Adsorption of Phenols in Water by Organically Modified Layered Niobate $K_4Nb_6O_{17}$

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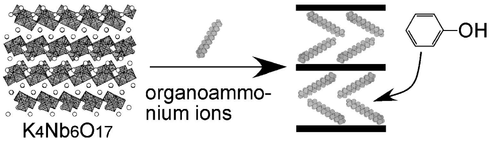
Intercalation compounds of layered niobate $K_4Nb_6O_{17}$ with organoammonium ions adsorbed 2,4-dicholorophenol and phenol dissolved in water. Their adsorption properties were greatly influenced by the organoammonium species pre-intercalated; modification by dioctadecyldimethylammonium ions gave peculiar affinity for 2,4-dichlorophenol.

Layered niobate $K_4Nb_6O_{17}$ forms intercalation compounds through displacement of interlayer K^+ ions for other species such as alkylammonium ions,[1,2] and has photocatalytic activities.[3] Because of these intercalating and photoactive properties, we may develop integrated materials where organic molecules adsorbed into the interlayer region are allowed to react photochemically; one of the authors found photoinduced electron transfer between the intercalated molecules and the niobate layers.[4]

Such an ''adsorption and photolysis'' concept will be utilized in another way: for example, removal of organic contaminants in water. When we use $K_4Nb_6O_{17}$ for such purposes, adsorption properties of the oxide should be a most important key. However, to our knowledge, solid–liquid adsorption behavior of $K_4Nb_6O_{17}$ has not been clarified well, in particular for electrically neutral molecules.

We report here the adsorption behavior of organically modified layered niobate $K_4Nb_6O_{17}$ for 2,4-dichlorophenol and phenol, which are often used as model compounds of organic pollutants, dissolved in water. Since the negatively charged $[Nb_6O_{17}]^{4-}$ layers can generally sandwich only cationic species, we modified the interlayer region to give affinity for the electrically neutral and hydrophobic adsorbates. Bulky organic cations were pre-intercalated to prepare hydrophobic interlayer environment (Scheme 1). Although this concept has been utilized for clay minerals in order to use them as adsorbents for organic pollutants in water,[5,6] investigations of layered niobates have not been reported. Our data show that adsorption property of $K_4Nb_6O_{17}$ is greatly altered by organic species used for the interlayer modification.



Scheme 1. Modification of $K_4Nb_6O_{17}$ for preparing hydrophobic interlayer spaces which can adsorb electrically neutral organic molecules.

$K_4Nb_6O_{17}$ synthesized according to the literature[7] was allowed to react with dodecyl-, dodecyltrimethyl-, and dioctadecyldimethyl-ammonium ions, which are abbreviated as $C_{12}N^+$, $C_{12}3MeN^+$, and $2C_{18}2MeN^+$, respectively. The reactions were carried out in aqueous solution containing excess amount of the organoammonium ions at 313–353 K for 2 weeks, followed by washing with water. The products are designated as, for example, $C_{12}N^+$–$K_4Nb_6O_{17}$. These organically modified niobates were then subjected to the adsorption experiment. The sample (0.5 g) was dispersed in a 0.1–10 mmol/dm^3 aqueous solution of 2,4-dichlorophenol or phenol (40 cm^3), and the mixture was shaken at 303 K for 24 h, by which treatment adsorption reached equilibrium. The adsorbed amount was estimated from the concentrations of adsorbate resided in water determined with UV spectroscopy.

The reactions of $K_4Nb_6O_{17}$ with organoammonium ions yielded the products where the organic species was intercalated. The intercalated structure was evidenced by X-ray diffraction (XRD) measurement, and composition of the products was determined by inductively-coupled plasma atomic emission spectroscopy (ICP) and thermogravimetry. Table 1 gives the gallery heights and compositions of the intercalated samples. The type of intercalation compounds listed in Table 1 distinguishes whether the guest species are located in every other interlayer spaces (A-type) or in all the interlayer regions (B-type),[2,8] because $K_4Nb_6O_{17}$ possesses two structurally unequal alternating interlayer regions with different intercalating reactivities.[9] This categorization leads to a deduction that quaternary ammonium ions ($C_{12}3MeN^+$ and $2C_{18}2MeN^+$) tend to give A-type intercalation compounds; B-type samples were not obtained under our reaction conditions. This is rationalized by bulkiness of their ammonium moieties which should kinetically retard incorporation into the interlayer regions. In addition, the quaternary ammonium species gives less dense packing of the alkyl chains; the interlayer volumes occupied by a carbon atom of organoammonium ions for the $C_{12}3MeN^+$– and $2C_{18}2MeN^+$–$K_4Nb_6O_{17}$ samples are larger than that for $C_{12}N^+$–$K_4Nb_6O_{17}$ (Table 1).

