

THEORY OF INTERFACIAL STEPWISE  
ION/COORDINATION PARTICLE  
EXCHANGE AND ITS APPLICATIONS

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INTERACTION OF TRACE METALS AND SUSPENDED  
MATTER IN SEAWATER — ION EXCHANGE pH RANGE

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ABSTRACT

This article summarizes the experimental results on the interaction among trace metals, particulate matter and organic material in seawater. Ion exchange pH ranges for fifty systems involving these three types of material are reported and the results explained according to simple equations and corresponding figures. The types of material involved include U(VI), Cu(II), Pb(II), Zn(II), Cd(II), Cr(III), Cr(VI); hydrous titanium oxide, Goethite, Hematite, amorphous hydrous ferric oxide,  $\delta$ -MnO<sub>2</sub>,  $\gamma$ -MnOOH, Manganite, Kaolinite, Illite, Montmorillonite, Humic Acid, Fulvic Acid, Lysine, Histidine, Aspartic Acid, Valine, Alanine, Threonine, Serine, Proline, Methionine, Arginine, Phenylalanine, etc. The equations and figures can be used to reveal (1) whether the interaction is cation ion exchange or anion ion exchange; (2) where the location of the pH curve is; (3) what the pH range of the reaction is; (4) how many ligands each metal ion replaces; and (5) how it can help to determine the reaction mechanism. Based on results involving organic matters, their effects on the interaction between trace metals and solids are quantified. The data indicate that whether an organic matter enhances or decreases the association between the trace metal and solids depends on the concentration of organic matter and its association constant with the metal ion.

INTRODUCTION

Some kind of surface interaction in association with suspended matter such as ion exchange, sorption, adsorption, partition, complexation or scavenging, plays an important role in the distribution and fate of trace metals in seawater (Goldschmidt, 1937; Krauskopf, 1956; Parks, 1975; Brewer, 1975; Turekian, 1977; Murray and Brewer, 1977; Sackett, 1978; Kitano et al., 1980; Li, 1981; 1982; Adamson, 1982; Whitfield and Turner, 1982; Pytkowicz, 1983). The suspended matter, or particulates, consists largely of organic matter, clay minerals, and metal hydroxides (Sackett, 1978), which are all known to be strong chelators and ion exchangers (Amphlett, 1964; Vesely and Pekarek, 1972a, b; Chang and Liu, 1974; 1978; Stumm and Morgan, 1981; Mantoura et al., 1978; Gamble et al., 1983). Previous studies often treated, successfully, the interaction of trace elements and particulates by surface complexation between ions and multiple surface sites, analogous to the complexation of ions and multi-ligands in an aqueous solution (James and Healy, 1972; Stumm et

al., 1976; 1980; Davis et al., 1978; Davis and Leckie, 1978a, b; Schindler, 1981; Balistrieri and Murray, 1982; 1983; Benjamin and Leckie, 1982). On the other hand, we prefer to treat the surface interaction by ion exchange (Chester, 1965; Chang and Liu, 1974; 1978; O'Connor and Kester, 1975; Sayles and Mangelsdorf, 1977; Sun, 1982). This article will discuss the theory and summarize the experimental results of Chang and co-workers performed at Shandong College of Oceanology and include fifty systems involving U(VI), Cu(II), Zn(II), Cd(II), Pb(II), Cr(III), Cr(VI), and hydrous titanium oxide, goethite, hematite, amorphous hydrous ferric oxide,  $\delta$ -MnO<sub>2</sub>,  $\gamma$ -MnOOH, manganite, kaolinite, illite, montmorillonite, humic acid (HA) and fulvic acid (FA), etc. interference of lysine, histidine, aspartic acid, valine, alanine, threonine, etc. for some systems are also reported. The results will be discussed according to the stepwise equilibrium theory proposed by Chang and Liu (1974).

This article (Part I) will concentrate on the discussion of pH range of ion exchange and the apparent equilibrium constant. A subsequent article (Part II) will discuss the reaction isotherms. A third article based on experiments performed at Oregon State University will focus on the reaction mechanism and will appear at a later date.

### THEORY ON THE pH RANGE OF THE ION EXCHANGE

It is well known that pH falls within a narrow range for the interactions between trace metal and solids (James and Healy, 1972; Chang and Liu, 1974; Balistrieri and Murray, 1982). Following the work of Chang and Liu (1974, 1978), we assume a simple ion exchange reaction between a solid ion exchanger RB<sub>m</sub> and a metal ion M in an aqueous solution (the valence of the ion is omitted for simplicity):



$$\text{and } K_{RM} = \frac{(RM)}{(M)(RB_m)}, \quad (2a)$$

$$K_{RB_m} = \frac{(RB_m)}{(R)(B)^m}, \quad (2b)$$

$$K = \frac{K_{RM}}{K_{RB_m}} = \frac{(RM)(B)^m}{(M)(RB_m)}, \quad (2c)$$

where  $K$  is the equilibrium constant, B is the ligand to be replaced on the solid R,  $m$  is the number of ligands replaced by each metal ion. For cation ion exchange with hydrous metal oxides and clay minerals, the proton is the most likely candidate to be replaced, thus

$$K = \frac{(RM)(H)^m}{(M)(RH_m)}. \quad (3)$$

Now we define the distribution coefficient ( $D$ ) and the percentage of ion exchange for M,  $E(\%)$ , respectively, as

$$D = (RM)/(M), \quad (4)$$

$$E(\%) = 100(RM)/[(M) + (RM)]. \quad (5)$$

Combining Eqs. (3) to (5) we obtain

$$D = E(\%) / [100 - E(\%)] = K(RH_m) / (H)^m \quad (6)$$

The logarithm of Eq. (6) gives

$$\text{pH} = \frac{-\log [K(RH_m)] + \log E(\%) - \log [100 - E(\%)]}{m} \quad (7)$$

These two equations can be represented by Figs. 1 and 2 (curve a), respectively.

