsulation procedures

Coating with poly(divinylbenzene) and poly(vinylbenzyl chloride)
$SiO_2/Al(OH)_3$ coated with poly(DVB) [$SiO_2/Al(OH)_3$/poly(DVB)]

Forty mg of $SiO_2/Al(OH)_3$ particles were mixed with 2.4×10^{-3}cm^3 of 4VP and dispersed in 4 cm^3 of MS with 1.2×10^{-2} cm^3 of DVB and 18 mg of BP. The entire system was heated at 110 °C for 24 h. The so obtained particles were collected by filtration and washed with hexane and an ethanol:water (1:1 vol) mixture.

"DY11 pigment" coated by poly(DVB) [DY11/poly(DVB)]

"DY11 pigment" was encapsulated by the same method as the core particles, i.e., $SiO_2/Al(OH)_3$/poly(DVB).

$SiO_2/Al(OH)_3$ coated with poly(VBC) [$SiO_2/Al(OH)_3$/poly(VBC)]

The $SiO_2/Al(OH)_3$ was encapsulated by VBC under essentially the same conditions as those described as $SiO_2/Al(OH)_3$/poly(DVB), except that one sample was prepared with 18 mg of BP, while the other was synthesized without BP.

Coating by (DVB-VBC) copolymer and subsequent sulfonation

Before proceeding to the A series (see below), in which VBC was polymerized with a cross-linking agent, DVB, in the presence of the inorganic cores, preliminary tests were carried out using the following conditions: 40 mg of $SiO_2/Al(OH)_3$ were mixed with 2.4×10^{-3} cm^3 of 4VP and dispersed in 4 cm^3 of MS with 6×10^{-3} cm^3 of DVB and 18 mg of BP. The entire system was heated at 110 °C for 3 h and then 6×10^{-3} cm^3 of VBC was added and the reaction continued for another 24 h. The so obtained particles were uniformly coated as illustrated in the transmission electron micrograph (Fig. 1).

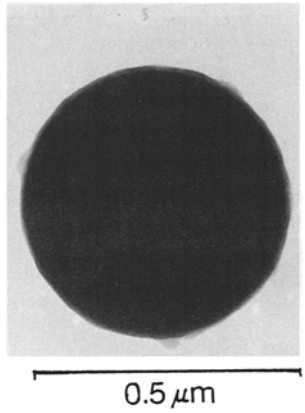


Fig. 1 Transmission electron micrograph (TEM) of a $SiO_2/Al(OH)_3$ core particle encapsulated by the (DVB–VBC) copolymer

The coating experiments of the $SiO_2/Al(OH)_3$ cores with DVB and VBC were carried out by three different methods as follows:

A series

In this series 120 mg of core [$SiO_2/Al(OH)_3$] particles mixed with 7.2×10^{-3} cm^3 of 4-vinylpyridine (4VP) were dispersed in 8 cm^3 of mineral spirits (MS) with 1.2×10^{-2}cm^3 of divinylbenzene (DVB), and then heated at 110 °C under stirring. After the reaction was carried out for 6 h, additional 2×10^{-3}cm^3 of DVB and 1.2×10^{-2} cm^3 of VBC were admixed and then kept at 110 °C for 18 h. The so obtained solids were filtered and washed with hexane and an ethanol:water (1:1 by vol) mixture (Sample A_0).

To sulfonate the polymer layer, 20 mg of coated particles (A_0) were dispersed in 4 cm^3 of an aqueous solution containing 17 mg Na_2SO_3 and reacted at 25 °C (Sample A_s–1), 45 °C (A_s–2), and 65 °C (A_s–3) for 24 h under stirring. The resulting dispersions were centrifuged at 4000 rpm for 15 min and the supernatant solutions were examined by UV spectroscopy to check whether there was an absorption band at 254 nm, which would indicate the existence of the sulfonated polymer detached from the coated particle surface. The settled solids were purified by rinsing with water, after they had been repeatedly dispersed in an ultrasonic bath, and then separated in an ultracentrifuge.