The obtained intercalation compounds of $K_4Nb_6O_{17}$ with organoammonium ions adsorbed 2,4-dichlorophenol in water ranging in concentration from 0.1 to 10 mmol/dm^3, although

Table 1. Structural and compositional data for $K_4Nb_6O_{17}$ intercalated with organoammonium species

Sample	Type of intercalation compound	Gallery height/nm	K^+ : organoammonium : Nb (molar ratio)	Interlayer volume occupied by one carbon atom (nm^3/carbon atom)[a]
$C_{12}N^+$–$K_4Nb_6O_{17}$	B	2.32	0.4 : 3.4 : 6.0	0.029
$C_{12}3MeN^+$–$K_4Nb_6O_{17}$	A	1.96	2.8 : 1.0 : 6.0	0.069
$2C_{18}2MeN^+$–$K_4Nb_6O_{17}$	A	4.08	3.0 : 0.8 : 6.0	0.065

[a] The interlayer volume occupied by a carbon atom of organoammonium ions is estimated from the gallery volume and content of the organoammonium ions. The gallery volume of the intercalation compounds is approximately determined as $a \times c \times$ (gallery height), where a and c are lattice parameters of $K_4Nb_6O_{17}$,[8] since the interlayer expansion in the b direction of the $K_4Nb_6O_{17}$ lattice on the intercalation corresponds to the gallery height.

Table 2. Amount of 2,4-dichlorophenol and phenol from 6 mmol/dm^3 of aqueous solutions onto $K_4Nb_6O_{17}$ modified with organoammonium ions

Sample	2,4-Dichlorophenol		Phenol	
	mmol/g[a]	mmol/C-mol[b]	mmol/g[a]	mmol/C-mol[b]
$C_{12}N^+$–$K_4Nb_6O_{17}$	0.58	0.021	0.30	0.011
$C_{12}3MeN^+$–$K_4Nb_6O_{17}$	0.80	0.063	0.50	0.039
$2C_{18}2MeN^+$–$K_4Nb_6O_{17}$	1.32	0.059	0.05	0.002

[a] Amount of the adsorbate in millimoles adsorbed onto 1 g of the sample.
[b] Adsorbed amount of the adsorbate in millimoles per 1 mol of carbon atom provided by the pre-intercalated organoammonium ions.

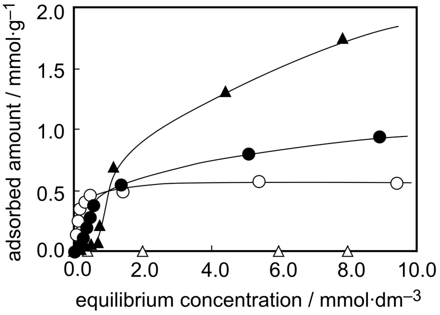


Figure 1. Adsorption isotherms of organically modified $K_4Nb_6O_{17}$ for 2,4-dichlorophenol; ○: $C_{12}N^+$–$K_4Nb_6O_{17}$, ●: $C_{12}3MeN^+$–$K_4Nb_6O_{17}$, ▲: $2C_{18}2MeN^+$–$K_4Nb_6O_{17}$, and △: unmodified $K_4Nb_6O_{17}$.

unmodified $K_4Nb_6O_{17}$ hardly adsorbed it. Figure 1 shows the adsorption isotherms at 303 K. The organically modified samples adsorbed more than 0.5 mmol/g of 2,4-dichlorophenol at 2 mmol/dm^3 of equilibrium concentration. This value is comparable with that observed for the adsorption of chlorophenols by organically modified clay minerals (e.g., montmorillonite modified with hexadecyltrimethylammonium ions adsorbs about 0.6 mmol/g of 3,5-dichlorophenol at 1 mmol/dm^3 of equilibrium concentration[5]). Further investigations using $2C_{18}2MeN^+$–$K_4Nb_6O_{17}$ indicated that the adsorption behavior obeys the isotherm at higher concentrations of 2,4-dichlorophenol up to 20 mmol/dm^3. Thermal analyses of the sample before and after the adsorption indicated little elimination of $2C_{18}2MeN^+$ ions during the adsorption process.