At the beginning of reaction,  $E(\%)$  is small so that

$$\text{pH}^0 = \frac{-\log [K(RH_m)] - 2}{m} \quad (8)$$

while at the end of reaction,  $E(\%)$  approaches 100, so that

$$\text{pH}^f = \frac{-\log [K(RH_m)] + 2}{m} \quad (9)$$

and the pH range for the cation ion exchange is

$$\text{pH range} = \frac{-\log [K(RB_m)] \pm 2}{m}$$

For an anion ion exchange reaction, B in (2) is replaced by (OH), thus

$$\text{pH range} = 14 + \frac{\log [K(ROH_m)] \pm 2}{m} \quad (11)$$

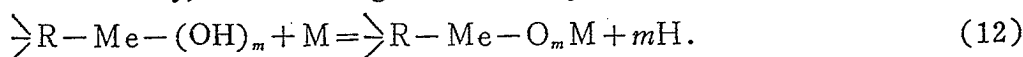
The relation between  $E(\%)$  and pH for an anion ion exchange is also shown in Fig. 2 (curve b). The  $E(\%)$  vs pH figure provides the following information:

(1) Whether cation ion exchange reaction (CIER) or anion ion exchange reaction (AIER) occurs (Chang and Liu, 1974): For instance, Cu, Zn, Pb, Mn, Cr(III), U(VI), Bi and Hg in seawater undergo CIER, with H on ferric hydroxide and the  $E(\%)$  vs pH correlation is a S-curve (curve a in Fig. 2). On the other hand, Sn, As, Mo and V undergo AIER with iron hydroxide, hence showing an inverse or mirror-image S-curve on the  $E(\%)$  vs pH plot (curve b in Fig. 2) (Chang and Liu 1974).

(2) The position of the curve indicates the affinity between the metal ion and the ion exchanger: For instance, the reactions with greater  $K$  are the ones with more stable ion exchange products. As a result, an ion that undergoes CIER more readily has a curve situated in the lower pH range than an ion of weaker affinity to the same solid.

(3) The ion exchange mechanism: The number of H or OH on the solid surface replaced by each metal ion can be estimated from the  $E(\%)$  vs pH curve because the pH varies over a range of  $4/m$  pH units (Eqs. (10) and (11)). For instance, a CIER that covers a pH range of 4 or 2 indicates that each cation replaces one or two protons, respectively. A non-integer pH range would suggest high valence or mixed-valence reactions. These results can be used for speciation studies.

In the above discussion,  $RB_m$  is a pure metal hydroxide or clay. In the situation that metal hydroxide coats a clay, the following reaction may occur:



If  $K_{RM} = \alpha_1$ ,  $K_{MeM}$  and  $(RB_m) = \alpha_2$  ( $Me(OH)_m$ ) where  $\alpha_1$  and  $\alpha_2$  are constants and  $K_{MeM}$  is

the association constant between  $\text{Me}(\text{OH})_m$  and  $\text{M}$ , and  $(\text{Me}(\text{OH})_m)$  is the concentration of  $\text{Me}(\text{OH})_m$ , then Eqs. (9) and (10) become

$$\text{pH}(\text{CIER}) = - \frac{\log \left[ \frac{\alpha_1 K_{\text{MeM}} \cdot \alpha_2 (\text{Me}(\text{OH})_m)}{K_{\text{RB}m}} \right] \pm 2}{m}, \quad (13)$$

$$\text{pH}(\text{AIER}) = 14 + \frac{\log \left[ \frac{\alpha_1 K_{\text{MeM}} \cdot \alpha_2 (\text{Me}(\text{OH})_m)}{K_{\text{RB}m}} \right] \pm 2}{m}. \quad (14)$$

In the situation that organic coating exists, equations similar to Eqs. (13) and (14) are also valid:

$$\text{pH}(\text{CIER}) = - \frac{\log \left[ \frac{\alpha'_1 K_{\text{OM}} \cdot \alpha'_2 (\text{O}(\text{OH})_m)}{K_{\text{RB}m}} \right] \pm 2}{m}, \quad (15)$$

$$\text{pH}(\text{AIER}) = 14 + \frac{\log \left[ \frac{\alpha'_1 K_{\text{OM}} \cdot \alpha'_2 (\text{O}(\text{OH})_m)}{K_{\text{RB}m}} \right] \pm 2}{m}, \quad (16)$$

where  $K_{\text{OM}}$  is the equilibrium constant between organic matter and trace metal, and  $(\text{O}(\text{OH})_m)$  is the concentration of the organic coating on the solid.

## EXPERIMENTS

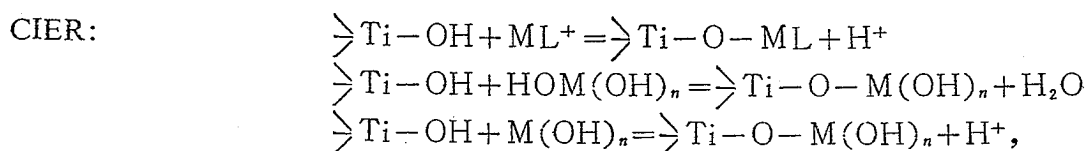
The experiments were all performed by Chang and the details have been given elsewhere (Chang & Liu 1978; Liu et al., 1980, 1981; Liu, 1983; Chang et al., 1982; Sun, 1982). Briefly, the metal hydroxides were prepared in the laboratory and analyzed by X-ray diffraction, IR spectroscopy and scanning electron microscopy in order to ensure purity. The illite, kaolinite and montmorillonite are natural products taken from ores in Nanjing, Suzhou and Heishan (all in China), respectively, but purified prior to the experiments to remove trace metals and organic material. Solids prepared by the same method were sieved by 40–80 mesh sieves prior to each series of experiments. One hundred mg of solids, about 100 ml natural seawater and trace metal solutions were put into 250 ml Erlenmeyer flasks. The pH of the solutions was adjusted by HCl or  $\text{NH}_4\text{OH}$  to produce equally-spaced pH values in the range of from 2 to 10.5. The final solution has a metal concentration of  $5 \times 10^{-8}$  moles/l. After having been shaken in a constant-temperature bath for two and a half hours, the solutions were filtered and the pH measured. The solids were washed by distilled water, followed by 10% HCl to release the trace elements on the surface of particles. Finally the trace metals in seawater and the HCl solutions were analyzed.

## RESULTS AND DISCUSSION

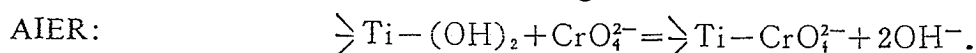
### 1. Hydrrous metal oxide

(1) Hydrous titanium oxide: The relationships between ion exchange percentage and pH for U(VI), Cr(VI), Cr(III), Cu(II), Zn(II) and Cd(II) (Chang and Liu, 1978; Zhang et al., 1982; Liu et al., 1980; 1981) are given in Fig. 3. A comparison of Figs. 2 and 3 shows clearly that Cr(III), Cd(II), Cu(II) and Zn(II) in seawater undergo CIER with hydrous titanium oxide, whereas Cr(VI) undergoes AIER. U(VI) undergoes CIER in spiked artificial seawater and in natural seawater at low pH range, but undergoes AIER at high pH range found in the oceans. These results are consistent with the chemical speciation of those elements reported in the literature (Stumm and Brauner, 1975; Zhang et al., 1983a, b).

