

Adsorption of benzene derivatives on allophane

Hiromasa Nishikiori*, Junichi Shindoh, Nobukazu Takahashi, Tomohiro Takagi,
Nobuaki Tanaka, Tsuneo Fujii

*Department of Environmental Science and Technology, Graduate School of Science and
Technology, Shinshu University, Wakasato, Nagano 380-8553, Japan*

Corresponding author: Hiromasa Nishikiori

Tel.: +81-26-269-5536

Fax: +81-26-269-5550

E-mail: nishiki@shinshu-u.ac.jp

Department of Environmental Science and Technology, Graduate School of Science and
Technology, Shinshu University, Wakasato, Nagano 380-8553, Japan

Abstract

The adsorption properties of benzene derivatives from water on allophane, extracted from soil, have been investigated by UV and FTIR spectroscopic measurements. Allophane adsorbs benzoic acid, phthalic acid, benzaldehyde, ethyl benzoate, and diethyl phthalate. Benzoic acid, phthalic acid, and benzaldehyde formed carboxylate anions on the positive sites of the hydrated alumina surface of allophane. In the case of adsorption from an acidic solution (pH 2), a small amount of a neutral species of benzoic acid was detected on the allophane. Ethyl benzoate and diethyl phthalate were adsorbed by an interaction between their carbonyl groups and the hydroxyl groups of the allophane. It was confirmed that allophane has an adsorption ability for the benzene derivatives that are not only ionic but also polar molecules. Allophane was found to be available as an absorbent for use in water purification by a simple procedure.

Keywords: Adsorption; Benzene derivatives; Allophane; IR spectra

1. Introduction

Some clay minerals have a high activity for ion exchange, adsorption, and catalyst uses, and they are also available for water purification (Bergaya et al., 2006; Cea et al., 2007; Xu et al., 1998). Environmental water purification is a very important subject in today's world because of the serious problems resulting from the bad management of some chemicals in the past. Clay minerals in soil spontaneously purge some chemicals in the natural world. The chemicals are expected to be decomposed while they are adsorbed on the clay minerals by the biological actions reported in a paper (Fisenko, 2004).

Some benzene derivatives, such as dialkyl phthalate, have been suspected of being endocrine disruptors. Besides polluting soil and groundwater, such compounds may affect animal/human fertility and reproduction.

Allophane, a natural clay mineral distributed throughout the world, is a hydrated aluminosilicate ($1-2\text{SiO}_2 \bullet \text{Al}_2\text{O}_3 \bullet 5-6\text{H}_2\text{O}$) having a 3.5–5.0 nm-sized hollow spherical structure with 0.3–0.5 nm-sized defects on its surface (Kitagawa, 1971; Henmi and Wada, 1976; Wada and Wada, 1977; Hall et al., 1985; van der Gaast et al., 1985). The walls in the hollow spheres consist of two layers, inner silica and outer alumina layers, and hydroxyl groups or water of hydration on their surface. Some studies suggest that these surfaces have a high ability to adsorb ionic or polar pollutants due to an amphoteric ion-exchange activity (Theng, 1972; Clark and McBride, 1984; Hanudin et al., 1999; Gustafsson, 2001; Hashizume et al. 2002; Jara et al., 2006) and high surface area (Kitagawa, 1971; Hall et al., 1985). Allophane has, in part, been applied to wall materials to control humidity in the air. However, only a small amount of allophane distributed throughout the world has been utilized, and its chemical properties have not been

effectively utilized. Basic studies on the adsorption of harmful aromatic molecules are needed. However, there is no report describing the detailed structure of aromatic molecules adsorbed on allophane.

In this study, we have investigated the absorption properties for benzene derivatives, i.e., benzoic acid, phthalic acid, benzaldehyde, ethyl benzoate, and diethyl phthalate, by allophane in order to assess its utilization as an absorbent for water purification. The adsorption was quantitatively evaluated by measuring UV absorption spectra, and the adsorption structure was determined by examining the IR spectra.

