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Anion Exchange Properties of Hydrous Metal Oxides. Analysis Based on Surface Complexation with Stability Constant Data Base

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Abstract

Ion exchange properties of hydrous metal oxides (HMeOs) for weak base anions were discussed in terms of surface complexation using the metal-ligand stability constant data base at relatively high ionic strength. The selectivity sequences of anion were correlated comparatively well with the orders of first stepwise stability constants (K_1) of the corresponding metal-ligand complexes. Conditions whether inner sphere or outer sphere surface complex forms could be evaluated by the difference in the stability constant between the OH^-/X^- (X^- : anion) and $\text{OH}^-/\text{H}_2\text{O}$ ligand exchange reactions. These calculations suggest that the anion exchange reaction of HMeO is controlled mainly by the interactions of anions or H_2O molecules with the central metal atoms.

Key words: anion exchange, selectivity, hydrous metal oxide, surface complexation model, stability constant

1 Introduction

Studies of anion exchange properties of HMeOs are important in the field not only of fundamental surface and separation chemistry but also of environmental- and geo-chemistry. From a standpoint of pollution control, there have been extensive studies on the adsorption of harmful anions (fluoride, arsenate, arsenite, selenate, selenite, phosphate, nitrate ions, etc.) on HMeO from lake, river, underground water, seawater, waste water, and drinking water. Several kinds of HMeO, e.g. hydrous iron oxide, hydrous aluminum oxide, etc. with crystalline or amorphous structure are a promising material for the removal of harmful anions from aqueous solutions. The anion exchange reactions of HMeOs progress involving the hydroxyl groups formed on the surface of metal oxide crystallites; they show different acid-base properties depending on the kinds and properties of central metal atoms of HMeO. Two kinds of anion exchange (adsorption) reactions are known with HMeO [1],

where $\boxed{\text{M}}$ is central metal atom of HMeO. Selectivity sequence of anion exchange can be obtained by measurement of distribution coefficient (K_d) of anions on HMeO from a diluted solution. Selectivity sequences on different kinds of HMeO vary depending on the kind of central metal atoms, as is shown in the next section.

It has been found that surface complexation model (SCM), which treats surface hydroxyl group as analogs of complexing ligand in solution, well describes the anion exchange behavior at the oxide/aqueous interface. The structure at the oxide/aqueous interface has been analyzed with several types of SCM: diffuse-layer model (DLM), constant capacitance model (CCM), triple-layer model (TLM), and extension of triple layer model (ETML) [2, 3]. Anions at the solution/solid interface can be classified mainly into two groups in the DLM: strongly bound anions which form inner sphere (IS) surface complex with the central metal atoms of HMeO and weakly bound ones which form outer sphere (OS) surface complex. In the latter, H_2O molecules are bound directly to the central metal atoms and anions in solutions interact outside the H_2O molecules. Formations and structures of IS and OS surface complexes can be schematically written as Figure. 1. The ionic strength dependence of anion adsorption can be used as a criterion for the formation of IS or OS surface complex. Anion uptake is rarely influenced by ionic strength in the case of IS surface complex,

Figure. 1 Schematic representations of inner and outer sphere surface complexations

while it decreases markedly with ionic strength in the case of OS surface complex [4]. Using these models, several parameters (equilibrium constant of complex formation, acid-base constants, etc.) are derived from experimental results of anion exchange. These parameters are useful to simulate the exchange behaviors over the wide conditions of exchange reactions which cannot be determined experimentally.

This paper shows that stability constant (SC) data base [5] compiled by IUPAC is useful to predict the selectivity sequence of anion on HMeO, especially consisting of trivalent and divalent metals. The correlation between the tendencies to form surface complex and to form the corresponding (inner-sphere) solute complex has been pointed out by W. Stumm for hydrous iron oxide and hydrous aluminum oxide, with $\text{Fe}(\text{OH})_2^+$ and $\text{Al}(\text{OH})_2^+$ ions as solute, respectively [6]. However, to the best of my knowledge, there have been no reports that use SC data base in a general way to predict selectivity sequence of anions on various kinds of HMeO. In addition to the prediction of selectivity sequence, SC data base is useful to distinguish whether IS or OS surface complex forms at a known condition. We studied only weak base anions in this paper, since the interaction between HMeO and weak base anions is simple because of no protonated species over a wide range of pH.