Based on the positions of the curves, the affinity of these metals with hydrous titanium oxide falls in the following sequence: Cr(III) > U(VI) > Cu(II)  $\cong$  Cd(II) > Zn(II), in good agreement with the results of Keen (1968). All reactions except U(VI) in the spiked artificial seawater cover a pH range of 4 units, thus each metal ion replaces one H or OH, perhaps by the following mechanism:



where M is the metal ion and L is the ligand associated with M.



The spiked U(VI) covers a pH range of 2 units, suggesting that each ion replaces two H. This is because  $\text{UO}_2^{2+}$  dominates in the spiked seawater and exchanges with two protons on hydrous titanium oxide. On the other hand, in the natural seawater concentration for U(VI),  $\text{UO}_2(\text{OH})^+$  exchanges with one H on the solid (Chang and Liu, 1974; 1977).

(2) Hydrous ferric oxide: The ion exchange percentages of Cu(II), Zn(II) and Cd(II) with the three major hydrous ferric oxides in the oceans, the amorphous hydrous ferric oxide, goethite, and hematite are plotted vs pH in Figs. 4—6 (Zhang and Liu, in press). The results indicate that among the three metal ions, Cu has the highest affinity to all three hydrous ferric oxides, whereas Cd has the lowest affinity, in agreement with the results of Balistrieri and Murray (1983). The positions of the curves also suggest that Cu has the highest affinity to amorphous hydrous ferric oxide, followed by goethite and hematite. Cd associates with amorphous hydrous ferric oxide most readily, followed by goethite and finally hematite. Zn associates better with amorphous hydrous ferric oxide and goethite than with hematite. pH varies over a range of 4 units, suggesting that each metal ion replaces a proton (Balistrieri and Murray, 1983). Such an event may indirectly suggest that Cu, Cd and Zn exist as single-charged species in seawater.

(3) Hydrous manganese oxide: The ion exchange percentages of Cd(II) on  $\delta$ - $\text{MnO}_2$ ,  $\gamma$ - $\text{MnOOH}$  and Manganite are plotted vs pH in Fig. 7. The results indicate that Cd(II) associates with  $\delta$ - $\text{MnO}_2$  more readily than with  $\gamma$ - $\text{MnOOH}$  and Manganite.

Fig. 8 shows  $E$  (%) vs pH for Cu, Pb, Zn and Cd on  $\gamma$ - $\text{MnOOH}$ . Cu associates with  $\gamma$ - $\text{MnOOH}$  the strongest, followed by Pb, then by Zn and finally by Cd (Takematsu, 1979).

All these ions undergo cation ion exchange and replace a proton on the solid.

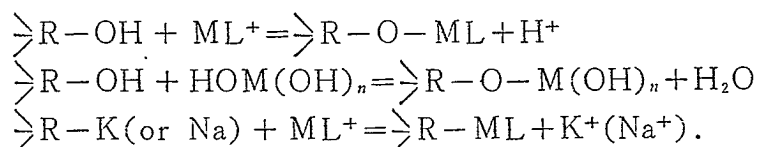
## 2. Clay minerals

Studies on the interactions between trace metals and clays in seawater are attracting more and more attention, but few comprehensive studies exist (Chester, 1965; O'Conner and Kester, 1975; Oakley et al., 1981; Sun, 1982).

The interactions of Cu, Pb, Zn and Cd with illite, kaolinite and montmorillonite have been studied, and the results for illite are presented in Fig. 9 (curves for kaolinite and montmorillonite are similar and are not shown here). The results indicate that Cu has the highest affinity with all three clays, followed by Pb and Zn, and finally by Cd. The results for Pb and Zn are so similar that they are almost indistinguishable.

All four trace metals associate the most with montmorillonite, followed by illite, then by kaolinite, in agreement with the results reported previously (Inskeep and Baham, 1983; Takematsu, 1979).

All reactions cover a pH range of 4 units and suggest the release of a single proton after ion exchange (DeMumbrum and Jackson, 1956; Hodgson et al., 1964; Chester, 1965; O'Conner and Kester, 1975). Possible reaction mechanisms are as follows:



Note that different batches of clay yield different quantitative results but the qualitative results are always the same.

## 3. Effect of organic matter on the interactions between trace metals and clays

Few systematic studies exist regarding the effect of organic matter on the distribution of trace metals on solids. Existing papers report contradictory results: some authors assert that organic matter favors the association of trace metals on solids (Vydra, 1963; Vydra and Markova, 1963; Siegel, 1966; Fukai et al., 1975; Reuter and Purdue, 1977; Davis and Leckie, 1978b; Anderson and Rubin, 1981), while others conclude that organic matter reduces the affinity between trace metals and solids (Richter and Theis, 1978; Leckie et al., 1978; Weaver and Birkner, 1978; Plausic et al., 1980).

It has been suggested that organic material of high molecular weight enhances the metal-solid interaction, whereas low-molecular weight organic matter reduces the reaction (Rashid et al., 1972; Reuter and Purdue, 1977). The theory is that high molecular weight organic matter (such as Humic acid, HA) does not easily dissolve in water, thus having a tendency to associate with solids, taking trace metals along with it. On the other hand, small organic compounds (such as fulvic acid, FA) dissolve in water, staying in the water along with their associated trace matter. But different authors are still reporting different results even for the same material. For instance, Vydra (1963) and Vydra and Markova's (1963) results for

EDTA contradict those of Plausic et al. (1980), and Siegel's results for glycine (1966) contradict those of Weaver and Birkner (1978).

