SPECIATION OF CADMIUM MIXED LIGAND COMPLEXES IN SALT WATER LAKES[+]

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ABSTRACT. Amalgam voltammetry has been used to study heavy metal interaction in model lake water in KNO_3 at 23 °C at concentration levels of genuine lake water. The hanging drop amalgam electrode was prepared in *situ* before exchanging the medium for the sample solution. Half-wave potentials at two metal ion concentrations were measured, one at the actual concentration in the lake while the other at a much lower one. The experimentally determined shifts in half-wave potentials are used to compute several formation constants.

At the natural $[CO_3^{2-}]$ of 0.5 M in the lake, the main contributor to the speciation of cadmium is $[Cd(CO_3Cl_2)]^{2-}$. At high $[Cd^{2+}]$, the DPASV detects the presence of free Cd^{2+} ions, hence, potential polluting effect, while the amalgam reports $[Cd(CO_3)_2Cl)]^{3-}$ to be dominant above $[CO_3^{2-}] = 0.8$ M. There is a variation in the number of complexes detected, their stabilities and percentage distribution in the two methods. Cd^{2+} ion concentration also affects the number of complexes formed and their stabilities.

KEY WORDS: Heavy metals, Hanging drop electrode, Amalgam voltammetry, Speciation, Cadmium mixed ligand complexes

INTRODUCTION

Most metals are toxic to living organisms and have a tendency to accumulate in food chains [1, 2]. In recent years, there has been a growing public concern and an increased general awareness of water problems. This awareness is attributed to the potential health risks associated with water pollution, a significant increase in media coverage of environmental issues, recreation and leisure time spent at tourist sites and a great political concern for environmental issues [3].

Millions of fish and flamingoes have been reported to have died in Lake Nakuru [4] with occasional temporary migration of flamingoes to some other places. The levels of heavy metals in the lake are likely to continue rising because the lake has inlets but no outlets coupled with the fact that there has been increased use of automobiles and agricultural practices in the catchment area [5]. However, increased inputs are balanced by precipitation of heavy metals [6, 7]. The free metal species is in dissolved or hydraded ionic forms [8] and is the most bioactive and the most toxic [9].

Lead is the most serious of the human toxic metals [10] although there is evidence that joint additive action of common pollutants is acutely toxic [11]. Interaction between all metal species depends on the stability of the different compounds as well as the rate of transfer [12]. Trace metal uptake varies in presence of different complexing agents [13]. An understanding of the transport, behaviour, effects and fate of such elements is, therefore, necessary.

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Speciation gives information on the mobility and therefore, availability which varies with the form [14]. It is found that most of the trace analytical methods fail because they give only the total amounts, not the species. Pre-concentration of metals is discouraged in order to maintain the distribution of the naturally occurring species [15]. Voltammetric techniques can be carried out at low total metal concentrations. Anodic stripping voltammetry has detection limits of about 10^{-9} M. In this research metal ions were not added, hence, no possible shift of species equilibria as a consequence because the values determined are in the order of 10^{-6} M.

Polarography displays its sensitivity to dissolved toxic metal species, and the distribution of the total trace metal content for the various chemical species in natural waters can ultimately be elucidated [14]. Speciation of cadmium in natural water has been determined [16] and the electrochemical approach to trace element speciation has been done [17]. However, not enough data are available on heavy metals, especially in salt water lakes. Hence, this study has been carried out. In this work, accurate potential measurements were done by investigating shifts in half wave potential or peak potential of the actual solution compared with one without any complex-forming species [18].

EXPERIMENTAL

Instrumentation

The EG and G Model 303 static mercury drop electrode was used. When a problem of mercury breaks arose, a soft plastic tubing syringe was attached to the tip of the capillary. Dispensing of a steady stream of mercury drops using the dispense function while slowly pulling on the syringe plunger effectively clears the problem. The EG and G Model 364 Polarographic Analyzer and EG Model 305 stirrer (Princeton Applied Research, Princeton NJ 08540, U.S.A.) were used. It is easy to operate by setting the right current range, the mode, scan rate and potential scan range. All the results were obtained using the differential pulse mode. All chemicals used were analar grade from Aldrich.

