p-Phenylenediammonium-Smectites as Adsorbents with Colorimetric Detection Ability for Phenols in Water

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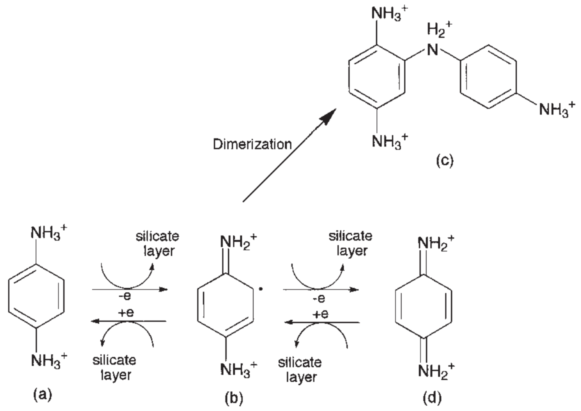
The ion exchange of *p*-phenylenediammonium and sodium-smectites (montmorillonite and synthetic saponite) resulted in the formation of *p*-phenylenediammonium radical cation and its dimer by the electron transfer from *p*-phenylenediammonium to smectites, as revealed by the color change (from colorless to green) as well as the visible absorption spectra. The *p*-phenylenediammonium-saponite thus obtained adsorbed phenols from aqueous solutions. The basal spacing of the *p*-phenylenediammonium-saponite increased upon the uptake of phenols, indicating a change in the microstructure. The uptake of phenols into the *p*-phenylenediammonium-saponite from aqueous solutions occurred through the formation of indoaniline dyes, as revealed by the color change from green to purple (for phenol) or purple-blue (for 2,4-dichlorophenol) as well as the absorption spectra. On the contrary, phenols were not intercalated into the interlayer space of the *p*-phenylenediammonium-montmorillonite.

There is a demand for materials with molecular recognition and separation abilities. The designing of adsorbents from inorganic[1,2] and organometallic[3] building units has thus been investigated. Organic modification of layered solids is a possible way of producing inorganic–organic hybrid materials, and nanoporous and hydrophobic properties have been imparted on the surface of smectites by cation exchange with organoammonium cations.[1,4,5] The resulting inorganic–organic hybrids have been applied as adsorbents for nonionic organic compounds from both vapor and water.[5,6] The combination of hosts with different layer charge densities and guests with different molecular geometries led to controlled adsorptive properties.[1,6–8] In addition to the nanostructures, the chemical interactions between adsorbates and organically modified smectites should play an important role in the adsorption of nonionic organic compounds.

Aliphatic ammonium ions have been extensively used to modify the surface properties of smectites.[6–9] On the contrary, there are relatively few examples of the adsorptive properties of smectites modified with aromatic ammonium ions[10–12] and the interactions between the interlayer aromatic ammonium ions and the organic nonionic species to be adsorbed have seldom been investigated. We have recently reported the adsorption behavior of phenols (phenol and 2,4-dichlorophenol) onto 1,1′-dimethyl-4,4′-bipyridinium (methylviologen: MV^{2+})-smectites (a natural montmorillonite (Kunipia F) and a synthetic saponite (Sumecton SA)) from aqueous solution.[13] The charge-transfer interactions between MV^{2+} and 2,4-dichlorophenol were thought to be a driving force for the adsorption as revealed by the color change in the MV^{2+}-saponite from colorless to yellow upon the adsorption of 2,4-dichlorophenol. We expect that the color-change signature upon the adsorption of a certain molecular species can be utilized as colorimetric sensing for the purpose of environmental pollutant detectors. In order to obtain adsorbents with better performances (such as clearer color-change, greater adsorption capabilities, and selective adsorption), efforts are being made by using clays with different origins and organic groups with different π-conjugated systems. In this paper, we report the adsorption of phenols (phenol and 2,4-dichlorophenol) from water on a natural montmorillonite (Kunipia F) and a synthetic saponite (Sumecton SA) modified with *p*-phenylenediammonium ions (abbreviated as PDA^{2+}, Scheme 1a).



Scheme 1. (a) PDA^{2+}, (b) PDA^{2+} radical cation, (c) PDA^{2+} radical dimer, and (d) *p*-benzoquinone diiminium ion.

