

Dynamic adsorption process of phthalate at goethite/aqueous interface: An ATR-FTIR study



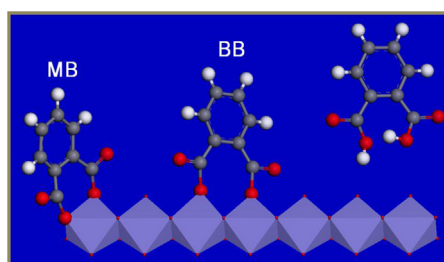
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HIGHLIGHTS

- Phthalate adsorption at the goethite/aqueous interface was studied using ATR-FTIR.
- Phthalate form one outer-sphere and two bidentate inner-sphere surface complexes.
- Outer-sphere complex is suppressed with increasing ionic strength.
- Adsorption follow pseudo-second-order kinetics and reach equilibrium within 60 min.

GRAPHICAL ABSTRACT



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ABSTRACT

Insights into the molecular-level behaviors of phthalate at the goethite/aqueous interface can further our understanding of the fate and transport of natural organic matter analogs in the environment. The motivation of this work is to explore the interfacial configuration and dynamic adsorption process of phthalate on goethite at the molecular scale. The flow-cell ATR-FTIR measurement, curve-fitting analysis, and pseudo-second-order kinetic simulation were used to investigate the adsorption mechanisms. The results showed that phthalate formed one electrostatic outer-sphere complex and two inner-sphere configurations in mononuclear bidentate and binuclear bidentate structures. The contribution of outer-sphere complex to the overall phthalate adsorption was suppressed with increasing ionic strength and decreasing pH values. The ratio of adsorption capacity between these two inner-sphere configurations was slightly affected under different experimental conditions. Furthermore, the dynamic adsorption process of these three interfacial configurations followed the pseudo-second-order kinetics model, and reached equilibrium rapidly within 60 min.

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1. Introduction

Phthalate is one of the ubiquitous low-molecular-weight carboxylic acid in the environment [1,2]. This carboxyl compound can readily adsorb onto minerals, thus altering its migration and susceptibility to transform in aquifers and soils. In addition, phthalate is deemed as an analog for natural organic matter (NOM) to investigate the mineral–NOM interactions, due to its high solubility in water, simple structure, as well as its similarity in functional

groups to NOM [3–6]. Therefore, knowledge on the molecular-level mechanisms of phthalate adsorption is critical in understanding the interactions of NOM on minerals.

Extensive research has been conducted about phthalate adsorption on metal oxides using Fourier-transform infrared (FTIR) spectroscopy, but no consistent conclusion is obtained in its interfacial structure on the molecular level. For example, Tejedor-Tejedor [7] indicated that phthalate adsorbed on goethite in the form of mononuclear monodentate (M–M) and binuclear bidentate (B–B) structures involving only one carboxylate group bound to the surface iron. The B–B configuration was also observed by Dobson and McQuillan [8] for phthalate adsorption on TiO₂, ZrO₂, Al₂O₃, and Ta₂O₅. However, Persson et al. [9,10] proposed phthalate

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adsorption on boehmite, aged γ - Al_2O_3 , and goethite in outer-sphere and mononuclear bidentate (M–B) structures. Furthermore, Hwang [1] found that phthalate formed three surface complexes on hematite, namely a fully deprotonated outer-sphere complex and two inner-sphere complexes with respect to a M–B and a B–B complex involving both carboxylate groups. The discrepancy in the proposed interfacial configuration motivated our further investigation at the molecular-scale understanding of phthalate adsorption. Here, goethite was chosen as the model adsorbent, due to its ubiquity in terrestrial soils and sediment [11,12]. Moreover, the existing literature on goethite provides valuable references for comparison [7,10].

In this study, we investigated the adsorption mechanisms of phthalate at goethite/aqueous interface as a function of pH and ionic strength via in situ flow-cell measurements of attenuated total reflectance (ATR) FTIR spectroscopy. In addition to the determination of interfacial configurations, our current work focused on the dynamic process of phthalate adsorption on the basis of curve-fitting analysis and kinetic model simulation. These results could further our understanding of the fundamental interactions between NOM and iron oxide surfaces.

2. Experimental

2.1. Materials

High-purity phthalic acid was purchased from Sigma–Aldrich. All chemicals were analytical grade or higher and were used as received. The samples were prepared in Milli-Q water (18.2 M Ω), which was boiled for 60 min and cooled with N_2 purging to remove CO_2 . Goethite was synthesized and characterized as shown in our previous reports [13,14]. The goethite had a N_2 -BET surface area of 84.7 m^2/g and a point of zero charge (PZC) of 8.9.

2.2. ATR-FTIR spectroscopy study

The ATR-FTIR spectra were recorded with a Nicolet 6700 spectrometer equipped with a liquid-nitrogen cooled MCT detector. The ATR crystal, a 45° ZnSe or Ge crystal, was mounted in a flow cell (PIKE Technologies, USA). The pH range for ZnSe crystal was within 5–9, and the ZnSe crystal could be etched below pH 5. Then, Ge crystal was used when $\text{pH} < 5$. All spectra were averaged with 256 scans at 4 cm^{-1} resolution. Data collection and analysis were carried out with OMNIC software (Thermo Fisher Scientific Inc., USA). The numbers and positions of the frequency were justified using the second derivative. The curve-fitting analysis of the overlap peak within the wavenumber range 1470–1330 cm^{-1} was conducted using the Gaussian line shape [15,16].