2. Experimental

2.1. Materials

Benzoic acid (reagent grade), phthalic acid (S, = special, grade), benzaldehyde (S grade), and ethyl benzoate (S grade), purchased from Wako Pure Chemicals, were used without further purification (Scheme 1). Diethyl phthalate (reagent grade) was purchased from Kanto Chemicals and was used without further purification. Water, which was deionized and then distilled, was used as a solvent. Hydrochloric acid (S grade) and sodium hydroxide (S grade), purchased from Wako Pure Chemicals, were used without further purification to control the acidity of the solutions. Allophane was extracted by elutriation of Kanuma soil from Tochigi, Japan (Wada and Wada, 1977; Hall et al., 1985; Wada, 2001). The soil grains were suspended in water and agitated on a reciprocal shaker. The clear suspension separated by centrifugation (Daiki Ataka MD-3) contained the allophane particles having an average diameter of 15 μm . The fine particles ($<0.2 \mu\text{m}$) were obtained by drying the supernatant resulting from filter pressing of

the almost clear dispersion at 0.85 MPa. The allophane sample was finally dried at 300°C. The ratio of Al/Si in the allophane was 1.25 by XPS analysis (ULVAC PHI5600). The specific surface area of the allophane was $312\text{ m}^2\text{ g}^{-1}$ by BET measurement (Micrometrics ASAP 2000).

(Scheme 1)

2.2. Measurements

Aqueous solutions of benzoic acid, phthalic acid, benzaldehyde, ethyl benzoate, and diethyl phthalate were adjusted to 1.0×10^{-4} and $1.0 \times 10^{-3}\text{ mol dm}^{-3}$. A 1.0 g allophane sample was dispersed in 30.0 cm^3 of the solutions. The dispersions were stirred for 1–30 days and then centrifuged. The UV absorption spectra of the clear solutions were measured as a function of time using a Shimadzu UV-2500PC spectrophotometer, and the amounts of the adsorbed compounds were estimated from the concentration differences. The spectral changes were mainly determined in the $1.0 \times 10^{-4}\text{ mol dm}^{-3}$ solutions of the benzene derivatives. In this study, the amounts of the benzene derivatives adsorbed on allophane were simply estimated by the UV absorption measurements of the $1.0 \times 10^{-3}\text{ mol dm}^{-3}$ solutions, in which the adsorption was almost saturated. The molar ratio of the benzene derivatives in these solutions to the aluminosilicate unit of allophane was ca. 1/100.

A 1.0 g allophane sample was dispersed in saturated aqueous solutions of benzoic acid, phthalic acid, ethyl benzoate, and diethyl phthalate, and in pure benzaldehyde. The pH value of the aqueous solution of benzoic acid was adjusted to 2.0–11 and was measured with a TOA HM-10P pH meter. These dispersions were stirred for 5 days and then centrifuged to obtain the allophane samples containing the adsorbed benzene derivatives. All samples and the pure benzene derivatives were pressed in KBr pellets for the FT-IR analysis (Shimadzu FTIR-8200

spectrophotometer). The spectra of the benzene derivatives adsorbed on allophane were obtained by subtracting those of allophane.

3. Results and discussion

3.1. Adsorption of esters

The spectrum of diethylphthalate exhibited two peaks at 235 and 276 nm and a strong band at less than 210 nm (Fig. 1). The intensity of these bands very slowly decreased with time and reached equilibrium after around 30 days, when the absorbance was reduced by 92%. The amounts of diethylphthalate and ethyl benzoate adsorbed per gram of allophane were 2.3 ± 0.2 and $1.6 \pm 0.1 \times 10^{-5}$ mol g⁻¹. The amounts of these compounds adsorbed on allophane increased with their concentration and approached their saturation similar to the Langmuir adsorption isotherm.

(Figure 1)

The IR peaks of the diethyl phthalate (Fig. 2) were located at 2985, 1728, and 1285 cm⁻¹ assigned to the CH₂/CH₃ antisymmetry stretching, the C=O stretching, and C—O—C antisymmetry stretching vibrations. The spectra of the diethyl phthalate adsorbed on allophane showed peaks at 2984, 1718, and 1292 cm⁻¹, the latter two peaks assigned to the C=O and C—O—C stretching vibrations, were shifted to the lower and higher wavenumber sides, respectively. The spectral shift indicates an interaction between the carbonyl group of the molecules and the hydroxyl groups on the surface of the allophane. Ethyl benzoate also exhibited spectral shifts from 1718 to 1713 cm⁻¹ for C=O and from 1278 to 1286 cm⁻¹ for C—O—C, which were similar to those of diethyl phthalate.