2 Selectivity sequences in the literatures

Selectivity sequences of anions on inorganic ion exchangers, reported until now are summarized in Table 1. The selectivity sequence varies depending on its crystal structure and the kind of central metal atom. The selectivity orders can be classified roughly into two groups: that ($\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$) reverse to the Hofmeister series and the others. The former is observed for HMeO with central metal ions (Al^{3+} , Fe^{3+} , tetravalent metals) belonging to hard acid. HMeO with central metal atoms (Bi^{3+}) belonging to rather soft acid (borderline acid) shows the different ($\text{Br}^- > \text{Cl}^-$) selectivity order, which follows the Hofmeister series ($\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$). The

strong base anion exchange resin with tetra-alkyl ammonium ions as a functional group (soft acid) also shows the selectivity order of Hofmeister series. These results suggest that the interaction between anion and the central metal of HMeO strongly affects the affinity of halide ion exchange properties and the concept of hard and soft acid and base (HSAB) [14] is useful to predict the selectivity order.

Table 1 Selectivity sequences of anion on hydrous metal oxides

Inorganic ion exchanger	Selectivity sequence	Ref.
ZnO nH ₂ O	CrO ₄ ²⁻ > C ₂ O ₄ ²⁻ > PO ₄ ³⁻ > SO ₃ ²⁻ > S ₂ O ₃ ²⁻ > I ⁻ > SO ₄ ²⁻ > Cl ⁻ > NO ₃ ⁻	[7]
PbO nH ₂ O	CrO ₄ ²⁻ > PO ₄ ³⁻ > Cl ⁻ > S ₂ O ₃ ²⁻ > SO ₃ ²⁻ > I ⁻ > SO ₄ ²⁻	[7]
Al ₂ O ₃ nH ₂ O	F ⁻ > IO ₄ ⁻ > IO ₃ ⁻ > BrO ₃ ⁻ > Cl ⁻ > Br ⁻ > ClO ₃ ⁻ > I ⁻	[4]
Fe ₂ O ₃ nH ₂ O (heating at 170°C)	OH ⁻ > AsO ₄ ³⁻ , B ₄ O ₇ ²⁻ > PO ₄ ³⁻ , F ⁻ > CO ₃ ²⁻ > CrO ₄ ²⁻ , SO ₃ ²⁻ > SO ₄ ²⁻ , IO ₄ ⁻ > S ₂ O ₃ ²⁻ > BrO ₃ ⁻ > NO ₂ ⁻ , NO ₃ ⁻ > Cl ⁻ > ClO ₃ ⁻ > Br ⁻ > ClO ₄ ⁻ , I ⁻	[7]
FeOOH	CO ₃ ²⁻ , HPO ₄ ²⁻ > SO ₄ ²⁻ , NO ₃ ⁻ , Cl ⁻ (α-FeOOH, pH 8) HPO ₄ ³⁻ > SO ₄ ²⁻ > NO ₃ ⁻ > CO ₃ ²⁻ , Cl ⁻ (β-FeOOH, pH8)	[8]
Fe ₂ O ₃ nH ₂ O (hematite)	Cr ₂ O ₇ ²⁻ > MoO ₄ ²⁻ > VO ₃ ⁴⁻	[7]
La ₂ O ₃ nH ₂ O	PO ₄ ³⁻ > C ₂ O ₄ ²⁻ > CrO ₄ ²⁻ > MnO ₄ ⁻ > I ⁻ > SO ₄ ²⁻ > Cl ⁻	[7]
Bi ₂ O ₃ nH ₂ O	CrO ₄ ²⁻ > C ₂ O ₄ ²⁻ > PO ₄ ³⁻ > SO ₄ ²⁻ > I ⁻ PO ₄ ³⁻ > SO ₄ ²⁻ > Br ⁻ > Cl ⁻ > NO ₃ ⁻	[7] [9]
SnO ₂ nH ₂ O	PO ₄ ³⁻ > C ₂ O ₄ ²⁻ > SO ₄ ²⁻ > Cr ₂ O ₇ ²⁻ > Cl ⁻ > MnO ₄ ⁻ > Br ⁻ > I ⁻ SO ₄ ²⁻ > Cl ⁻ > I ⁻ > Br ⁻ > NO ₃ ⁻	[7] [10]
TiO ₂ nH ₂ O	As(OH) ₄ ⁻ > Te ₂ O ₃ ⁻ > Se ₂ O ₃ ⁻ > IO ₃ ⁻ > BrO ₃ ⁻ > ClO ₃ ⁻ SO ₄ ²⁻ > Br ⁻ , Cl ⁻ > I ⁻ , NO ₃ ⁻	[11] [10]
SiO ₂ nH ₂ O (Mg ²⁺ loading)	PO ₄ ³⁻ > C ₂ O ₄ ²⁻ > SO ₄ ²⁻	[7]
CeO ₂ nH ₂ O	F ⁻ > HPO ₄ ²⁻ > SO ₄ ²⁻ > Cl ⁻ , NO ₃ ⁻ (pH 5) As(OH) ₄ ⁻ > B(OH) ₄ ⁻ > HPO ₄ ²⁻ > NO ₃ ⁻ , Cl ⁻ , F ⁻ (pH 9)	[12]
ZrO ₂ nH ₂ O	PO ₄ ³⁻ > F ⁻ > Cl ⁻ , SO ₄ ²⁻ , NO ₃ ⁻ , Br ⁻	[13]