B series

The procedure was essentially the same as in series A, except that the timing of the addition of the second batch of DVB and VBC was varied. Sixty mg of $SiO_2/Al(OH)_3$ cores mixed with 3.6×10^{-3} cm^3 of 4VP were dispersed in 4 cm^3 of MS with 6×10^{-3} cm^3 of DVB and heated at 110 °C under stirring. After the reaction was carried out for a given time as indicated in Table 1, additional 1×10^{-3} cm^3 of DVB and 6×10^{-3} cm^3 of VBC were added and then the entire system was kept at 110 °C for another 24 h.

In order to examine the amount of the poly(DVB) deposited by the first step reaction, a parallel experiment was carried out in each case without the second addition of monomers. The so obtained materials were analyzed by thermogravimetric analysis (TGA), which yielded the amounts of the polymers deposited on the inorganic particles by the first step alone and by the complete synthesis.

Transmission electron microscopy (TEM) observations of samples of the B series confirmed that all particles were uniformly coated by the polymer. Figure 2 compares the amount of deposited (DVB–VBC) copolymer by the second-step reaction with the weight of polyDVB alone generated by the first step reaction (relative to the total particle weight), as determined by the TGA. It is apparent that the first coating using DVB was essentially completed within 12 h with ~4 wt% of deposited polymer.

To sulfonate coated particles synthesized by the two-step process, 20 mg of solids were dispersed in 4 cm^3 of water containing 17 mg of Na_2SO_3 and heated at 70 °C for 24 h. The sulfonated products denoted B_s-1 through B_s-6 refer to original samples B_o-1 through B_o-6 (Table 1).

C series

In this series, 1-vinylpyrrolidone (VPo) was used instead of 4VP as a coupling agent. Six hundred mg of $SiO_2/Al(OH)_3$ cores premixed with 5.4×10^{-2} cm^3 of VPo were dispersed in 60 cm^3 of MS by sonication and then 1.35×10^{-1} cm^3 of VBC, 4.5×10^{-2} cm^3 of DVB, and 75 mg of BP were added. The entire system was heated at 110 °C for 24 h under stirring. After completion of the coating reaction, the particles were washed with hexane and an ethanol:water (1:1 by vol) mixture (Sample C_o).

The polymer coated particles were sulfonated under different conditions, as shown in Table 2. Thirty mg of sample C_o were dispersed by sonication in 4 cm^3 of water or in a mixture of water and acetone, which contained 40 mg of Na_2SO_3. The sulfonation reaction was carried out at 25 ° or 55 °C for 40 h. These sulfonated particles were denoted as samples C_s-1 through C_s-6 (Table 2).

Table 1 Encapsulation of alumina-coated silica with the DVB/VBC copolymer by the procedure of series B

Sample	B_o-1	B_o-2	B_o-3	B_o-4	B_o-5	B_o-6
Reaction time before the second addition of DVB-VBC (hours)	0	3	6	12	18	24

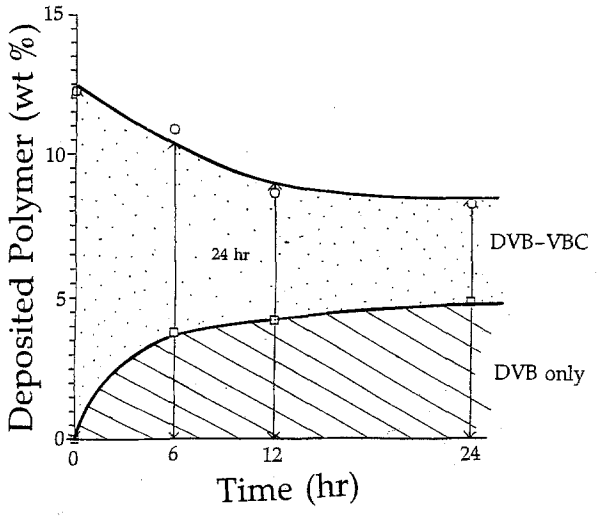


Fig. 2 The weight percent of deposited polymers relative to the total weight of the coated particles produced by a two-step process (Table 1). The amounts of deposited polymers synthesized by the first step (□, DVB alone), when the reaction was carried out for times as given on the abscissa. The total amounts of deposited polymers by the first and the second reactions; the second step reaction (DVB and VBC) carried out for an additional 24 h after completion of the first step reaction is shown by ○