The spectra of aqueous phthalate in 0.1 M NaCl solutions were obtained by subtracting the spectrum of background electrolyte solutions from the sample spectrum. The interfacial spectra of phthalate were measured with goethite film on the ZnSe crystal in the same way as our previous report [13,14]. Briefly, 400 μL of goethite suspensions (1 g/L) was spread on the crystal surface and dried in an oven at 50 °C for 1 h. Prior to use, the crystal was gently rinsed with Milli-Q water to remove loosely deposited goethite particles. Concentration of phthalic acid was fixed at 1 mM in 0.01, 0.1, and 1 M NaCl solution. The background electrolyte was passed through the flow cell at the rate of 0.4 mL/min, and the background spectrum was collected until the equilibrium was established. The solution was then changed to the sample with the same pH value and NaCl concentration as that in the background. The adsorbed spectra were recorded as a function of time for 150 min.

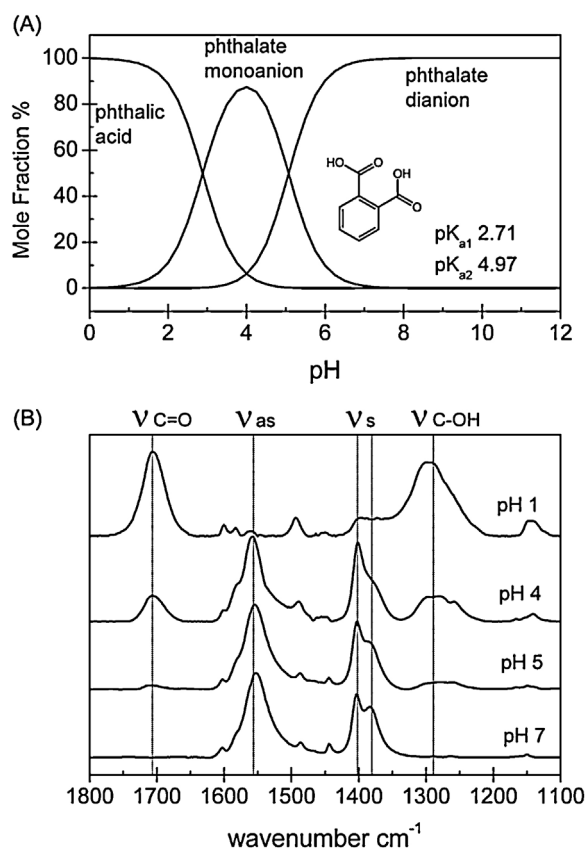


Fig. 1. (A) Distribution of phthalic acid, phthalate monoanion and dianion in solution as a function of pH at the ionic strength of 0.1 M. (B) FTIR spectra of 10 mM dissolved phthalic acid at pH 1, 4, 5, and 7 in 0.1 M NaCl solution. Spectra were normalized to the peak with the strongest intensity.

3. Results and discussion

3.1. ATR-FTIR spectroscopy of dissolved phthalate

Phthalic acid has two carboxylic groups with $\text{pK}_{\text{a}1} = 2.71$ and $\text{pK}_{\text{a}2} = 4.97$ at the ionic strength of 0.1 M, and thus exists as three aqueous species in the pH range 0–12 (Fig. 1A). The spectra of soluble phthalate at pH 1, 4, and 7 in Fig. 1B represent the phthalic acid, monoanionic phthalate, and dianionic phthalate species, respectively. The observed frequencies and peak assignments of dissolved phthalate are listed in Table 1.

As for phthalate dianion, the bands at 1485 and 1443 cm^{-1} were associated with benzene ring vibrations [1,7,17–19]. The two peaks at 1383 and 1402 cm^{-1} were clearly resolved in the characteristic symmetric ν_{COO^-} region [1,9,19,20]. Similarly, the second derivative of the strong peak in the asymmetric ν_{COO^-} region revealed two components at 1554 and 1564 cm^{-1} , though it was seemed as a broad band at around 1552 cm^{-1} [9]. The appearance of asymmetric

Table 1
Peak positions and assignments for dissolved phthalate.

pH 1	pH 4	pH 7	Assignment
1709	1710		$\nu(\text{C}=\text{O})$
1565	1562	1564	$\nu_{\text{as}}(\text{COO})$
1556	1556	1554	$\nu_{\text{as}}(\text{COO})$
1494	1489	1485	$\nu_{\text{CC}}(\text{ring})$
1448	1445	1443	$\nu_{\text{CC}}(\text{ring})$
1402	1402	1402	$\nu_{\text{S}}(\text{COO})$
1386	1384	1383	$\nu_{\text{S}}(\text{COO})$
1290	1290		$\nu(\text{C}-\text{OH})$

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