Experimental

Materials. Na^+-montmorillonite (Kunipia F, obtained from Kunimine Ind. Co.) and a synthetic Na^+-saponite (Sumecton SA, obtained from Kunimine Ind. Co., synthesized by a hydrothermal reaction) were used as the host materials. Cation exchange capacities (CECs) of Na^+-montmorillonite and Na^+-saponite are 119 and 71 meq (100 g clay)$^{-1}$, respectively.[14] *p*-Phenylenediamine dihy-

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drochloride was purchased from Tokyo Kasei Ind. Co. and used as received.

Preparation of PDA^{2+}-Smectite Intercalation Compounds. PDA^{2+}-smectites were prepared from Na$^+$-montmorillonite and Na$^+$-saponite by cation exchange reactions with PDA^{2+} dichloride. An aqueous suspension (100 cm^3) of smectite (1.0 g) was mixed with an aqueous PDA^{2+} dichloride solution (100 cm^3) for 1 day, where the added PDA^{2+} dichloride amount was 5 times in excess of CEC. After the aqueous phase was separated by centrifugation, the solid product was washed with methanol until negative $AgNO_3$ test was obtained and subsequently dried under a reduced pressure.

Adsorption of Phenols. The adsorption isotherms of phenols (phenol and 2,4-dichlorophenol) for the PDA^{2+}-smectites were obtained as follows: the adsorbents (10 mg) were allowed to react with 50 cm^3 of aqueous solutions of phenols (pH = 7, 0.1–1.7 mmol dm^{-3}) in 50 cm^3 glass vessels for 1 day at room temperature under dark. The dissociation constants of phenols (9.84 for phenol[15] and 7.85 for 2,4-dichlorophenol[16]) and initial concentrations of aqueous phenols solutions show that the ionized fractions of phenols are in the ranges from 2×10^{-4} to 1×10^{-3} (molar ratio of phenolate ion to phenol) and from 2×10^{-3} to 1×10^{-2} (molar ratio of 2,4-dichlorophenolate ion to 2,4-dichlorophenol). Blank samples containing 50 cm^3 of aqueous solution, without adsorbents, were also prepared to estimate vaporization losses and the adsorption of phenols on the glass vessel. After the resulting solids were separated by centrifugation, the concentrations of the remaining phenol and 2,4-dichlorophenol in supernatant were determined by high-performance liquid chromatography (HPLC). Concentrations of aqueous solutions of phenol and 2,4-dichlorophenol were calculated from the measured HPLC peak areas using a series of external standards. Desorption of PDA^{2+} adsorbed on smectites was not observed, as evidenced by the absence of PDA^{2+} in supernatant by HPLC.

Preparation of Aqueous Suspensions for Vis Spectra. Visible absorption spectra were recorded for the suspension containing the PDA^{2+}-saponite and phenols. In order to avoid the sedimentation of the PDA^{2+}-saponite, the final concentration of aqueous suspension of the PDA^{2+}-saponite was adjusted to be 20 mg dm^{-3}. The aqueous PDA^{2+}-saponite suspension (5 cm^3, 40 mg dm^{-3}) was mixed with 5 cm^3 of aqueous solutions of phenols (phenol and 2,4-dichlorophenol) (0, 0.04, or 0.4 mmol dm^{-3}, pH = 7) for 1 day at room temperature.

Characterization. XRD patterns were recorded on a Rigaku RAD I B powder diffractometer equipped with monochromatic Cu Kα radiation, operated at 20 mA, 40 kV. UV–vis absorption spectra were recorded on a Shimadzu UV-3100PC spectrometer. The diffuse reflectance spectra were recorded on a Shimadzu UV-3100PC spectrometer equipped with an integrated sphere attachment. TG-DTA curves were obtained by a Rigaku TAS 200 instrument with a heating rate of 10 K/min under air using α-Al_2O_3 as the standard material. CHN analysis was performed on a Perkin Elmer 2400 II instrument. HPLC was carried out with a Hewlett Packard instrument with a UV–vis detector (HP 1100) monitored at 284 (± 20) nm using an octadecylsilane column (Eclipse® XDB-C18). Carrier solutions were 0.1% aqueous phosphoric acid solution and methanol mixed at a ratio of 20:80 (the aqueous phosphoric acid solution/methanol, v/v).