Poly(DVB) latex

Poly(DVB) latex was prepared as a reference material. Into 300 cm^3 of MS were added 0.6 cm^3 of 4VP, 4 cm^3 of DVB,

Table 2 Sulfonation conditions of polymer-coated particles, sample C_o

Sample	Sample C_o (mg)	Na_2SO_3 (mg)	H_2O (cm^3)	Acetone (cm^3)	Temp. (°C)
C_s-1	30	40	4.0	0	55
C_s-2	30	40	3.5	0.5	55
C_s-3	30	40	3.0	1.0	55
C_s-4	30	40	4.0	0	25
C_s-5	30	40	3.5	0.5	25
C_s-6	30	40	3.0	1.0	25

Reaction time in all cases was 40 h.

and 1.35 g of BP and heated at 110 °C for 24 h. The particles so obtained were collected by filtration and washed with hexane and an ethanol:water (1:1 by vol) mixture.

Techniques

The polymer coating was inspected by transmission electron microscopy (TEM). Electrophoretic mobility was measured with both the DELSA 440 (Coulter Electronics) and PenKem 3000 systems, keeping the ionic strength constant at 1×10^{-3} mol dm^{-3} (KCl).

For the thermogravimetric analysis (TGA), each sample was heated from 80 °C to 900 °C at a rate of 10 °C/min in air. The net mass of the polymer on inorganic particles was estimated by subtracting the weight loss of the core materials from the weight change of the coated particles, taking the dehydration of the core particles into account.

Results

The electrophoretic mobility of monodispersed silica particles as a function of the pH in 1×10^{-3} mol dm^{-3} KCl yields the isoelectric point (i.e.p.) at pH = 3.5 (Fig. 3), in agreement with the literature data [1, 13]. It was found that the i.e.p. of silica in the presence of so-called indifferent electrolytes (e.g., KCl) was independent of the electrolyte concentration [8].

The same figure also shows the electrophoretic mobilities as a function of the pH of: a) silica coated with aluminum (hydrous) oxide, $SiO_2/Al(OH)_3$, b) $SiO_2/Al(OH)_3$ presaturated in $Al(OH)_3$, and c) pure aluminum (hydrous) oxide, all in the presence of 1×10^{-3} mol dm^{-3} KCl. The i.e.p. of the pure $Al(OH)_3$ was at pH = 9.2, which is characteristic of this compound [14, 15], while for $SiO_2/Al(OH)_3$ in the electrolyte solution presaturated with $Al(OH)_3$, it was at pH = 6.5. However, the same $SiO_2/Al(OH)_3$ in 1×10^{-3} mol dm^{-3} KCl exhibited three different values of the i.e.p: at pH 6.2, 4.7, and 3.1.

Figure 4 displays analogous data for the pure poly(DVB) latex, for $SiO_2/Al(OH)_3$ core particles coated by poly(DVB), [$SiO_2/Al(OH)_3$/poly(DVB)], for core particles with the incorporated dye, Direct Yellow 11, as well as for the latter pigment coated with poly(DVB). The dye-containing particles remain negatively charged (no i.e.p.) over the entire pH range, while the same sample coated by poly(DVB) showed an i.e.p. at pH ~ 4.5. Moreover, the i.e.p. for $SiO_2/Al(OH)_3$/poly(DVB) was at pH = 6.6, which was almost the same as that of the poly(DVB) latex.

The electrokinetic behavior of particles of the A series is shown in Fig. 5. The coated particles before sulfonation (sample A_o) were positively charged over the entire pH region, while the sulfonation of the polymer coatings introduced negative groups resulting in the charge reversal from positive to negative at appropriate pH values, which depended on the reaction temperature of sulfonation; the lowest value was observed with systems produced at the highest temperature, i.e., 65 °C.