Sampling

Water samples were collected from lake Nakuru which is a salt water lake and analysis of different ions done using standard methods.

Procedure for differential pulse anodic stripping voltammetry (DPASV)

The supporting electrolyte, KNO_3 was prepared at a concentration higher than 1.44 M so that when a certain volume of this solution was used, the total ionic strength remained constant. A 4.0 x 10^{-4} M Cd^{2+} working standard solution was prepared from analar grade $Cd(NO_3)_2$ and the desired concentrations were found by dilution. Two concentration levels of cadmium ions were used, one at the metallic concentration as determined in the lake water which was 1.3 x 10^{-6} M and the other at 9.6 x 10^{-8} M, a much lower value. Right volumes of the supporting electrolyte and ligand solutions that gave the desired concentrations were put in a 10 mL polarographic cell cup, maintaining a constant ionic strength.

Oxygen was removed by bubbling with N_2 gas, followed by plating at a constant potential for some period with stirring using a hanging drop as the cathode. Stripping was allowed, the anodic curve recorded and the peak height values of the potential noted. The concentration of the less basic ligand was kept constant while that of the more basic one varied in an increasing manner.

Amalgam voltammetry

This work is an application of the theoretical approach described earlier [1, 18, 19]. The electrolytic preparation was done by mixing KNO_3 and the desired solution of Cd^{2+} ion. To work at 1.3 x 10^{-6} M, 32.5 Φl of the 4.0 x 10^{-4} M Cd $^{2+}$ M solution was used while for 9.6 x 10^{-8} M, 2.4 Φl was taken. Each solution was transferred into a 10 mL volumetric flask containing 7.2 mL of 2 M KNO_3 and filled to the mark using distilled de-ionized water. The solution mixture was then transferred to a polarographic cell cup.

Nitrogen gas was bubbled through for 5 minutes, and then platted for 90 seconds to a hanging mercury drop (small size) at a constant potential and at a given time. Stirring was done using a magnetic stirrer and the solution allowed to equilibrate for half a minute after which stripping was done and the polarograph recorded. This gives the $E_{1/2}$ for the metal ion. To form the amalgam with the ligand, the procedure for the cadmium metal was repeated, except, instead of allowing stripping to take place, the ionic solution was removed and the electrode system carefully washed several times with distilled de-ionized water. If the amalgam drop fell during this procedure, the experiment had to be repeated. Finally, the solution containing a ligand at a known concentration was inserted. Oxygen was removed from the solution by bubbling with pure N_2 for 5 minutes, deposition (plating) done for a varied period of time then stripping and the anodic DP voltammetric curve recorded.

Treatment of results

Two most important methods of studying labile metal complexes by using voltammetric data are reported [20, 21]. Both methods utilize the shift of the half-wave potential with increasing concentration of ligand-forming species [1]. For mixed ligands, the method described [22] was used to compute stability constants. The determined stability constants were used to compute percentage distribution of the various species in the lake water by computer modelling at the ionic strength of the lake.

RESULTS AND DISCUSSION

Temperature of the laboratory was air conditioned at 23 °C. The ionic strength of the lake was found to be 1.44 M while the pH for the lake medium was 10. The levels of heavy metals in the lake were: $[Pb^{2+}]$ = 8.5 x 10^{-6} M; $[Cd^{2+}]$ = 1.3 x 10^{-6} M; $[Cu^{2+}]$ = 8.7 x 10^{-6} M; $[Zn^{2+}]$ = 8.8 x 10^{-6} M. Thus the determined $[Cd^{2+}]$ in the lake = 1.3 x 10^{-6} M, and the lower value found by dilution = 9.6 x 10^{-8} M. Stability constants are reported in logarithm. 1 mL of NH_4NO_3 was added to the solution to suppress precipitation of complexes.