Results and Discussion

Preparation of PDA^{2+}-Smectite Intercalation Compounds. The basal spacings of the PDA^{2+}-montmorillonite and the PDA^{2+}-saponite were 1.27 and 1.34 nm, respectively. The gallery heights of the PDA^{2+}-montmorillonite and the PDA^{2+}-saponite were determined by subtracting the thickness of the silicate layer (0.96 nm) from the observed basal spacings to be 0.31 and 0.38 nm, respectively. Taking the gallery heights and the thickness of PDA^{2+} (ca. 0.3 nm) into consideration, we conclude that the adsorbed PDA^{2+} cations are thought to be arranged as a monomolecular layer with their molecular planes parallel to the silicate layers. The slight difference in the basal spacing between montmorillonite (1.27 nm) and saponite (1.34 nm) systems reflects the difference in the adsorbed water amounts. The adsorbed amounts of PDA^{2+} on montmorillonite and on saponite were determined by the C content (ca. 4 and 2 mass% for the PDA^{2+}-montmorillonite and for the PDA^{2+}-saponite, respectively) to be 119 and 64 meq (100 g clay)$^{-1}$, respectively. These values were close to the CECs of the smectites. Thus, quantitative ion exchange reaction between sodium ions and PDA^{2+} was confirmed.

The color of Na$^+$-smectites changed from colorless to green by the reaction with PDA^{2+}. In the diffuse reflectance spectrum of the PDA^{2+}-saponite (Fig. 1a), absorption bands were observed in the wavelength regions of 420–520 and 550–700 nm, which were different from the absorption bands observed for an aqueous PDA^{2+} dichloride solution (285 nm). A similar spectrum was obtained for the PDA^{2+}-montmorillonite (Fig. 1b). It was reported that the absorption bands of *p*-phenylenediamine radical cations formed by bromine oxidation in aqueous solution appeared at 460 and 490 nm.[17] It was also reported that an absorption band ascribable to *p*-phenylenediamine radical dimer formed by the reactions between the radical cations appeared at 550 to 700 nm.[17] Thus, the absorption bands observed for the PDA^{2+}-smectites in the wavelength regions of 420–520 and 550–700 nm were ascribable to PDA^{2+} radical cation (Scheme 1b) and PDA^{2+} radical dimer (Scheme 1c), respectively.

It was reported that aromatic amines such as benzidine converted to their colored derivatives when they interacted with

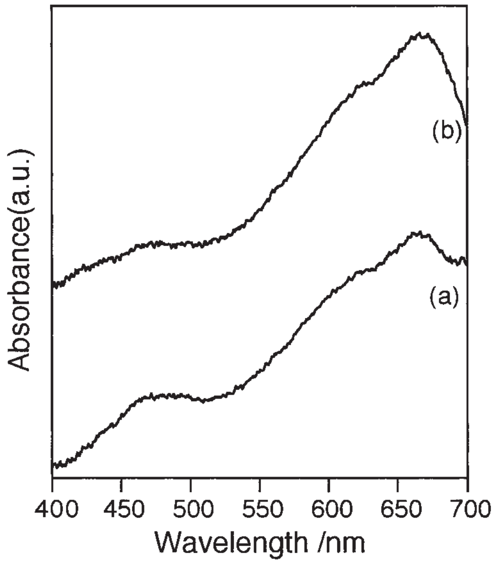


Fig. 1. Diffuse reflectance spectra of (a) PDA^{2+}-saponite and (b) PDA^{2+}-montmorillonite.

smectites.[18,19] Electron transfer from adsorbed aromatic amines to dangling bonds at the crystal edges of smectites and to Fe^{3+} in octahedral sheet has been thought to lead the formation of the radical cations (semiquinone) of aromatic amines. In the present system, it is thought that the formation of PDA^{2+} radical cation and its dimer through the electron transfer from PDA^{2+} to smectites caused the change in the color from colorless to green. Considering the very low iron content of saponite, we think that the dangling bonds at the crystal edges of saponite act as an electron acceptor.

Adsorption of Phenols on the PDA^{2+}-Smectites. The adsorption isotherms of phenol and 2,4-dichlorophenol for the PDA^{2+}-smectites are shown in Fig. 2. According to the Giles classification, the isotherms of phenol and 2,4-dichlorophenol for the PDA^{2+}-smectites were type-S.[20] A small amount of 2,4-dichlorophenol was adsorbed on the PDA^{2+}-saponite when the equilibrium concentration was low (Fig. 2). With the increase in the equilibrium concentration, the amount of the adsorbed 2,4-dichlorophenol increased. There is a step in the adsorption isotherm at the equilibrium concentration of ca. 0.7 mmol dm^{-3}. Further adsorption was not observed when the concentration was higher than 1.4 mmol dm^{-3} and the maximum uptake was 10 mg g^{-1}.