Most of the HMeOs shows high selectivity for strong base oxo-anions (phosphate, arsenate, carbonate ions, etc). Since they have a tendency to bind cations (for example protons) easily, they can form IS surface complexes smoothly. For halate anions, several HMeOs show the selectivity order of IO₃⁻ > BrO₃⁻ > ClO₃⁻ which agrees in the decreasing of order of ionic radius. The pH dependence of halate ion adsorption on γ-Al₂O₃ shows the formation of OS surface complex [3]. In the case of OS surface complex, it is reasonable to think that the affinity of anions are controlled mainly by the electrostatic interaction between anions and the positively charged HMeO surface, therefore it decreases with an increase in the radius of "hydrated" ions (with a decrease of ionic radius).

3 Surface complexation based on solute complexation

3.1 Anion exchange selectivity

The anion exchange reaction of HMeO can be written by eqs. 1 and 2 for IS and OS surface complexation reactions, respectively. The protonation reaction (eq. 2) has the same physical meaning as H₂O coordination at the inner sphere of central metal. When the random mixing can be assumed for exchanged anions with a constant number of exchange site, the anion exchange reaction can be treated as a homogeneous solution reaction of complex formation. The complexation reaction of cations for various ligands are

summarized as stability constant (S) data base by IUPAC [5]. The first stepwise stability constant (K_1) can be written as follows,

where metal ion M^{n+} is in a hydrated form. Since metal ions are hydrated before the complexation reaction, the stability constant corresponds to the value of H_2O/X^- ligand exchange.

The anion exchange reaction of HMeO can be written by two step reaction as follows,

where $K_{1,OH}$ and $K_{1,X}$ are the stability constants given as follows. A random mixing of anions on HMeO is assumed and the electrostatic term is ignored since high ionic strength is assumed.

The selectivity of anion exchange can be evaluated from the value of $K_{1,X}$, since the stability constant ($K_{1,OH}$) of H_2O coordination is constant. We cannot distinguish the complexation state (IS or OS state) directly from the stability constant, since it can be calculated from the concentrations of metal-ligand complex, metal ions, and ligand irrespective of the state of metal-ligand complex.

3.2 The pH dependence of anion exchange

The pH dependence of anion exchange can be calculated using the $K_{1,X}$ and $K_{1,OH}$ values. The rate (R_X) of ion exchange are given as follows,

$$\begin{aligned} R_X &= [MX] / ([MX] + [M(OH)]) \\ &= K_{1,X}[X] / (K_{1,OH}[OH] + K_{1,X}[X]) = K_{1,X}[X] / (K_{1,OH}K_w/[H] + K_{1,X}[X]) \end{aligned} \quad (6)$$

where K_w is dissociation constant of H_2O . The pH dependence of anion exchange can be calculated when $K_{1,X}$ and $K_{1,OH}$ are available.