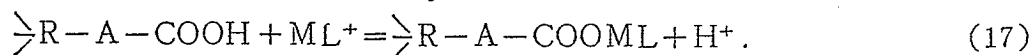
In order to understand why the contradiction existed and perhaps provide a logical explanation, we studied the effect of HA, FA and 14 amino acids on the association of Cu, Zn and Cd with illite, kaolinite and montmorillonite. The results are summarized here; details will be published elsewhere (Liu, 1983). The effect of various concentrations of FA, histidine and Lysine on the reaction between Cu (II) and illite is shown on Figs. 10—12, respectively. Fig. 13 shows the change of  $E(\%)$  with the concentration of Lysine. Fig. 14 and Table 1 show the effect of organic matter on the shift of  $E(\%)$  vs pH curves where pH is the difference in the position of pH curves with and without organic matter. Fig. 15 and Table 2 reveal the effect of histidine, poline, alanine, serine and lysine on the interaction of Cu (II) and illite in seawater. These results indicate that:

(1) From Figs. 10—12 it is obvious that the effect of organic matter on the interaction between trace metals and solids depends on the organic matter concentration. The  $E(\%)$  vs pH curves first shift toward the left at low organic matter concentrations (stronger association) before shifting toward the right (weaker association) above a certain organic matter concentration. (Only part of the experimental data are shown for clarity of Figs. 10 to 12). The change of  $E(\%)$  vs lysine concentration for the Cu (II)-illite system in seawater at pH 8 is shown in Fig. 13. The results indicate that low concentrations of lysine enhance metal and solid association whereas high concentrations impede the association. This phenomenon may explain why different investigators reported contradictory results.

The logarithm of lysine concentration (0 to 0.35 ppm) is plotted vs the shift in position of the  $E(\%)$  vs pH curve in Fig. 14. A linear correlation is found; that is, in the low concentration range the higher the lysine concentration the stronger is the metal-solid association. The points in the high concentration range (only the 3.0 ppm lysine curve is shown in Fig. 12) do not fall on the same line, perhaps because a different reaction mechanism is involved in the ion exchange reaction.

(2) Based on Figs. 10—12 and 15, it is clear that the interaction between Cu(II) and illite is still a CIER and each metal ion also still replaces only one proton. Thus the presence of organic matter does not significantly change the reaction mechanism.

(3) The reaction mechanism among the three types of material, trace metal, organic matter, and particulates, may be shown schematically as follows:



But in the solution amino acid and metal ion form chelators. The association constant for the chelator  $K_{\text{OM}(2)}$ , is much greater than that for reaction (17),  $K_{\text{OM}(1)}$ . At low concentrations of organic matter, it is mainly associated with particulates, and the trace metal interacts with organic matter mainly via reaction (17). When the organic matter concentration becomes higher than a certain value, more and more organic matter is left in the aqueous phase and competes with the particulates for the trace metal. As a result, low concentrations

of organic matter enhance the association of metal ion and solid, whereas high concentrations impede the reaction.

(4) The effect of organic matter on the distribution of trace metals on solids is not a function of molecular weight. Instead, the effect depends on the concentration of the organic matter (Figs. 10—15) and on the equilibrium constant between the organic matter and the trace metal.

(5) The qualitative effect of the organic matter on the interaction of trace metal and particulates are shown on Figs. 10—15. Further, the quantitative effects can be calculated from Eqs. (15) and (16), and the resultant log  $K$  values are given in Table 1, along with the shift in the  $E$  (%) vs pH curves ( $\Delta\text{pH}$ ). Log  $K$  for various amino acids correlate linearly with  $\Delta\text{pH}$  (Fig. 16).

#### 4. Further analysis of the ion exchange pH range

The above discussion indicates that the validity of Eqs. (15) and (16) can be tested by changing the organic matter concentration. We now change the amount of particulates, that is, the amount of ( $\text{RB}_m$ ) in Eqs. (8)—(10) in order to test their validity. Fig. 17 shows the  $E$  (%) vs pH plots for the reaction between Cu, Zn, Cd and various amounts of hematite in seawater. The results indicate that increasing ( $\text{RB}_m$ ) shifts the position of the pH curve toward the left as expected (Eqs. 8 and 9). However, the total pH range for the reaction remains the same at 4 pH units, also as expected (Eq. 10). These results are consistent with the data of Balistrieri and Murray (1982, 1983).

## CONCLUSION

We have presented the results on the interactions of trace metals and particulates in seawater, with or without organic matter. The results are summarized in Table 2 where the pH range of ion exchange, the probable species of trace metal exchanged, and the resulting species on the solid surface are listed. All metals studied except Cr(VI) undergo cation ion exchange reaction, while Cr(VI) undergoes anion ion exchange reaction. U(VI) undergoes CIER at natural seawater concentration at low pH ranges and in artificial seawater with higher U concentration. At high pH range, however, U(VI) seems to undergo AIER. All metals except U(VI) and Cr(VI) exchange with a proton on the solid while U(VI) replaces 2 protons and Cr(VI) replaces 2 OH group. These results indicate simple ion exchange reactions and can be represented by Eqs. (9)—(11), (15) and (16). Experimental results over wide ranges of organic matter concentration indicate that the presence of organic matter at low concentrations enhances the interaction between trace metals and particulates. At the high concentration range, organic matter impedes the association between a trace metal and a solid.



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**Table 1** The association constant between trace metals and amino acids on illite, and the leftward shift in the  $E(\%)$  vs pH curves under the influence of the amino acids at  $2 \mu\text{m}$ .

Amino acid	M. W.	log $K_{\text{OM}(i)}$	Amino acid concentration		$\Delta\text{pH}$	$\Delta\text{pH}'^*$
			ppm	$\mu\text{M}$		
Histidine	137.2	10.20	0.25	1.83	0.50	0.55
Poline	115	8.83	0.20	1.74	0.40	0.46
Alanine	89.1	8.14	0.15	1.68	0.35	0.42
Serine	105.1	7.89	0.20	1.70	0.40	0.42
Lysine	146	7.56	0.30	2.05	0.40	0.39

\*  $\Delta\text{pH}'$  values normalized to  $2\mu\text{M}$  by assuming a linear correlation between log (concentration) and  $\Delta\text{pH}$ .

**Table 2** Summary of ion exchange pH range, probable species of metal ions exchanged from seawater and the species produced for the interactions among metals, organic matter and particulates.