The isotherms indicate that adsorption behavior for 2,4-dichlorophenol depends on the organic modification. The A-type samples ($C_{12}3MeN^+$– and $2C_{18}2MeN^+$–$K_4Nb_6O_{17}$) show S-shaped isotherms. This type of isotherms indicates relatively weak adsorbent–adsorbate interactions, represented by downward curvature, at low equilibrium concentrations (<1 mmol/dm^3), while cooperative adsorption by, for example, hydrophobic interactions gives upward curvature at high concentrations.[10] The weak adsorption at low concentrations will be brought about by the residual hydrophilic interlayer regions, which are shared by remaining K^+ ions, in these samples.

The intercalation compounds with quaternary ammonium ions ($C_{12}3MeN^+$–$K_4Nb_6O_{17}$ and $2C_{18}2MeN^+$–$K_4Nb_6O_{17}$) adsorbed larger amount of 2,4-dichlorophenol than the sample with primary ammonium ions ($C_{12}N^+$–$K_4Nb_6O_{17}$) at higher concentrations (>2 mmol/dm^3). Table 2 compares the amount of adsorbed 2,4-dichlorophenol from an aqueous solution initially containing 6 mmol/dm^3 of the adsorbate. When the adsorbed amount is expressed in the unit of millimoles of adsorbed 2,4-dichlorophenol per 1 mole of carbon atoms of the pre-intercalated organoammonium ions, the amounts of adsorbate taken up by the samples modified with quaternary ammonium are similar to each other but much larger than that adsorbed by $C_{12}N^+$–$K_4Nb_6O_{17}$. This discrepancy would be due to the difference in packing of the alkyl chains; the quaternary ammonium ions less densely intercalated are presumed to provide larger spaces for accommodating the adsorbate.

A noticeable behavior of $2C_{18}2MeN^+$–$K_4Nb_6O_{17}$ was observed for the adsorption of phenol; the sample little adsorbed phenol in the concentration region of 0.1–10 mmol/dm^3. Table 2 exemplifies that $2C_{18}2MeN^+$–$K_4Nb_6O_{17}$ adsorbed very small amount of phenol, while that the other samples took up certain amounts the adsorbate. Although it is reasonable that phenol, more hydrophilic than 2,4-dichlorophenol, is less adsorbed to some extent by the hydrophobic interlayer regions of the organically modified niobates, the $2C_{18}2MeN^+$–$K_4Nb_6O_{17}$ sample shows unusual reduction in the adsorbed amount. We cannot fully rationalize this adsorption behavior at present. A possible explanation is that the intercalated $2C_{18}2MeN^+$ ions give highly organophilic interlayer regions to strongly prevent uptake of the relatively hydrophilic adsorbate; because of the bulkiness of the alkyl moieties, the amount of carbon atoms intercalated in $2C_{18}2MeN^+$–$K_4Nb_6O_{17}$ is rather larger than those in the other samples. However, we regard that this property is important because such adsorption property is helpful to apply the organically modified niobate for selective adsorption of organic contaminants.

In conclusion, layered niobate $K_4Nb_6O_{17}$ properly pre-intercalated with organic species can adsorb electrically neutral organic molecules, exemplified by phenols, dissolved in water. The adsorption property can be tuned by the pre-intercalated organoammonium ions. In particular, adsorption behavior of $2C_{18}2MeN^+$–$K_4Nb_6O_{17}$ should be regarded as a clue to selective adsorption. The results should also be useful for constructing intercalation-based systems of layered niobates with electrically neutral species.

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8 The difference in the types of intercalation compounds is regarded as that in "staging" of the interlayer structure; the A- and B-type structures corresponds to second- and first-staging, respectively. This difference is distinguished by the XRD patterns,[2] and the deduction is verified by whether or not the gallery height estimated on the basis of the assumed structural type is rational. Composition of the samples is also helpful to confirm the deduction; for the A-type intercalates, molar ratio of the intercalated cation to Nb atom does not exceed 2 to 6 because the guest cations can compensate less than half of negative charges provided by the $[Nb_6O_{17}]^{4-}$ layers. The organic contents of the A-type samples listed in Table 1 satisfy this limitation.
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