For a mixed complex with a stability constant k_{ij}, the first subscript i is the number of bonded ligand molecules that vary in concentration while j is that for the fixed one. k_{i0} is stability constant for a single ligand indicated simply as k_i. Levels of $[CO_3^{2-}]$ and $[OH^-]$ in the lake in its natural state are indicated by dotted lines in the figures.

Carbonato/chloro complexes

Table 1 shows that at high $[Cd^{2+}]$, the amalgam method is more sensitive than the DPASV and identifies the complex formed with k_{12}. However, the DPASV system reports more stabilized complexes formed than the amalgam, except particularly the destabilized complex with k_{21}. At low $[Cd^{2+}]$, the DPASV method reports complexes that are slightly more stable than the amalgam with an exception of the complex with k_{30}.

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Table 1.   Stability constants of carbonato/chloro mixed ligand complexes at both levels of Cd^{2+} by the two methods.

Stability Constant	High [Cd^{2+}]		Low [Cd^{2+}]	
	DPASV	Amalgam	DPASV	Amalgam
k_{10}	4.09	3.90	3.94	2.80
k_{12}	-	5.75	22.08	18.13
k_{20}	5.02	4.70	4.61	4.29
k_{21}	0.96	7.38	6.08	6.00
k_{30}	4.55	4.40	4.52	5.07
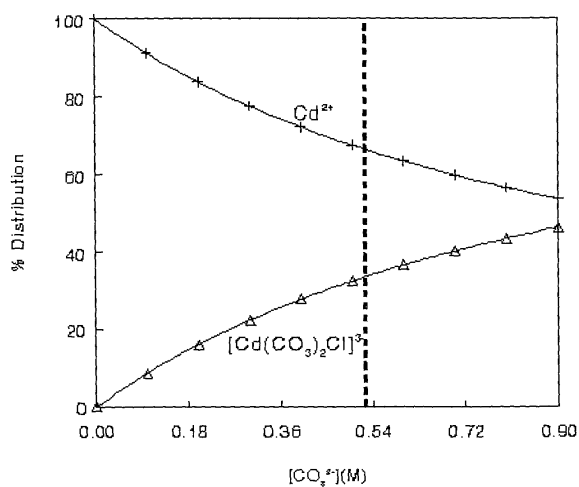
Figure 1.1. % Distribution of carbonato/chloro Cd at 1.3 x 10^{-6} M in simulated lake water.
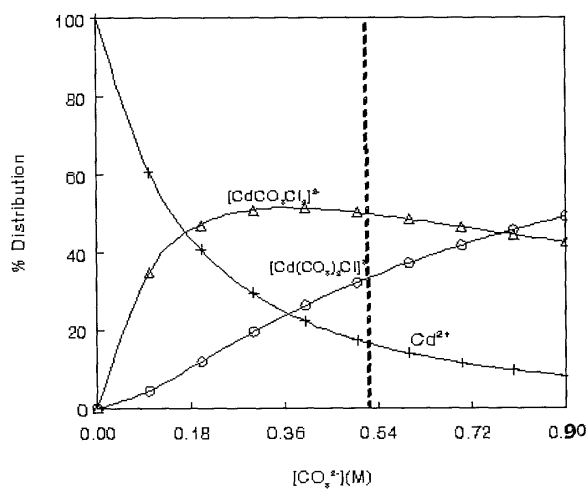
Figure 1.2. % Distribution of carbonato/chloro Cd/Hg at 1.3 x 10^{-6} M in simulated lake water.
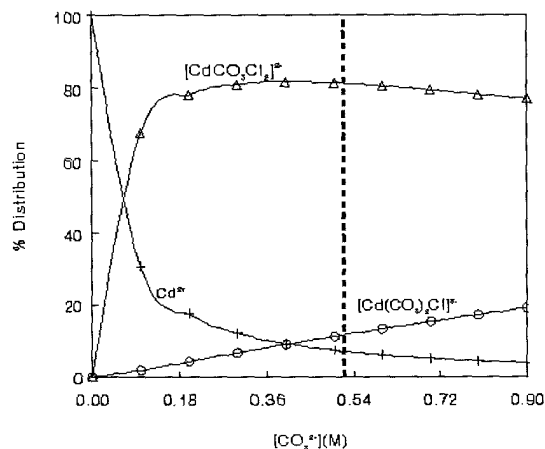
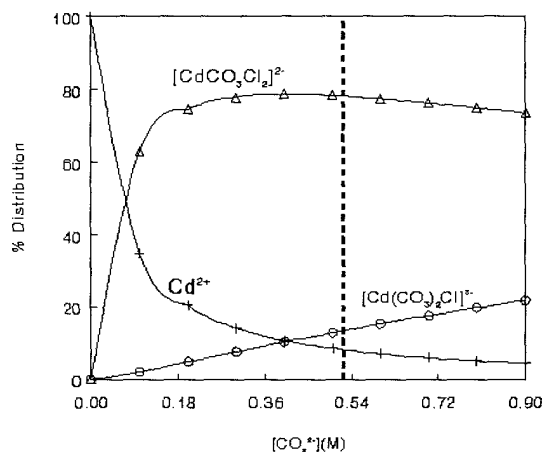Figure 1.3. % Distribution of carbonato/chloro Cd at 9.6 x 10^{-8} M in simulated lake water.