System	pH range of ion exchange	Probable species of metal ions exchanged from seawater	Exchange mechanism (species produced)
Hydrous titanium oxide			
	2(1.0—3.0)	$\text{UO}_2^{2+}$ (concentrated seawater)	Ti-O- $\text{UO}_2$
U(VI)	4(1.5—5.5)	$\text{UO}_2(\text{OH})_3^-$ (natural seawater) $\text{UO}_2(\text{CO}_3)_3^{4-}$	Ti-O- $\text{UO}_2$
Cr(III)	4(1.5—5.5)	$\text{Cr}(\text{OH})_3$	Ti-O- $\text{Cr}(\text{OH})_2$
Cr(VI)	2(6.0—8.0)	$\text{CrO}_4^{2-}$	$(\text{Ti})_2\text{CrO}_4$
Cu(II)	4(3.0—7.0)	$\text{CuCl}_2$ or $\text{CuCl}^+$	Ti-O-( $\text{CuCl}^+$ )
Zn(II)	4(5.0—9.0)	$\text{ZnCl}^+$ or $\text{ZnOH}^+$	Ti-O-( $\text{ZnCl}^+$ )
Cd(II)	4(2.5—6.5)	$\text{CdCl}^+$ or $\text{CdCl}_2$	Ti-O-( $\text{CdCl}^+$ )
Goethite			
Cu(II)	4(3.0—7.0)	$\text{CuCl}^+$ or $\text{CuCl}_2$	Fe-O-( $\text{CuCl}^+$ )
Zn(II)	4(4.2—8.2)	$\text{ZnCl}^+$ or $\text{ZnOH}^+$	Fe-O-( $\text{ZnCl}^+$ )
Cd(II)	4(5.5—9.5)	$\text{CdCl}$ or $\text{CdCl}_2$	Fe-O-( $\text{CdCl}^+$ )
Hematite			
Cu(II)	4(3.0—7.0)	$\text{CuCl}$ or $\text{CuCl}_2$	Fe-O-( $\text{CuCl}^+$ )

(to be continued)

Table 2 (continued)

System	pH range of ion exchange	Probable species of metal ions exchanged from seawater	Exchange mechanism (species produced)
Zn(II)	4(4.2—3.2)	ZnCl <sup>+</sup> or ZnOH <sup>+</sup>	Fe-O-(ZnCl <sup>+</sup> )
Cd(II)	4(6.0—10.0)	CdCl <sup>+</sup> or CdCl <sub>2</sub>	Fe-O-(CdCl <sup>+</sup> )
Amorphous hydrous iron oxide			
Cu(II)	4(3.0—7.0)	CuCl <sup>+</sup> or CuCl <sub>2</sub>	Fe-O-(CuCl <sup>+</sup> )
Zn(II)	4(4.0—8.0)	ZnCl <sup>+</sup> or ZnOH <sup>+</sup>	Fe-O-(ZnCl <sup>+</sup> )
Cd(II)	4(5.5—9.5)	CdCl <sup>+</sup> or CdCl <sub>2</sub>	Fe-O-(CdCl <sup>+</sup> )
$\delta$ -MnO <sub>2</sub>			
Cu	4(0.5—4.5)	CuCl <sup>+</sup> or CuCl <sub>2</sub>	Mn-O-(CuCl <sup>+</sup> )
Zn	4(1.2—5.2)	ZnCl <sup>+</sup> or ZnOH <sup>+</sup>	Mn-O-(ZnCl <sup>+</sup> )
Cd	4(1.5—5.5)	CdCl <sup>+</sup> or CdCl <sub>2</sub>	Mn-O-(CdCl <sup>+</sup> )
$\gamma$ -MnOOH			
Cu	4(1.0—5.0)	CuCl <sup>+</sup> or CuCl <sub>2</sub>	Mn-O-(CuCl <sup>+</sup> )
Zn	4(2.7—6.7)	ZnCl <sup>+</sup> or ZnOH <sup>+</sup>	Mn-O-(ZnCl <sup>+</sup> )
Cd	4(3.0—7.0)	CdCl <sup>+</sup> or CdCl <sub>2</sub>	Mn-O-(CdCl <sup>+</sup> )
Manganite			
Cu	4(1.5—5.3)	CuCl <sup>+</sup> or CuCl <sub>2</sub>	Mn-O-(CuCl <sup>+</sup> )
Zn	4(2.0—6.0)	ZnCl <sup>+</sup> or ZnOH <sup>+</sup>	Mn-O-(ZnCl <sup>+</sup> )
Cd	4(3.3—7.5)	CdCl <sup>+</sup> or CdCl <sub>2</sub>	Mn-O-(CdCl <sup>+</sup> )
Cu			
Kaolinite	4(5.0—9.0)	CuCl <sup>+</sup> , CuCl <sub>2</sub>	C-O-(CuCl <sup>+</sup> )
Illite	4(5.0—9.0)	CuCl <sup>+</sup> , CuCl <sub>2</sub>	C-O-(CuCl <sup>+</sup> ) CK <sup>+</sup> + CuCl <sup>+</sup> = C - CuCl <sup>+</sup> + K <sup>+</sup>
Montmorillonite	4(4.5—8.5)	CuCl <sup>+</sup> , CuCl <sub>2</sub>	C-O-(CuCl <sup>+</sup> ) CK <sup>+</sup> + CuCl <sup>+</sup> = C - CuCl <sup>+</sup> + K <sup>+</sup>
Zn			
Kaolinite	4(6.0—10.0)	ZnCl <sup>+</sup> , ZnOH <sup>+</sup>	C-O-(ZnCl <sup>+</sup> )
Illite	4(6.0—10.0)	ZnCl <sup>+</sup> , ZnOH <sup>+</sup>	C-O-(ZnCl <sup>+</sup> ) CK <sup>+</sup> + ZnCl <sup>+</sup> = C - ZnCl <sup>+</sup> + K <sup>+</sup>
Montmorillonite	4(5.5—19.5)	ZnCl <sup>+</sup> , ZnOH <sup>+</sup>	C-O-(ZnCl <sup>+</sup> ) CK <sup>+</sup> + ZnCl <sup>+</sup> = C - ZnCl <sup>+</sup> + K <sup>+</sup>
Cd			
Kaolinite	4(7.5—11.5)	CdCl <sup>+</sup> , CdCl <sub>2</sub>	C-O-(CdCl <sup>+</sup> )
Illite	4(7.5—11.5)	CdCl <sup>+</sup> , CdCl <sub>2</sub>	C-O-(CdCl <sup>+</sup> ) CK <sup>+</sup> + CdCl <sup>+</sup> = C - CdCl <sup>+</sup> + K <sup>+</sup>
Montmorillonite	4(7.0—11.0)	CdCl <sup>+</sup> , CdCl <sub>2</sub>	C-O-(CdCl <sup>+</sup> ) CK <sup>+</sup> + CdCl <sup>+</sup> = C - CdCl <sup>+</sup> + K <sup>+</sup>

(to be continued)

Table. 2 (continued)