(Figure 2)

3.2. Adsorption of aldehyde and carboxylic acids

The UV peak and shoulder of benzoic acid before the addition of allophane were located at 230 and 274 nm. The spectra of the allophane suspension showed a peak at 224 nm and a shoulder at around 280nm due to formation of the benzoate anion. The absorbance decreased rapidly within 1 day (Fig.3a). The spectra of benzaldehyde exhibited a peak at 250 nm and a shoulder at around 280nm (Fig. 3b). The spectral intensity for both compounds gradually decreased with time and attained equilibrium after around 10 days. The absorbance for benzoic acid and benzaldehyde decreased by 87% and 96%, respectively. The adsorption rates were somewhat faster than that for diethyl phthalate. The pH values in the suspensions of both benzoic acid and benzaldehyde were around 6. The amounts of benzoic acid and benzaldehyde adsorbed per gram of allophane were 3.6 ± 0.2 and $6.2 \pm 0.3 \times 10^{-6}$ mol g⁻¹, respectively. The adsorption isotherm of these compounds was similar to that of Langmuir type.

(Figure 3)

Benzoic acid exhibited peaks specific of carboxylic acid at 1689 cm⁻¹ for the C=O stretching, at 1427 cm⁻¹ for the O–H in-plane bending (aggregate), at 1326 cm⁻¹ for the O–H in-plane bending (isolate), and at 1294 cm⁻¹ for the C–O stretching (Fig. 4). These C–O stretching and O–H in-plane bending were coupled. Phthalic acid exhibited peaks similar to benzoic acid at 1687 cm⁻¹ for the C=O stretching and at 1402 and 1280 cm⁻¹ for the coupling mode of the C–O stretching and O–H in-plane bending (not shown here). The spectra of the compounds adsorbed on the allophane showed peaks at 1562 and 1435 cm⁻¹ for the benzoic acid, and at 1560 and 1433 cm⁻¹ for the phthalic acid assigned to the COO⁻ antisymmetry and symmetry stretching band, respectively. These carboxylic acids were adsorbed on allophane as carboxylate anions (Klug

and Forsling, 1999; Rosenqvist et al., 2003; Lee and Reeder, 2006). The spectrum of the benzaldehyde-adsorbed allophane exhibited peaks at 1605 and 1497 cm^{-1} for the skeletal vibration of the benzene ring and at 1566 and 1437 cm^{-1} for the COO^- antisymmetry and symmetry stretching bands, respectively (Guil et al., 2005). The peaks typical of benzaldehyde at 1703 cm^{-1} for the C=O stretching, 1390 cm^{-1} for the C–H bending, and 1204 cm^{-1} for the C–CO in-plane bending were weak. Benzaldehyde was also adsorbed and formed benzoate anion on allophane due to nucleophilic attack on the carbonyl group by the surface oxygen as reported for ZnO (Bowker et al., 1983). A shoulder was found at 1690–1680 cm^{-1} , which indicates that the C=O groups of benzaldehyde, in part, interacted with the hydroxyl groups of allophane.

(Figure 4)

3.3. pH dependence of adsorption of carboxylic acid

The adsorption amount of benzoic acid depended on the pH value of the suspension (Fig. 5). The dissociation constant of benzoic acid, pK_a , is 4.2. The pK_a of the $-\text{AlOH}_2^+$ group on allophane is reported to be around 6 (Clark and McBride, 1984; Hanudin et al., 1999). The intensity of the IR bands of benzoic acid adsorbed at pH 5.0 was clearly higher than that adsorbed at pH 11 because the electrostatic interaction between the benzoate anion and the $-\text{AlOH}_2^+$ group enhanced its adsorption on allophane (Clark and McBride, 1984; Hanudin et al., 1999; Klug and Forsling, 1999). The spectrum of benzoic acid adsorbed at pH 2 was somewhat different from the other spectra. A very weak carboxylate band and a peak at around 1655 cm^{-1} were observed. The latter band originated from the carboxyl C=O interacting with the hydroxyl groups of

allophane because the peak was shifted to a lower wavelength compared to that of pure benzoic acid. A small amount of protonated benzoic acid was adsorbed on the allophane.