Figure 1.4. % Distribution of carbonato/chloro Cd/Hg at 9.6 x 10^{-8} M in simulated lake water.

Figures 1.1-1.4 show that at the natural $[CO_3^{2-}]$ level of 0.5 M in the lake medium and at high $[Cd^{2+}]$, the DPASV identifies the dominant species to be the free Cd^{2+} ions. Throughout the $[CO_3^{2-}]$ changes, the only complex, $[Cd(CO_3)_2Cl]^{3-}$ rises steadily but does not overtake the free Cd^{2+} ions. The existence of the free Cd^{2+} ions poses a danger to the ecosystem, hence, toxicity of cadmium. The amalgam method on the other hand, reports $[Cd(CO_3Cl_2]^{2-}$ as the most dominant complex but is eventually overtaken by $[Cd(CO_3)_2Cl]^{3-}$ at high $[CO_3^{2-}]$. This technique also reports that decrease in $[CO_3^{2-}]$ in the lake leads to dominance of the free Cd^{2+} ions.

At low $[Cd^{2+}]$, both methods report the complex $[Cd(CO_3Cl_2]^{2-}$ to be the main contributor to the speciation of cadmium at the normal $[CO_3^{2-}]$ in the lake. The proportion of this complex persistently remains fairly constant and dominates throughout the $[CO_3^{2-}]$ changes with a steady rise in distribution of $[Cd(CO_3)_2Cl]^{3-}$ which, however, remains in low amounts.

Hydroxo/chloro complexes

Table 2 shows that at both levels of cadmium using the two methods, the DPASV system reveals the formation of the complex with k_{12} as the most stable one. Only the DPASV is sensitive in identifying the complex with k_{21} at low $[Cd^{2+}]$. From Figures 2.1-2.4 it can be observed that at high $[Cd^{2+}]$, the DPASV system identifies the free Cd^{2+} ions as dominant throughout the pH changes. The complexes $[Cd(OH)Cl_2]^-$, $[Cd(OH)Cl]^0$ and $[Cd(OH)_2Cl]^-$ exist in small amounts. The amalgam system reports the complex $[Cd(OH)Cl_2]^-$ as the main contributor to the speciation of cadmium while $[Cd(OH)_2Cl]^-$ is minor with increase in OH^- concentration.

At low $[Cd^{2+}]$ and at low $[OH^-]$, the DPASV identifies the free Cd^{2+} ions to be dominant but is overtaken by the complex $[CdOH)Cl_2]^-$ at high pH. The complexes $[Cd(OH)Cl]$ and $[Cd(OH)_2Cl]^-$ exist only in small proportions. The amalgam method reports the free Cd^{2+} ions dominate throughout the pH changes, while the complexes $[Cd(OH)Cl_2]^-$, $[Cd(OH)Cl]^0$ and $[Cd(OH)_2Cl]^-$ are in small proportions. However, the $[OH^-]$ in the lake medium is very low, hence, the contribution by these complexes to the speciation of Cd is negligible.