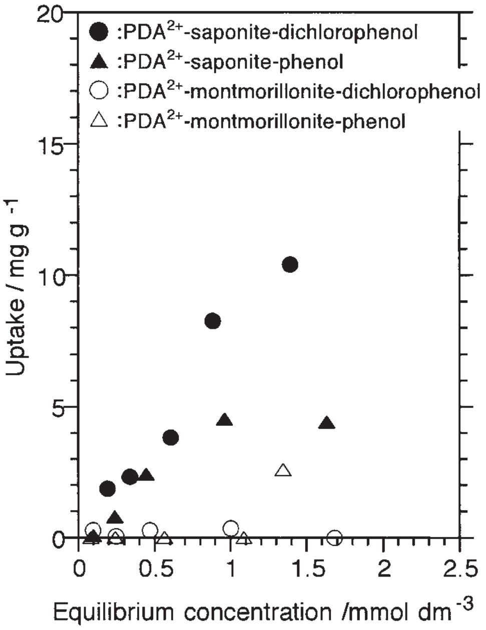
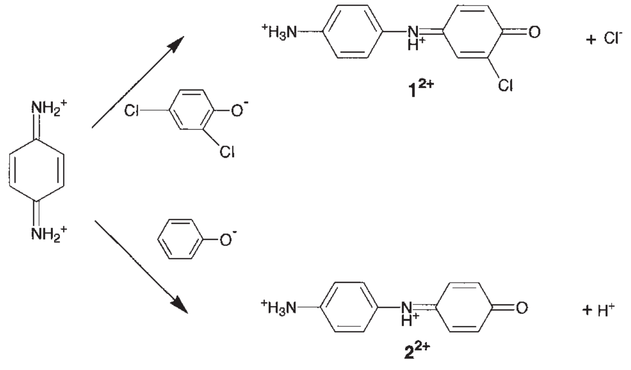


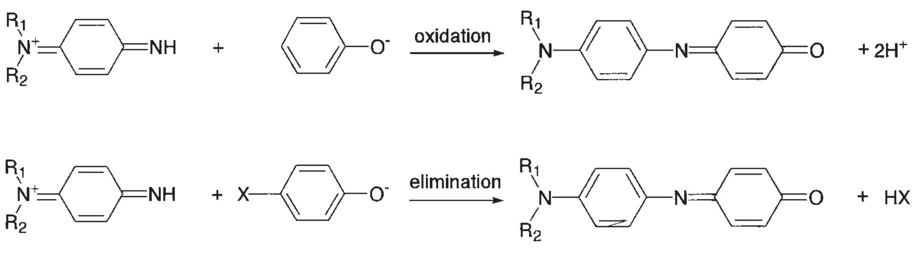
Fig. 2. Adsorption isotherms of phenol and 2,4-dichlorophenol on PDA^{2+}-smectites from aqueous solution.

It is worth noting as a merit of the present systems that the color apparently changed from green to purple. It has been known that the coupling reactions between *p*-benzoquinone diimines and various phenolate anions lead to the formation of indoaniline cyan dyes (Scheme 2).[21,22] We expect that the intercalation of 2,4-dichlorophenol into the PDA^{2+}-saponite was caused by the coupling reaction[22] between 2,4-dichlorophenolate ion and *p*-benzoquinone diiminium ion (Scheme 1d), which was formed by the oxidation of PDA^{2+} radical cations by silicate layer, to form an indoaniline dye, $\mathbf{1}^{2+}$ (Scheme 3). The adsorption of 3,5-dichlorophenol onto organically modified clays was reported,[7] however, the color change has never been observed except for the MV^{2+}-saponite system, which we have reported recently.[13]

The aqueous suspensions of the PDA^{2+}-saponite changed its color from green to purple-blue by the addition of 2,4-dichlorophenol. In order to understand the mechanism of the color change, the absorption spectrum of aqueous suspension containing the PDA^{2+}-saponite and 2,4-dichlorophenol was measured. The absorption spectrum of the mixture of aqueous 2,4-dichlorophenol solution (0.2 mmol dm^{-3}) and aqueous PDA^{2+}-saponite suspension (20 mg dm^{-3}) is shown in Fig. 3d, together with that of aqueous PDA^{2+}-saponite suspension (20 mg dm^{-3}) (Fig. 3a). The absorption spectrum of the mixture of aqueous 2,4-dichlorophenol solution and aqueous PDA^{2+}-saponite suspension showed absorption bands at 620 and 680 nm (Fig. 3d). The absorption bands ascribable to an indoaniline dye, **1** (Scheme 3), of *p*-benzoquinone diimine and 2,4-dichlorophenolate ions in aqueous solution were observed at 550 and 650 nm (Fig. 4a).[23] Thus, it was thought that the color change was due to the formation of $\mathbf{1}^{2+}$ between the interlayer *p*-benzoquinone diiminium and 2,4-dichlorophenolate ions



Scheme 3.