System		pH range of ion exchange	Probable species of metal ions exchanged from seawater	Exchange mechanism (species produced)
<b>Pb**</b>				
Kaolinite		4(6.0—10.0)	PbCl <sup>+</sup> , PbCl <sub>2</sub>	C-O-(PbCl <sup>+</sup> )
Illite		4(6.0—10.0)	PbCl <sup>+</sup> , PbCl <sub>2</sub>	C-O-(PbCl <sup>+</sup> )
Montmorillonite		4(5.8—9.8)	PbCl <sup>+</sup> , PbCl <sub>2</sub>	C-O-(PbCl <sup>+</sup> )
<b>Cu***</b>				
Illite	25°C	4(6.0—10.0)	CuCl <sup>+</sup> , CuCl <sub>2</sub>	C-O-(CuCl <sup>+</sup> )
	18°C	4(6.0—10.0)	CuCl <sup>+</sup> , CuCl <sub>2</sub>	C-O-(CuCl <sup>+</sup> )
	35°C	4(6.0—10.0)	CuCl <sup>+</sup> , CuCl <sub>2</sub>	C-O-(CuCl <sup>+</sup> )
Kaolinite	25°C	4(5.8—9.8)	CuCl, CuCl <sub>2</sub>	C-O-(CuCl <sup>+</sup> )
Montmorillonite	25°C	4(5.5—9.5)	CuCl <sup>+</sup> , CuCl <sub>2</sub>	C-O-(CuCl <sup>+</sup> )
<b>Cu-Illite***</b>				
Aspartic acid		4(5.8—9.8)	CuCl <sup>+</sup> , CuOrg <sup>+</sup>	C-O-(Org-Cu <sup>+</sup> )
Threonine		4(5.8—9.8)	CuCl <sup>+</sup> , CuOrg <sup>+</sup>	C-O-(Org-Cu <sup>+</sup> )
Valine		4(5.7—9.7)	CuCl <sup>+</sup> , CuOrg <sup>+</sup>	C-O-(Org-Cu <sup>+</sup> )
Alanine		4(5.65—9.65)	CuCl <sup>+</sup> , CuOrg <sup>+</sup>	C-O-(Org-Cu <sup>+</sup> )
Histidine	0.25 ppm	4(5.4—9.4)	CuCl <sup>+</sup> , CuOrg <sup>+</sup>	C-O-(Org-Cu <sup>+</sup> )
	2.5 ppm	4(6.5—10.5)	CuCl <sup>+</sup> , CuOrg <sup>+</sup>	C-O-(Org-Cu <sup>+</sup> )
Lysine	0.35 ppm	4(5.5—9.5)	CuCl <sup>+</sup> , CuOrg <sup>+</sup>	C-O-(Org-Cu <sup>+</sup> )
	0.1 ppm	4(5.9—9.9)	CuCl <sup>+</sup> , CuOrg <sup>+</sup>	C-O-(Org-Cu <sup>+</sup> )
	3.0 ppm	4(6.3—10.2)	CuCl <sup>+</sup> , CuOrg <sup>+</sup>	C-O-(Org-Cu <sup>+</sup> )

Note: Experiments marked “\*”, “\*\*” and “\*\*\*” were performed using different batches of clays.

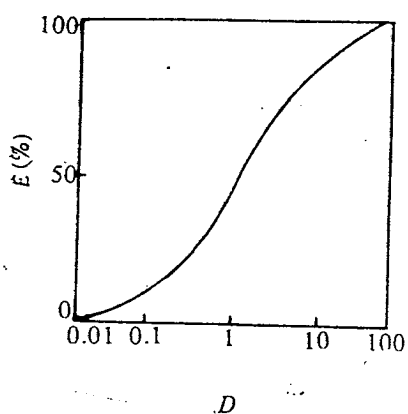


Fig. 1. Percentage of ion exchange vs the distribution coefficient.

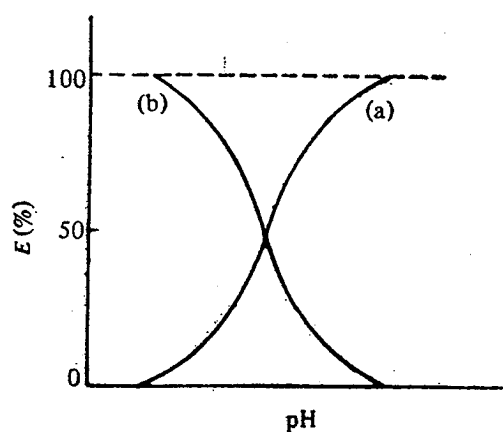


Fig. 2. Percentage of ion exchange vs pH for (a) the cation ion exchange reaction and (b) the anion ion exchange reaction.

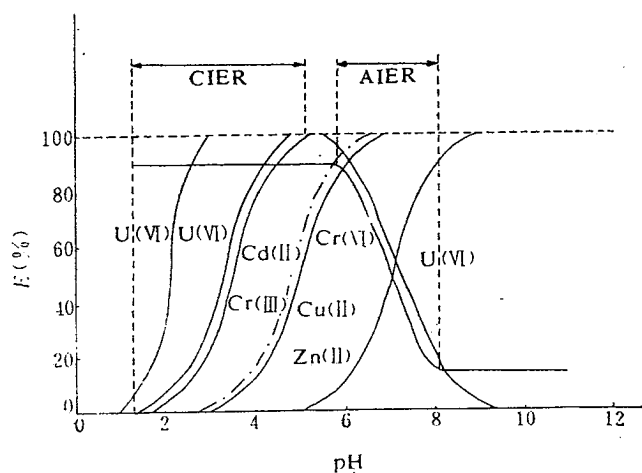


Fig. 3. Percentage of ion exchange vs pH for the interaction between U(VI) (both in artificial and natural seawaters), Cr(III), Cd(II), Cu(II), Cr(VI), Zn(II) and hydrous titanium oxide in seawater. The metal ion concentrations are all at  $5 \times 10^{-8}$  moles except for the artificial seawater which contains  $0.4 \mu$  moles of U(VI), (the U(VI)<sub>1</sub> curve).

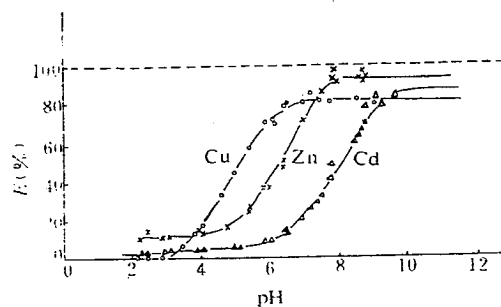


Fig. 4. Percentage of ion exchange vs pH for the interaction between Cu(II), Zn(II), Cd(II) and hydrous ferric oxide in seawater.