Fig. 3 Electrophoretic mobility as a function of the pH of silica particles (●); silica particles coated with aluminium (hydrous) oxide, $SiO_2/Al(OH)_3$ (○); $SiO_2/Al(OH)_3$ in the solution presaturated with aluminium hydroxide (△); and pure $Al(OH)_3$ (□), all at 0.001 mol dm^{-3} KCl

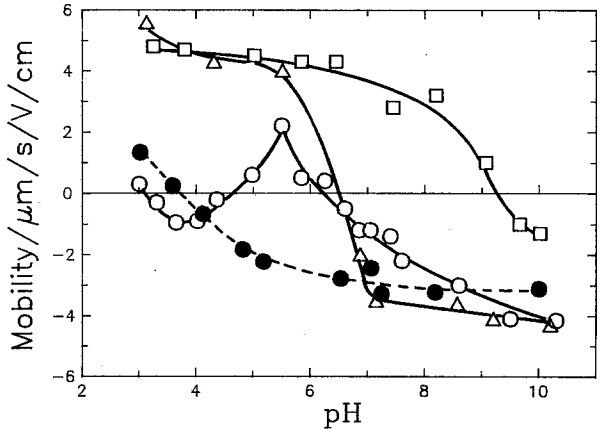
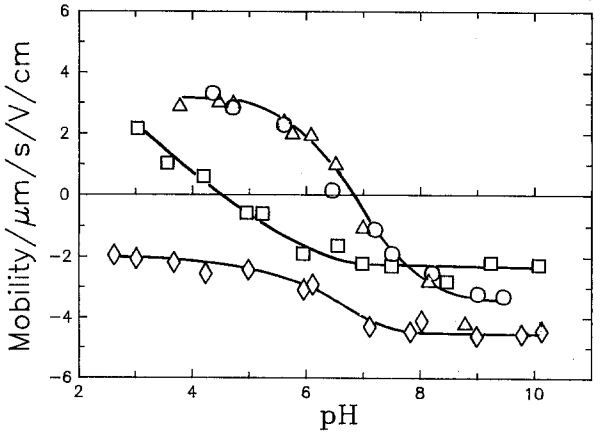


Fig. 4 Electrophoretic mobilities as a function of the pH of poly(DVB) latex (○); of $SiO_2/Al(OH)_3$ coated with poly(DVB) [$SiO_2/Al(OH)_3$/poly(DVB)] (△); of the cores with incorporated dye DY11 (◇); and of the same pigment coated by poly(DVB) (□), all at 0.001 mol dm^{-3} KCl



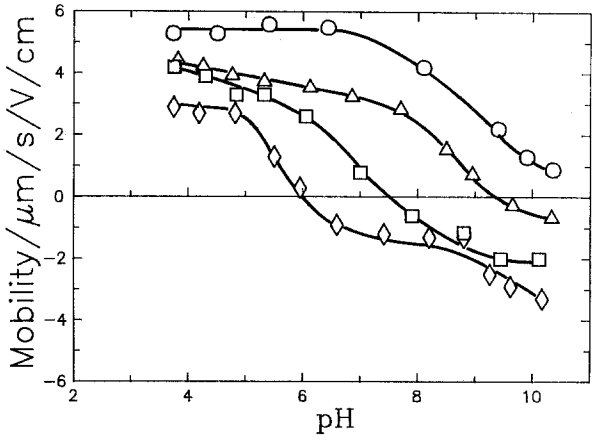


Fig. 5 Electrophoretic mobilities as a function of the pH of samples of the A series. Unsulfonated, sample A_0 (○); sulfonated samples; A_s-1 (△); A_s-2 (□); and A_s-3 (◇), all at 0.001 mol dm^{-3} KCl

In the B series, the inorganic cores were first coated with poly(DVB) and then a poly(VBC) shell was added onto the particle surface using different reaction conditions. This system was designed to prevent possible leaching of dyes from composite pigments by trapping their bulky molecules into the poly(DVB) network structure and simultaneously controlling the surface charge by the introduction of sulfonate groups at the outer layer after a nucleophilic displacement of the CH_2Cl group.