X= anion (e.g. halide)

Scheme 2.

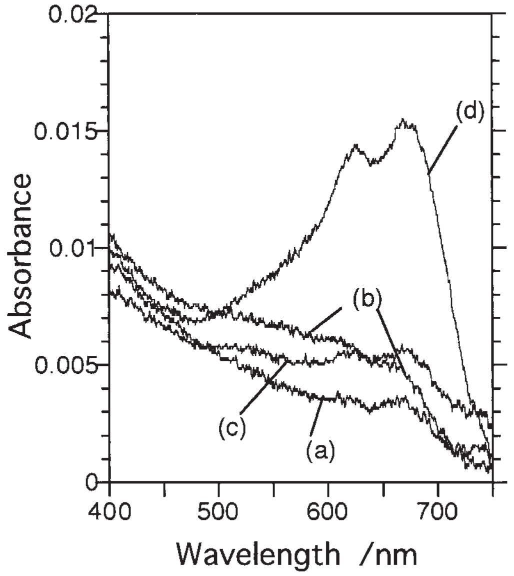


Fig. 3. Absorption spectra of the mixtures of the PDA^{2+}-saponite (20 mg dm^{-3}) and aqueous solutions of phenols. (a) PDA^{2+}-saponite, (b) PDA^{2+}-saponite + phenol (0.2 mmol dm^{-3}), (c) PDA^{2+}-saponite + 2,4-dichlorophenol (0.02 mmol dm^{-3}), and (d) PDA^{2+}-saponite + 2,4-dichlorophenol (0.2 mmol dm^{-3}).

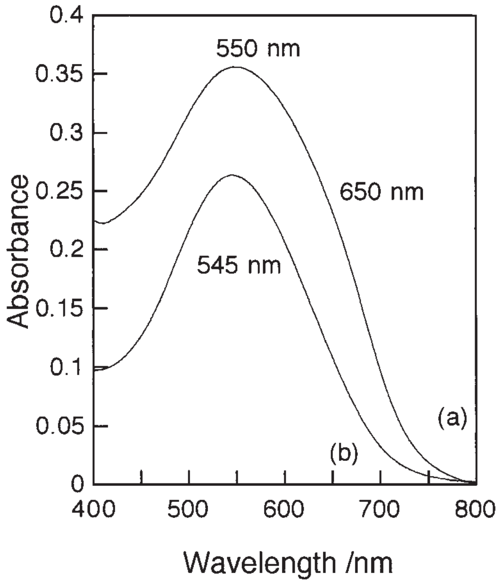


Fig. 4. Absorption spectra of aqueous solutions of (a) **1** and (b) **2**.

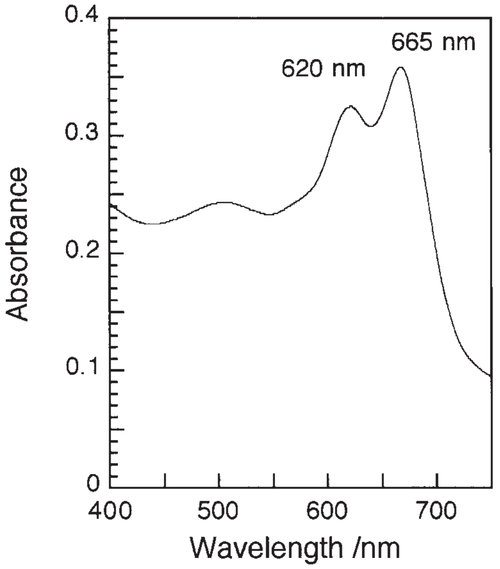


Fig. 5. Absorption spectrum of the mixture of saponite (1 g dm^{-3}) and aqueous solution of **1**.

(Scheme 3). The interactions between surfaces of silicate layer and $\mathbf{1}^{2+}$ were thought to be one possible reason for the difference in the absorption maxima seen in Figs. 3d and 4a.