The conditions that the OS surface complexation reaction takes place can be calculated using the $K_{1,OH}$. Since the OS surface complex forms when M-X interaction is markedly weaker than the M - OH_2 interaction, the reaction is controlled mainly by the reaction of H_2O coordination on central metal. The rate (R_{aq}) of aqua-complex is given as,

$$R_{aq} = [M] / ([M] + [M(OH)]) = (K_{1,OH} K_w [H]^{-1} + 1)^{-1} \quad (7)$$

Equation 7 shows that the conditions that OS complex forms depends only on pH, but not on anion concentration.

4 Results and Discussion

4.1 Selectivity sequence

The first stepwise stability constants ($K_{1,X}$) of di- and tri-valent metal ions for halide and oxo anions are summarized in Figure 2. They are obtained by averaging the $K_{1,X}$ values at ionic strength between 0.5 and 2, since the influence of electrostatic interaction decreases at high salt concentration due to the shielding effect of electric field by added salt (ions). The $K_{1,X}$ value varies depending on central metal ions similar to the experimental results in Table 1. The selectivity sequences for HMeO can be predicted from these $K_{1,X}$ values as follows,

[Central metal]

The selectivity sequences agree comparatively well with those in Table 1. Similar to the experimental results, the HSAB relationship is observed; the HMeOs with hard acid metals (Fe^{3+} , Zn^{2+}) shows high selectivity for F^- , while those with borderline acid (Bi^{3+} , Pb^{2+}) relatively high selectivity for I^- . Although experimental results are not available, the selectivity sequences of hydrous magnesium oxide and hydrous cadmium oxide can be predicted as follows,

[Central metal]

Since Cd^{2+} belongs to soft acid, the predicted selectivity sequence for halide ions agrees with the Hofmeister series. The $K_{1,X}$ values of tetraalkyl ammonium ions for anions are given in the bottom of Figure 2 as a model functional group of strong base anion exchange resin. The selectivity sequence ($\text{I}^- > \text{Br}^- > \text{Cl}^-$) for halide ions follows the normal Hofmeister series, suggesting that these anions interact with the functional group in a hydrated state. This also follows the HSAB rule.

4.2 pH dependence of anion exchange

The pH dependence of anion exchange can be evaluated using eq. 6 when ligand concentration and $K_{1,\text{OH}}$ are known in addition to the $K_{1,X}$ values. The calculated pH dependences of Cl^- and F^- exchanges and the experimental result [15] for Cl^- exchange are shown in Figure 3 at a solute concentration of 0.1 M. Since the

Figure 2 First stepwise stability constant of metal ions for various anions.

Figure 3 The calculated and experimental pH dependences of anion exchange. $\log K_{1,\text{OH}} = 7.3$.

Since the

exchange capacity of $\text{MgO} \cdot n\text{H}_2\text{O}$ is not available, the R_X value cannot be calculated from the experimental uptake curve. Therefore, the pH values that start anion exchange is meaningful at present. The starting pH value agrees well between the calculated and experimental results for Cl^- exchange on hydrous magnesium oxide.

The conditions that form IS or OS surface complex can be calculated using eqs. 6 and 7. The pH dependences of Cl^- and H_2O exchanges with hydroxylated Fe^{3+} are given in Figure 4. The Cl^- exchange depend on solute concentration according to eq.6; the exchange

curve shift to lower pH region with the decrease of solute concentration. While the H_2O exchange does not depend on solute concentration according to eq. 7. Fig. 4 shows that the IS surface complex forms at 1M FeCl_3 while the $\text{OH}^-/\text{H}_2\text{O}$ exchange is predominant and the OS surface complex forms in the region of FeCl_3 concentration below 0.1 M. This shows that the structure of surface complex varies depending on solute concentration. The conditions whether IS or OS complex forms can be written as follows,

$$K_{1,X} [X] > 1 \quad (\text{formation of IS surface complex})$$

$$K_{1,X} [X] < 1 \quad (\text{formation of OS surface complex})$$

In the system with lower $K_{1,X}$, for examples $\text{Mg}^{2+}\text{-Br}^-$, $\text{Zn}^{2+}\text{-Br}^-$, and $\text{Fe}^{3+}\text{-ClO}_3^-$ systems, the OS surface complex tends to form at low solute concentrations.

Figure 4 The pH dependences of Cl^-/OH^- and $\text{Cl}^-/\text{H}_2\text{O}$ exchanges with Fe^{3+} system.

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