The effects of the sulfonation of two B_o samples (Table 1) on their electrophoretic behavior are displayed in Fig. 6. The mobilities of reference particles are not the same, because every sample was synthesized under different experimental conditions. After sulfonation, the mobilities are much lower and even charge reversal from positive to negative was observed; the i.e.p. of B_s-1 was at pH = 6.5 and that of B_s-5 was at pH = 5.9.

Electrophoretic mobilities of samples of the C_s series (Table 2), all shown to be negatively charged, were little affected by a change in the pH (Fig. 7). It is noteworthy that particles coated with the unsulfonated polymer also remained negatively charged even in acidic media.

Discussion

Extensive studies of the electrophoretic mobility and of the surface charge of silica in the presence of the so-called indifferent electrolytes showed that the i.e.p. and the point of zero charge (pzc) depended on the sample history, with most of the i.e.p. values ranging between pH = 2 and 4 [13, 14, 16]. The i.e.p. of the amorphous monodispersed silica used in this work was at pH ~ 3.5 and independent of the electrolyte concentration. The adsorption of ions or molecules at the solid/liquid interface affects the electrokinetic behavior of dispersed particles in general [17–20], and of silica in particular. In the latter case the effect of hydrolyzable ions, such as of aluminum, was especially pronounced [21, 22]. This cation can produce three charge reversal (CR) regions, yielding several isoelectric points, the first of which is characteristic of pure silica particles. The second is determined by the adsorption of hydrolyzed metal ions, and the third i.e.p. is due to the coating by the metal hydroxide nucleated on the core surface. When the coating is complete, the i.e.p. is the same as that of the coating material.

The results presented in Fig. 3 follow the same trends. Thus, the i.e.p. at pH ~ 3.1 corresponds to pure silica, after the coating of aluminum hydrous oxide was completely

Fig. 6 Electrophoretic mobilities as a function of the pH of unsulfonated sample B_o-1 (○) and of its sulfonated form, B_s-1 (●), of unsulfonated B_o-5 (□), and of its sulfonated form, B_s-5 (■), all at 0.001 mol dm^{-3} KCl

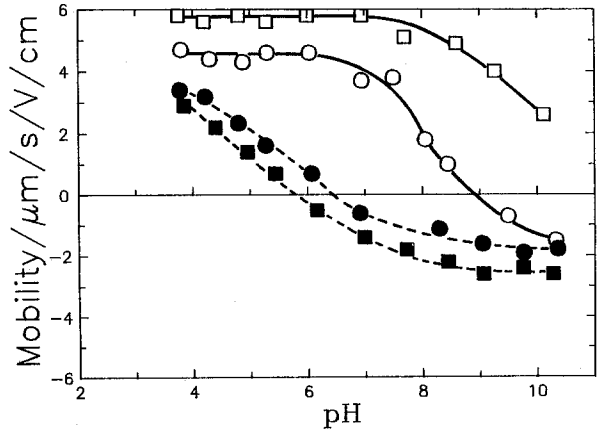
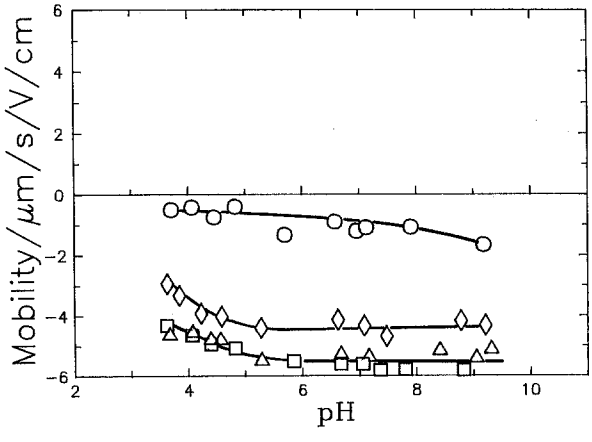


Fig. 7 Electrophoretic mobilities as a function of the pH of the samples of the C series: unsulfonated sample C_o (○); sulfonated samples C_s-1 (△); C_s-3 (□); and C_s-4 (◇), all at 0.001 mol dm^{-3} KCl



dissolved in acidic media. The second i.e.p. at pH 4.7 is most likely caused by the adsorption of the nonstoichiometric aluminum basic sulfate species of the composition $Al(OH)_{3-2x}(SO_4)_x$ on the surface of silica particles, while the last value (at pH 6.2) is characteristic of the fully coated silica particles with aluminum hydroxide which incorporates sulfate ions.