(Figure 5)

4. Conclusions

UV and IR spectroscopic measurements revealed that allophane adsorbed benzoic acid, phthalic acid, benzaldehyde, ethyl benzoate, and diethyl phthalate. Benzoic acid, phthalic acid, and benzaldehyde formed benzoate or phthalate anions on the positive sites of the hydrated alumina surface of allophane. In the case of adsorption from an acidic solution, a small amount of a neutral species of benzoic acid was detected. Ethyl benzoate and diethyl phthalate were adsorbed by interaction of the carbonyl groups and the hydroxyl groups of allophane. Allophane was found to be useful as an absorbent for water purification.

Acknowledgments

This work was supported in part by a Grant-in-Aid for Scientific Research (A No. 14208070) from the Ministry of Education, Culture, Sports, Science and Technology of the Japanese Government. The authors thank Dr. T. Matsumoto of Tochigi Research Institute for kindly providing the allophane.

References

Bergaya, F., Theng, . K.G., Lagaly, G., 2006. Handbook of clay science. Elsevier, Amsterdam.

- Bowker, M., Houghton, H., Waugh, K. C., 1983. The interaction of acetaldehyde and acetic acid with the ZnO surface. *J. Catal.* 79, 431–444.
- Cea, M., Seaman, J.C., Jara, A.A., Fuentes, B., Mora, M.L., Diez, M.C., 2007. Adsorption behavior of 2,4-dichlorophenol and pentachlorophenol in an allophanic soil. *Chemosphere* 67, 1354–1360.
- Clark, C.J., McBride, M.B., 1984. Cation and anion retention by natural and synthetic allophane and imogolite. *Clays Clay Miner.* 32, 291–299.
- Fisenko, A.I., 2004. A new long-term on site clean-up approach applied to non-point sources of pollution. *Water Air Soil Pollution* 156, 1–27.
- Guil, J.M., Homs, N., Llorca, J., Ramírez de la Piscina, P., 2005. Microcalorimetric and infrared studies of ethanol and acetaldehyde adsorption to investigate the ethanol steam reforming on supported cobalt catalysts. *J. Phys. Chem. B* 109, 10813–10819.
- Gustafsson, J.P., 2001. Modelling competitive anion adsorption on oxide minerals and an allophane-containing soil. *Eur. J. Soil Sci.* 52, 639–653.
- Hall, P.L., Churkman, G.J., Theng, B.K.G., 1985. Size distribution of allophane unit particles in aqueous suspensions. *Clays Clay Miner.* 33, 345–349.
- Hanudin, E., Matsue, N., Henmi, T., 1999. Adsorption of some low molecular weight organic acids on nano-ball allophane. *Clay Sci.* 11, 57–72.
- Hashizume, H., Theng, B.K.G., Yamagishi, A., 2002. Adsorption and discrimination of alanine and alanyl-alanine enantiomers by allophane. *Clay Miner.* 37, 551–557.

Henmi, T, Wada, K., 1976. Morphology and composition of allophane. Am. Mineralogist 61, 379–390.

Jara, A.A., Violante, A., Pigna, M., Mora, M.L., 2006. Mutual interactions of sulfate, oxalate, citrate, and phosphate on synthetic and natural allophanes. Soil Sci. Soc. Am. J. 70, 337–346.

Kitagawa, Y., 1971. The “unit particle” of allophane. Am. Mineralogist 56, 465–475.

Klug, O., Forsling, W., 1999. A spectoscopic study of phthalate adsorption on γ -aluminum oxide. Langmuir, 15, 6961–6968.

Lee, Y.J., Reeder, R.J., 2006. The role of citrate and phthalate during Co(II) coprecipitation with calcite. Geochim. Cosmochim. Acta 70, 2253–2263.

Rosenqvist, J., Axe, K., Sjöberg, S., Persson, P., 2003. Adsorption of dicarboxylates on nano-sized gibbsite particles: effects of ligand structure on bonding mechanisms. Colloids and Surfaces A: Physicochem. Eng. Aspects 220, 91–104.

Theng, B.K.G., 1972. Adsorption of ammonium and some primary n-alkylammonium cations by soil allophane. Nature 238, 150–151.

van der Gaast, S.J., Wada, K., Wada, S.-I., Kakuto, Y., 1985. Small-angle X-ray powder diffraction, morphology, and structure of allophane and imogolite. Clays Clay Miner. 33, 237–243.