Indoaniline dye, **1**, was adsorbed on saponite from aqueous solution; the adsorbed amount of **1** was 0.04 mmol g^{-1}. The absorption spectrum of the aqueous suspension containing **1** and saponite showed absorption bands at 620 and 665 nm (Fig. 5). Judging from the adsorbed amount of **1** and absorbance (0.36 at 665 nm), we estimated the molar extinction coefficients of **1** to be 9×10^3 dm^3 mol^{-1} cm^{-1} at 665 nm.[24] Considering the molar extinction coefficients of **1** and the absorbance (0.015 at 680 nm) obtained from the absorption spectrum of the mixture of aqueous 2,4-dichlorophenol solution and aqueous PDA^{2+}-saponite suspension, we estimated the amount of the formed $\mathbf{1}^{2+}$ on the PDA^{2+}-saponite to be 0.08 mmol g^{-1}. This value was close to the value of the amount of the immobilized 2,4-dichlorophenol on the PDA^{2+}-saponite (10 mg g^{-1}, 0.06 mmol g^{-1}), indicating that almost all of the immobilized 2,4-dichlorophenol contributed to the coupling reactions. This was supported by the fact that desorption of 2,4-dichlorophenol from the PDA^{2+}-saponite-2,4-dichlorophenol (the immobilized amount was 0.06 mmol g^{-1}) was not observed by washing with methanol repeatedly.

The formation of indoaniline dye, $\mathbf{1}^{2+}$, was attempted by FT-IR, FT-Raman, and ^{13}C NMR spectra. Taking the adsorbed amount of PDA^{2+} on saponite (0.32 mmol g^{-1}) and the amount of the immobilized 2,4-dichlorophenol (0.06 mmol g^{-1}) into consideration, we conclude that a large part of the adsorbed PDA^{2+} (ca. 80 molar %) did not participate in the coupling reactions. Therefore, it was difficult to distinguish $\mathbf{1}^{2+}$, which was a minor constituent in the PDA^{2+}-saponite-2,4-dichlorophenol, from these spectra.

The change in the XRD pattern of the PDA^{2+}-saponite by the reaction with aqueous 2,4-dichlorophenol solution is shown in Fig. 6. When the PDA^{2+}-saponite was treated with an aqueous solution of 2,4-dichlorophenol at low concentrations ($<$ca. 0.7 mmol dm^{-3}), the basal spacing increased from 1.34 to 1.39 nm. When the reaction was conducted from higher concentration ($>$ca. 0.7 mmol dm^{-3}), the basal spacing of the PDA^{2+}-saponite increased to 1.45 nm. Thus, 2,4-dichlorophenol was intercalated into the interlayer to change the microstructure.

The organoclay (tributyl(hexadecyl)phosphonium-clay) was reported to act as electrode modifier of a carbon paste electrode for the electrochemical detection of 2,4-dichlorophenol in water.[25] 2,4-Dichlorophenol can be detected at the concentration of 0.02 mmol dm^{-3} by using the technique. In the present system, a slight change in the absorption spectrum in the wavelength region from 600 to 700 nm was observed upon the reaction with a relatively dilute aqueous solution of 2,4-dichloro-

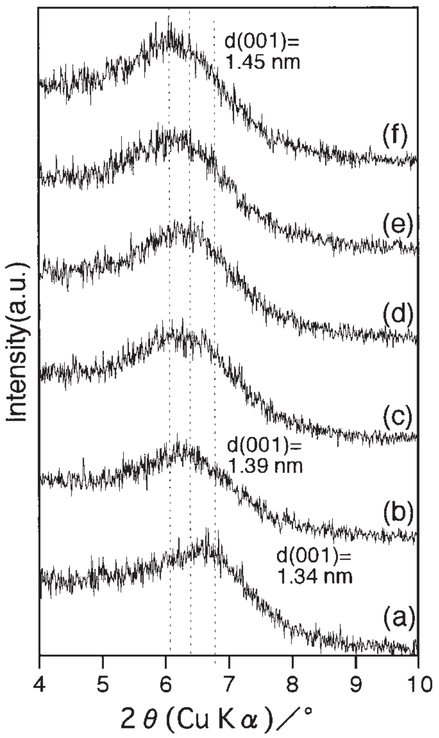


Fig. 6. XRD patterns of PDA^{2+}-saponite dispersed in aqueous 2,4-dichlorophenol solutions at the equilibrium concentrations of (a) 0 mmol dm^{-3}, (b) 0.19 mmol dm^{-3}, (c) 0.33 mmol dm^{-3}, (d) 0.60 mmol dm^{-3}, (e) 0.88 mmol dm^{-3}, and (f) 1.4 mmol dm^{-3}.

phenol (0.02 mmol dm^{-3}) (Fig. 3c). The large molar extinction coefficient of indoaniline dye, **1** (9 × 10^3 dm^3 mol^{-1} cm^{-1} at 665 nm), is worth noting as a merit for the detection of 2,4-dichlorophenol in water by visible spectra. The formation of cationic dye naturally indicates that the desorption as 2,4-dichlorophenol is less plausible. This point is another merit of the present system.