Table 2. Stability constants for hydroxo/chloro mixed ligand complexes at both levels of Cd^{2+} by the two methods.

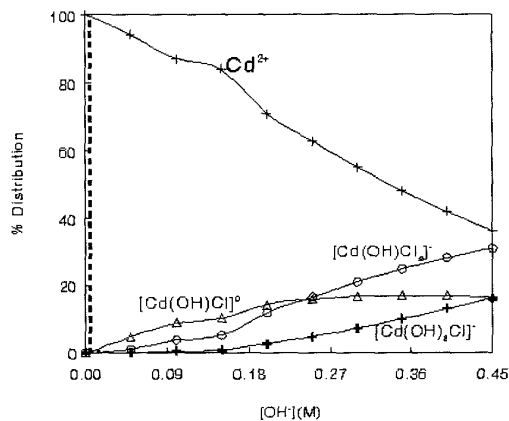| Stability Constant	High $[Cd^{2+}]$		Low $[Cd^{2+}]$	
	DPASV	Amalgam	DPASV	Amalgam
k_{10}	3.19	2.95	2.99	2.83
k_{12}	16.75	5.54	63.48	8.19
k_{20}	4.36	4.15	4.12	4.00
k_{21}	-	-	5.00	-
k_{30}	5.48	5.30	5.19	5.14

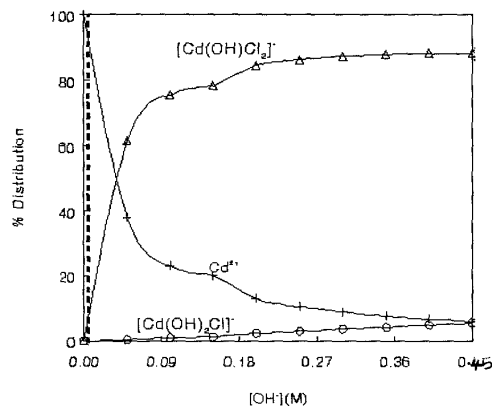Figure 2.1. % Distribution of hydroxo/chloro Cd at 1.3 x 10^{-6} M in simulated lake water.

Figure 2.2. % Distribution of hydroxo/chloro Cd/Hg at 1.3 x 10^{-6} M in simulated lake water.
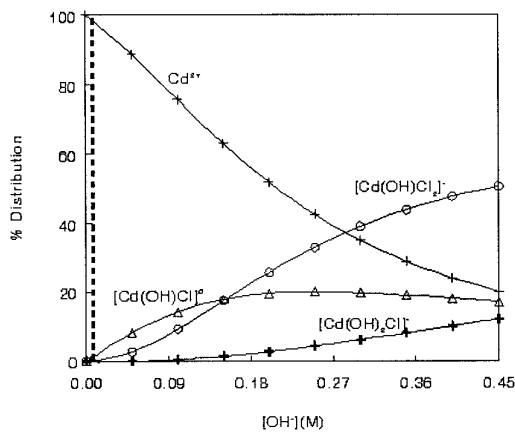

Figure 2.3. % Distribution of hydroxo/chloro Cd at 9.6 x 10^{-8} M in simulated lake water.
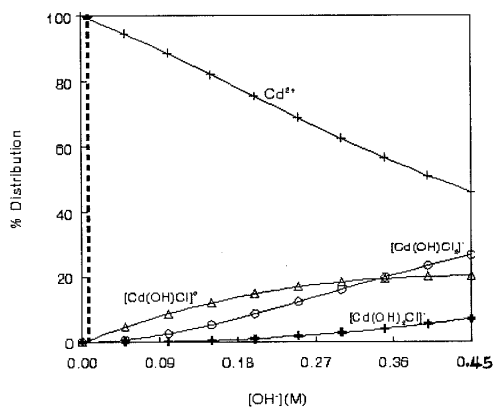

Figure 2.4. % Distribution of hydroxo/chloro Cd/Hg at 9.6 x 10^{-8} M in simulated lake water.