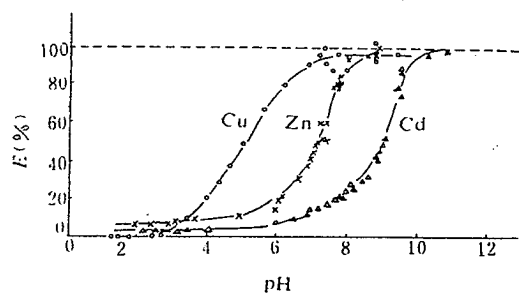


Fig. 5. Percentage of ion exchange vs pH for the interaction between Cu(II), Zn(II), Cd(II) and Goethite.

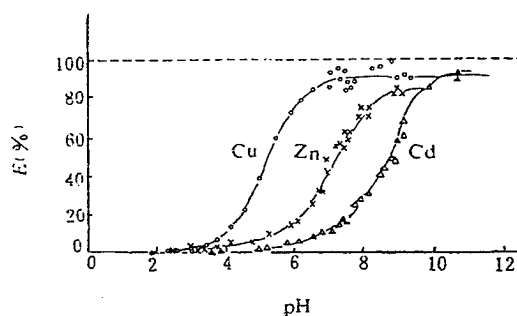


Fig. 6. Percentage of ion exchange vs pH for the interaction between Cu(II), Zn(II), Cd(II) and Hematite.

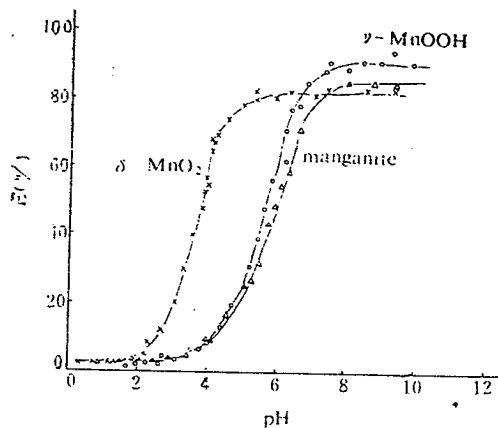


Fig. 7. Percentage of ion exchange vs pH for the interaction between Cd(II) and hydrous manganese oxide.

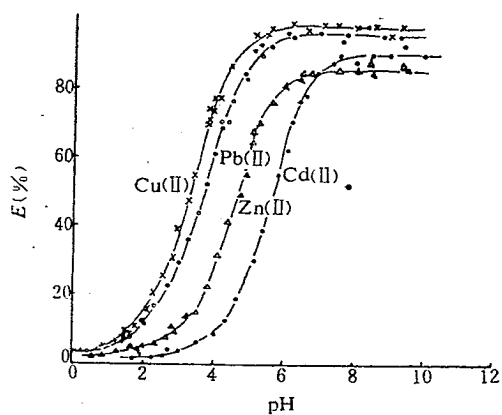


Fig. 8. Percentage of ion exchange vs pH for the interaction between Cu(II), Pb(II), Zn(II), Cd(II) and  $\gamma$ -MnOOH.

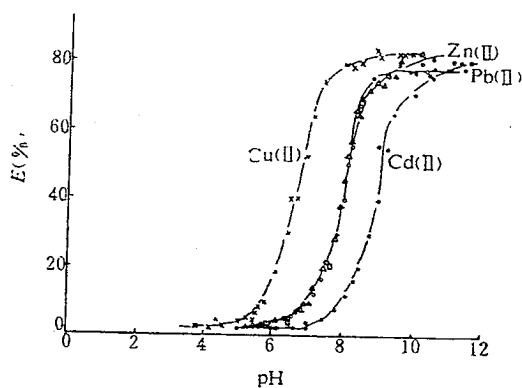


Fig. 9. Percentage of ion exchange vs pH for the interaction between Cu(II), Pb(II), Zn(II), Cd(II) and illite.

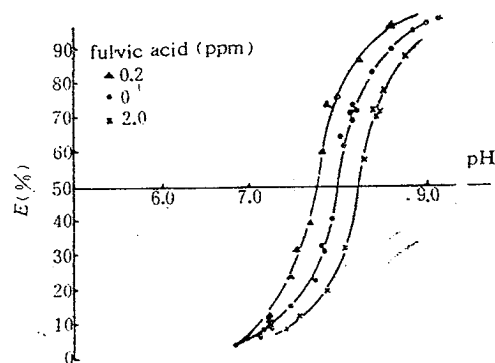


Fig. 10. The effect of fulvic acid on the  $E(\%)$  vs pH graph for the Cu(II)-illite system in seawater.

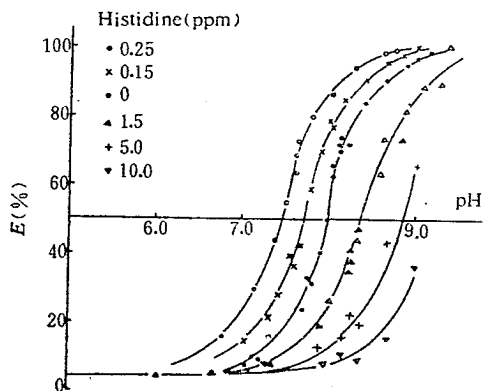


Fig. 11. The effect of histidine on the  $E(\%)$  vs pH graph for the Cu(II)-illite system in seawater.

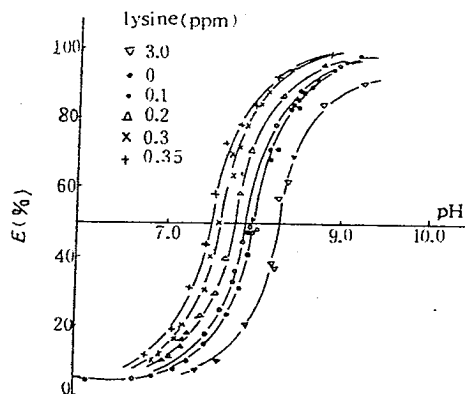


Fig. 12. The effect of lysine on the  $E(\%)$  vs pH graph for the Cu(II)-illite system in seawater.

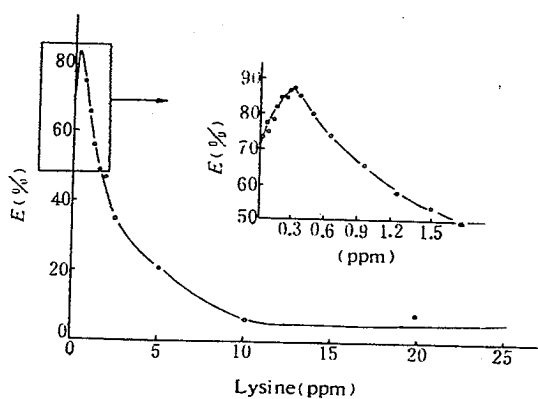


Fig. 13. Percentages of ion exchange at various lysine concentrations for the Cu(II)-illite system in seawater at pH 8.