Wada, S., Wada, K., 1977. Density and structure of allophane. Clay Miner. 12, 289–298.

Wada, S., 2001. A procedure for separation and purification of allophane from weathered pumice. Clay Sci. Soc. Jpn. 40, 242–248 (in Japanese).

Xu, S., Lehmann, R.G., Miller, J.R., Chandra, G., 1998. Degradation of polydimethylsiloxanes (silicones) as influenced by clay minerals. Environ. Sci. Technol. 32, 1199–1206.

Figure captions

Figure 1 Change in the UV absorption spectra and absorbance at 235 nm of diethyl phthalate in an aqueous dispersion of allophane. Initial concentration of diethyl phthalate is 1.0×10^{-4} mol dm $^{-3}$.

Figure 2 IR spectra of (1) diethyl phthalate and (2) diethyl phthalate adsorbed on allophane.

Figure 3 UV absorption spectra of (a) benzoic acid and (b) benzaldehyde in the aqueous suspensions of allophane. Initial concentration of diethyl phthalate is 1.0×10^{-4} mol dm $^{-3}$.

Figure 4 IR spectra of (a) benzoic acid and (b) benzaldehyde (1) before and (2) after adsorption on allophane.

Figure 5 IR spectra of the benzoic acid adsorbed on allophane at different pH.

Scheme 1 Benzene derivatives used in this study.

Figure 1

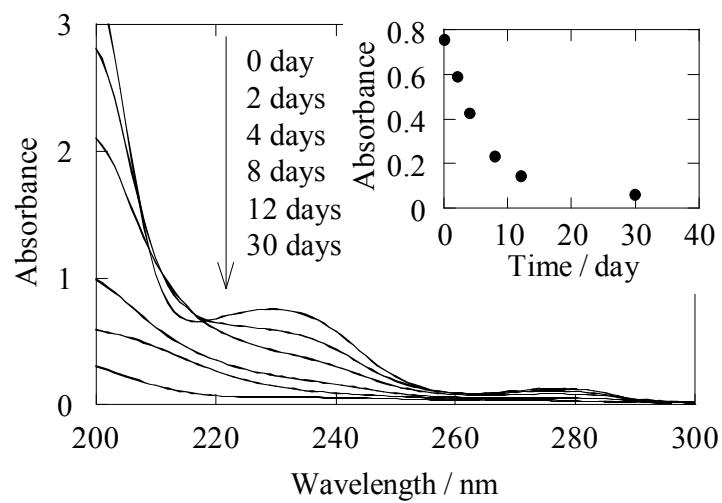


Figure 2

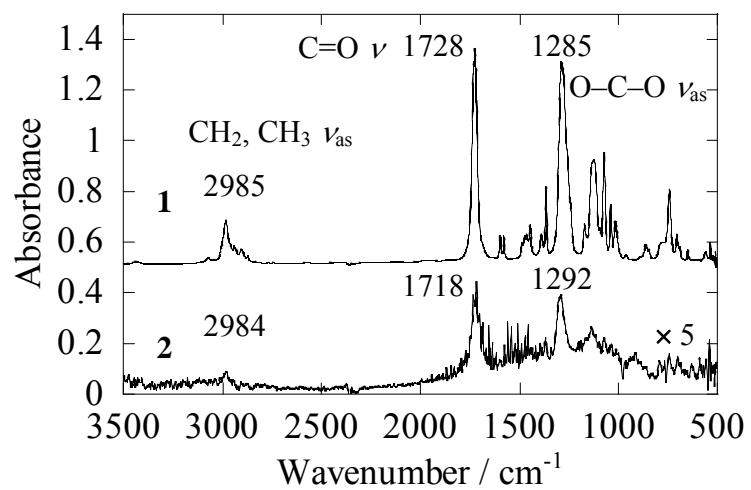
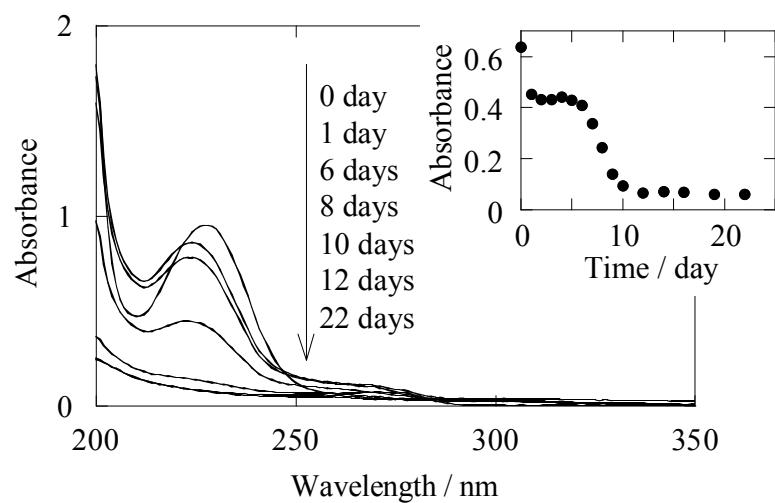