As to the adsorption capabilities, the amount of immobilized 2,4-dichlorophenol on the PDA^{2+}-saponite (10 mg g^{-1}) is in the same range of the amounts of dichlorophenol adsorbed on the reported organoclays (ca. 2 and ca. 80 mg g^{-1} at the equilibrium concentration of 1.0 mmol dm^{-3}, for the trimethylphenylammonium-smectite and the hexadecyltrimethylammonium-smectite, respectively).

Beside the adsorption of 2,4-dichlorophenol, the PDA^{2+}-saponite adsorbed phenol from aqueous solution (Fig. 2). When the equilibrium concentration was low (<ca. 0.1 mmol dm^{-3}), a small amount of phenol was adsorbed. There is an upsweep in the adsorption isotherm at the equilibrium concentration of ca. 0.1 mmol dm^{-3}. No further adsorption of phenol on the PDA^{2+}-saponite was observed when the concentration was higher than 1.0 mmol dm^{-3}; the maximum adsorbed amount was 5 mg g^{-1}. A possible driving force for the intercalation of phenol into the interlayer space of the PDA^{2+}-saponite was the coupling reaction between *p*-benzoquinone diiminium and phenolate ions to form an indoaniline dye, **2^{2+}** (Scheme 3). The amount of the immobilized phenol (5 mg g^{-1}, 0.05 mmol g^{-1}) was small compared to that of 2,4-dichlorophenol on the PDA^{2+}-saponite (10 mg g^{-1}, 0.06 mmol g^{-1}). It has been thought that the adsorption of aromatic compounds on organically pillared clays occurred on hydrophobic siloxane surfaces in the interlayer space.[10,26] Since phenol is less hydrophobic (higher water solubility) than 2,4-dichlorophenol (the solubilities in water are 87 and 4.4 g kg^{-1} for phenol[16] and 2,4-dichlorophenol,[27] respectively), the interactions between siloxane surface and phenol are weaker. Phenols were primarily adsorbed on the siloxane surface of saponite and subsequently these adsorbed phenols reacted with *p*-benzoquinone diiminium ions. Therefore, the amount of phenol adsorbed on the PDA^{2+}-saponite was small compared to that of 2,4-dichlorophenol.

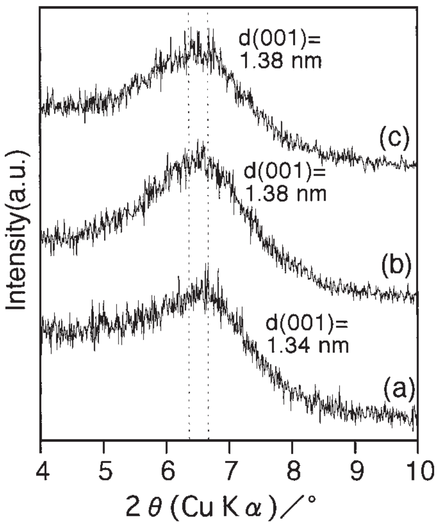


Fig. 7. XRD patterns of PDA^{2+}-saponite dispersed in aqueous phenol solutions at the equilibrium concentrations of (a) 0 mmol dm^{-3}, (b) 0.24 mmol dm^{-3}, and (c) 0.96 mmol dm^{-3}.

The basal spacing of the PDA^{2+}-saponite increased from 1.34 nm (Fig. 7a) to 1.38 nm (Fig. 7b) after the reactions of aqueous phenol solutions. The slight difference in the basal spacing (1.38 nm for the PDA^{2+}-saponite-phenol and 1.45 nm for the PDA^{2+}-saponite-2,4-dichlorophenol systems) was probably due to a difference in the arrangement of the formed indoaniline dyes as well as the adsorbed amounts of water.

By the reaction of the PDA^{2+}-saponite with aqueous phenol solution, the color of the aqueous suspension of the PDA^{2+}-saponite changed from green to purple. The absorption spectrum (Fig. 3b) showed a broad band in the wavelength range from 450 to 700 nm, which was absent for an aqueous phenol solution (270 nm) and aqueous PDA^{2+}-saponite suspension (Fig. 3a). The absorption band ascribable to an indoaniline dye, **2** (Scheme 3), in aqueous solution appeared at 545 nm (Fig. 4b).[23] Thus, the formation of **2^{2+}** between *p*-benzoquinone diiminium and phenolate ions (Scheme 3) was thought to cause the change in the color.