The mobility of $SiO_2/Al(OH)_3$ cores, dispersed in the electrolyte solution saturated with $Al(OH)_3$, exhibited only one i.e.p. (at pH ~6.5). Under these conditions the coating on the particles remains unchanged because the solution is already saturated with different aluminum species, which prevent dissolution of the coated layer. The reported i.e.p. of pure $Al(OH)_3$ is at pH ~9.2. The reason for the difference observed with the core particles used in this work is due to sulfate ions contained in their structure, which are known to lower the value of the i.e.p. The same effect was observed before with monodispersed chromium hydroxide particles precipitated in the presence of sulfate ions [23].

The synthesis of $SiO_2/Al(OH)_3$/poly(VBC) demonstrated that VBC could be used for encapsulation without BP in the same way as DVB at 110 °C. This finding represents an important advantage for the coating of pigments, because the possible decomposition of dye molecules by a radical initiator is avoided. It was also observed by TEM that the addition of the initiator reduces the thickness of the encapsulating poly(VBC).

The experiments with the series A (Fig. 5) indicated that the nucleophilic displacement is facilitated by an increase in temperature, when the sulfonation of the CH_2Cl group was carried out in an aqueous Na_2SO_3 solution for 24 h. The UV spectra of the Na_2SO_4 solution after the removal of the sulfonated particles showed an absence of the absorption band at 254 nm, implying that there was no polymer detached from the particle surfaces of samples A_s-1, A_s-2, or A_s-3 as a result of the sulfonation treatment. It would appear that the DVB co-monomer effectively fixes the sulfonated polymer chains onto the particle surface by crosslinkages. This finding is in agreement with previous reports showing that the surface charge of coated particles can be altered by introducing negative groups by functionalization of the polymer with subsequent sulfonation [24, 25].

The electrophoretic behavior of samples in the B series illustrated in Fig. 6 demonstrated that a longer polymerization time in the first step of the two-step encapsulation process produced higher positive charge of the coated particles. After the sulfonation of samples covered by the (DVB–VBC) copolymer, the mobilities became less positive and eventually underwent charge reversal to negative at a sufficiently high pH value. The shift in the i.e.p. was larger in the dispersion prepared with the longer polymerization time in the first step. This observation indicates that the surface charge properties of the sulfonated particles (B_s-series) are dominated by the VBC coating.

Figure 7 showed that the $SiO_2/Al(OH)_3$ particles encapsulated by (DVB–VBC) copolymer using VPo as a coupling agent (sample C_o) have very low negative mobilities over the entire pH region, which observation differes greatly from the results obtained with the analogous system using 4VP as a coupling agent.

In an attempt to swell the poly(VBC) layer and to facilitate the exchange of sulfate for chloride groups, acetone was added during the sulfonation process. The results in Fig. 7 indicate that the so treated sample C_s-3 had similar mobilities as samples C_s-1 sulfonated in the pure aqueous medium at the same temperature. Even an increase in the sulfonation temperature from 25 °C to 55 °C had an insignificant effect on the electrophoretic mobilities of the resulting particles (as seen by a comparison of the sample C_s-1 with C_s-4). Although the addition of acetone did not contribute much to an increase in the degree of sulfonation, it greatly facilitated the process of dispersing the hydrophobic coated particles in an aqueous solution.

The data displayed in Fig. 4 show that the DY11 containing pigment is negatively charged over the entire pH range, due to the strongly acidic nature of the dye that contains many sulfate groups. The same pigment coated with poly(DVB) exhibits that i.e.p. at pH ~4.5, which is somewhat lower than that of the poly(DVB) (pH ~6.5); apparently, the dye still has some effect on the surface charge characteristics despite the polymer coating.

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