Figure 3

(a)



(b)

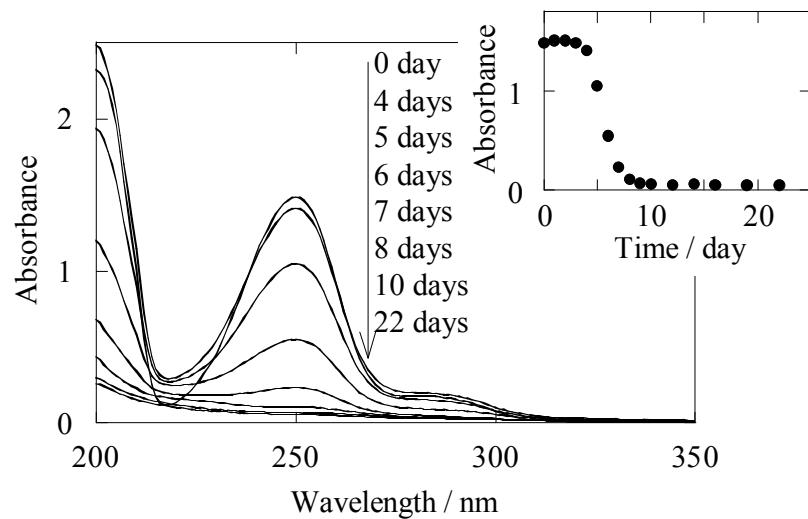
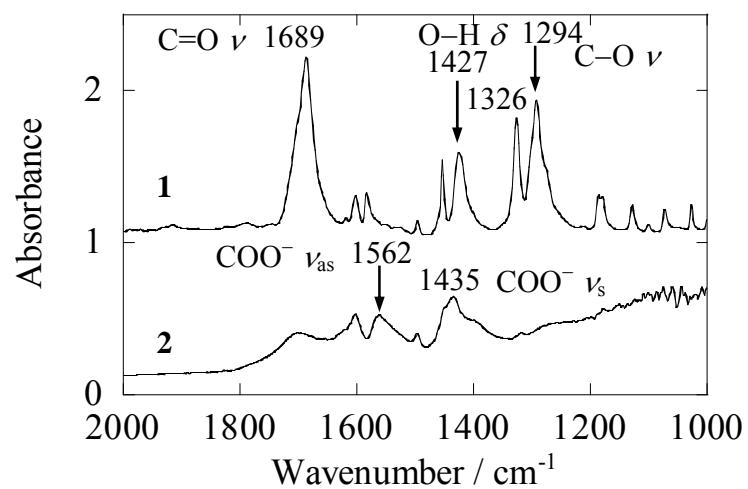


Figure 4

(a)



(b)