The adsorption of phenol on organically modified smectites from aqueous solution was reported.[7,12,26] Hexadecyltrimethylammonium-smectite did not adsorb phenol. Phenol interacted strongly with water and was not attracted sufficiently to the hydrophobic surface of the hexadecyltrimethylammonium-smectite.[7] When tetramethylphosphonium-smectite was used as adsorbent, the adsorbed amount was ca. 30 mg g^{-1} at the equilibrium concentration of 1.2 mmol dm^{-3}.[26] Recently, the adsorption of phenol on the clay modified with cationic dyes (i.e., crystal violet) from aqueous solution was reported and the amount of the adsorbed phenol was ca. 8 mg g^{-1}.[12] The uptake of phenol on the PDA^{2+}-saponite (5 mg g^{-1}) is comparable to those on organically modified clays reported previously.

On the contrary, the uptake of phenol by the PDA^{2+}-montmorillonite from dilute aqueous solution (<ca. 1.1 mmol dm^{-3}) (Fig. 2) is very low. Even when the concentration was higher than 1.1 mmol dm^{3}, the adsorbed amount of phenol was still very low (less than 3 mg g^{-1}). Similarly, only a very small amount of 2,4-dichlorophenol was immobilized on the PDA^{2+}-montmorillonite from aqueous solutions (Fig. 2). As expected from the adsorption isotherms, the basal spacing (1.27 nm) did not change due to the reactions of aqueous solutions of phenols with the PDA^{2+}-montmorillonite. We thought that the difference in the adsorption capabilities of the PDA^{2+}-saponite and the PDA^{2+}-montmoriilonite was derived from the layer charge density and isomorphous substitution. It is known that the expandability of the interlayer space of smectite correlates to electrostatic interaction, which depends on layer charge and position of cations.[28] This difference motivates the study on the adsorption of various organic nonionic compounds onto dye-modified clay because one can expect molecular recognition and colorimetric sensing ability in a certain system.

Conclusions

The reactions of PDA^{2+} dichloride with sodium-smectites (montmorillonite and synthetic saponite) led the formation of green-colored PDA^{2+}-smectite intercalation compounds, which included PDA^{2+} radical cations, its dimer, and *p*-benzoquinone diiminium ions. Phenol and 2,4-dichlorophenol were immobilized in the interlayer space of the PDA^{2+}-saponite from aqueous solutions, while the PDA^{2+}-montmorillonite did not immobilize two phenols, as shown by the adsorption isotherms of phenols for the PDA^{2+}-smectites as well as the changes in the basal spacings of the PDA^{2+}-smectites. The coupling reactions between *p*-benzoquinone diiminium ions and phenolate or 2,4-dichlorophenolate ions played an important role in the uptake of phenols as revealed by the color change of the PDA^{2+}-saponite from green to purple (for phenol) or purple-blue (for 2,4-dichlorophenol) and spectral changes in the aqueous suspensions of the PDA^{2+}-saponite. The present finding on the adsorption behavior can be a way of constructing adsorbents with detection ability for various phenolic compounds in water.

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23 The preparation of indoaniline dyes (**1** and **2**) was carried out as described in Ref. 22. An aqueous *p*-phenylenediamine solution (5×10^{-2} mmol dm^{-3}) and an aqueous solution of phenol or 2,4-dichlorophenol (5×10^{-2} mmol dm^{-3}) were mixed at room temperature and subsequently an aqueous $K_3[Fe(CN)_6]$ solution (the molar ratios of phenols to $K_3[Fe(CN)_6]$ were 1:2 (phenol:$K_3[Fe(CN)_6]$) and 1:4 (2,4-dichlorophenol:$K_3[Fe(CN)_6]$) was added to each mixture). The reactions were conducted in phosphate buffer solution (pH = 6.8).

24 The adsorption of indoaniline dye, **1**, from aqueous solution on saponite was conducted as follow; saponite (10 mg) was allowed to react with aqueous solution of **1** (prepared as described in Ref. 23) for 1 day at room temperature. The adsorbed amount of **1** was estimated from the difference in the concentration of the aqueous solution between initial and equilibrium concentration by vis spectra (665 nm).

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