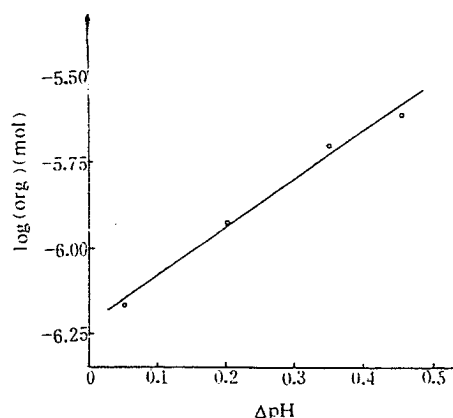


Fig. 14. Logarithm of lysine concentration (in moles/l) vs the leftward shift in position of the  $E(\%)$  vs pH curves shown in Fig. 12.

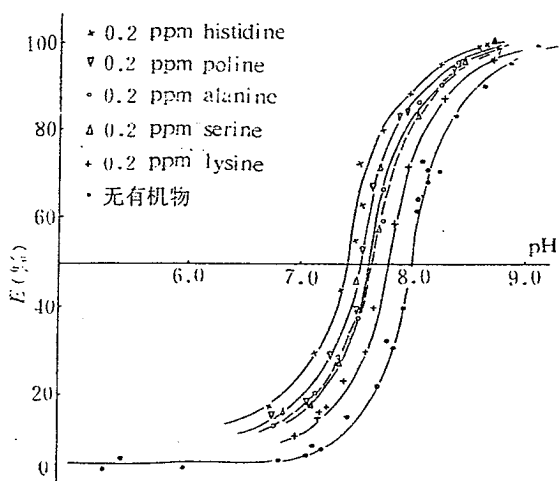


Fig. 15. The effect of histidine, poline, alanine, serine and lysine on the  $E(\%)$  vs pH graph for the Cu(II)-illite system in seawater.

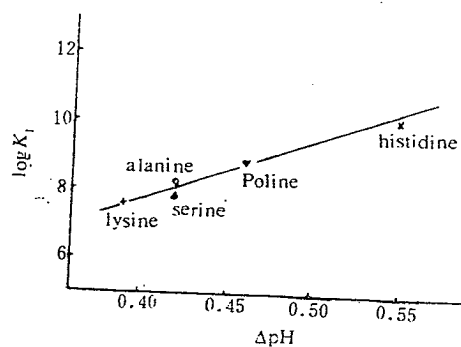


Fig. 16.  $\log K_1$  for various amino acids vs the leftward shift in position of the  $E(\%)$  vs pH curves shown in Fig. 15. The  $\Delta\text{pH}$  values have been normalized to  $2\mu\text{M}$  in amino acid concentration by assuming that the linear correlation in Fig. 14 is valid.

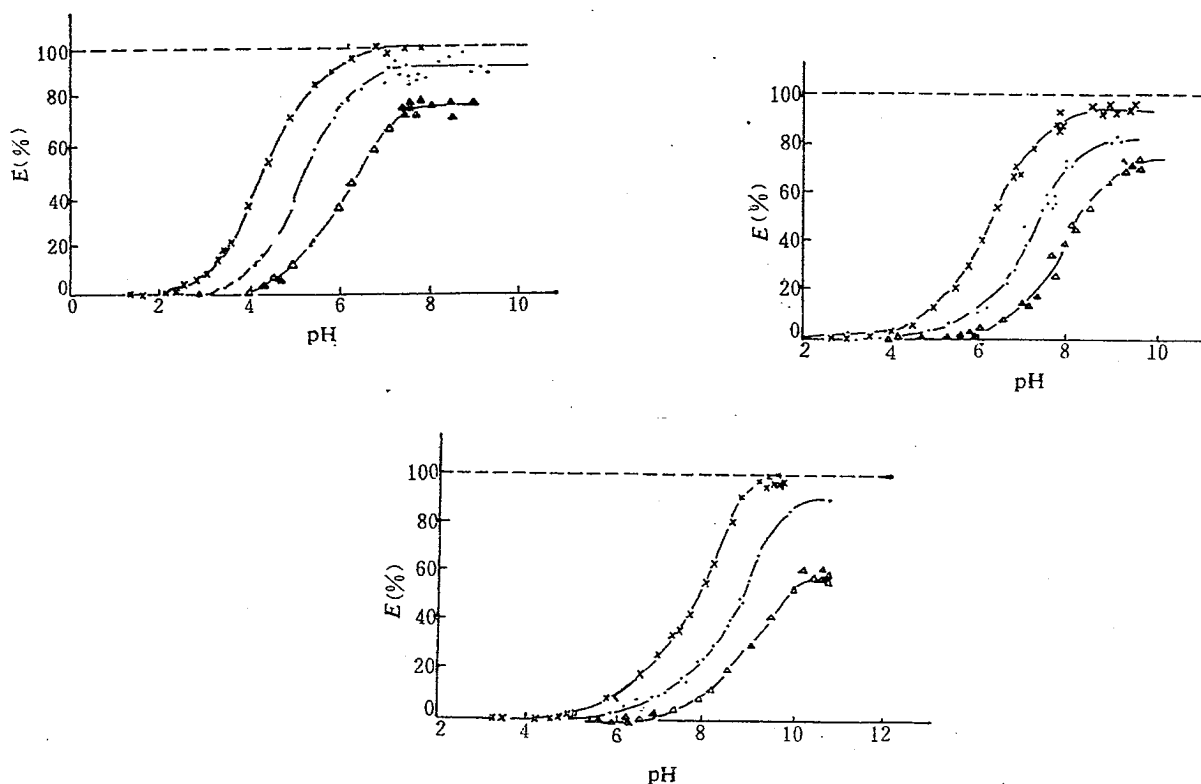


Fig. 17. Effect of the amount of solids on the  $E$  (%) vs pH curves for Cu, Zn and Cd.

- ×  $10.000 \pm 0.003$ g hematite/l.
- $1.0000 \pm 0.0005$ g hematite/l.
- Δ  $0.1000 \pm 0.0003$ g hematite/l.

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