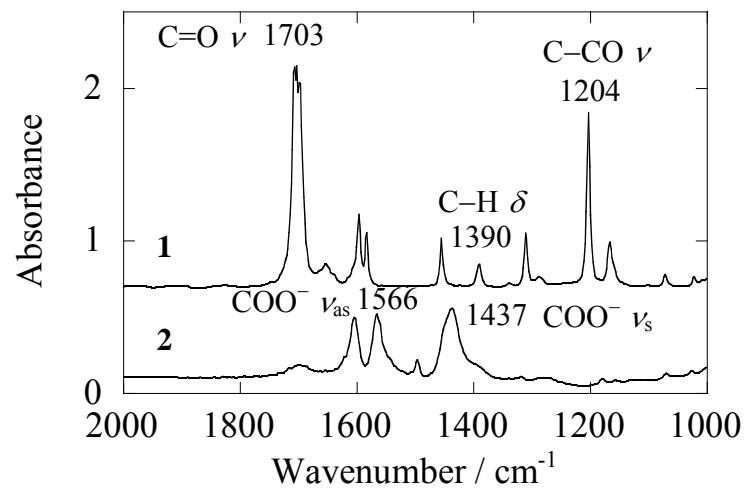
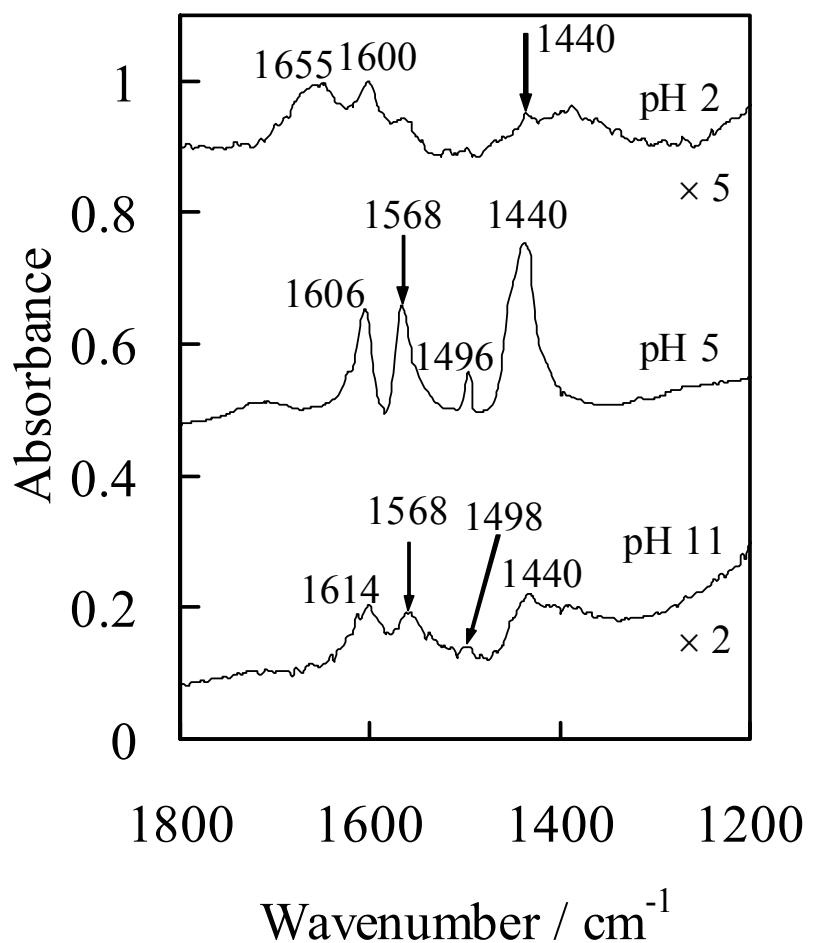
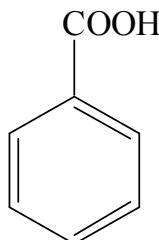


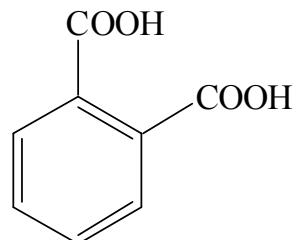
Figure 5



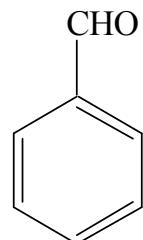
Scheme 1



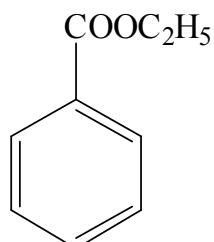
Benzoic acid



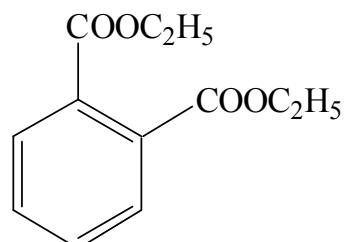
Phthalic acid



Benzaldehyde



Ethyl benzoate



Diethyl phthalate