Hydroxo/fluoro complexes

Table 3 shows that complexes reported by the DPASV are slightly more stable than those identified by the amalgam. However, the complex with k_{12} at high $[Cd^{2+}]$ as reported by the DPASV is highly stabilized compared to that identified by the amalgam but the observation at low $[Cd^{2+}]$ is reversed. Furthermore, the DPASV is more sensitive and identifies a weakly stable complex with k_{11} that is not reported by the amalgam at low $[Cd^{2+}]$. At the natural level of the $[OH^-] = 9.5 \times 10^{-5}$ M, the dominant species are the free Cd^{2+} ions and therefore, this system is potentially toxic. However, since the natural $[OH^-]$ in the lake medium is very low, the contribution by these complexes to the speciation of Cd is not quite significant. At both levels of $[Cd^{2+}]$ and as the $[OH^-]$ increases, the two methods report the complex $[Cd(OH)F_2]^-$ dominates over the free Cd^{2+} ions.

At low $[Cd^{2+}]$, the DPASV method identifies an additional complex, $[Cd(OH)_2F]^-$, that exists in nearly a constant and insignificant proportion with increase in $[OH^-]$. Although the two techniques detect several complexes in this system (Figures 3.1-3.4), the natural level of the $[OH^-]$ in the lake is quite low, hence, their contribution to the speciation of cadmium is minor.

Table 3.   Stability constants of hydroxo/fluoro mixed ligand complexes at both levels of Cd^{2+} by the two methods.

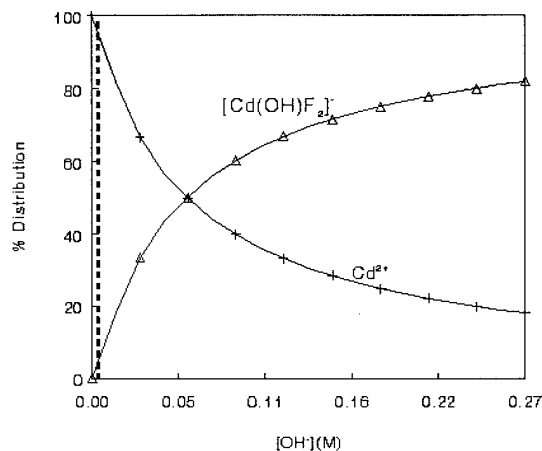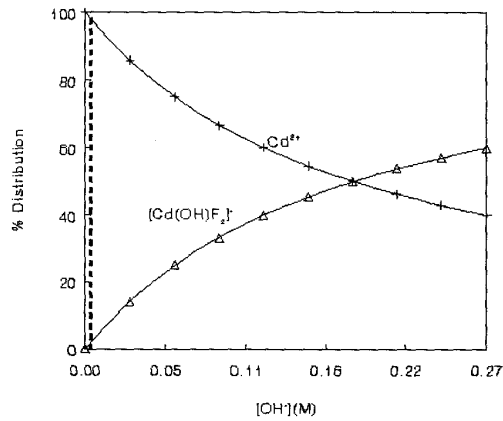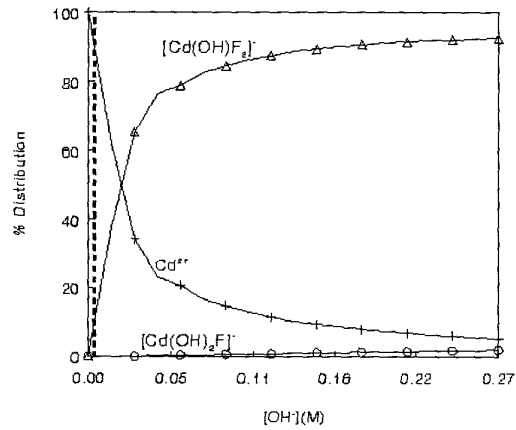| Stability Constant	High $[Cd^{2+}]$		Low $[Cd^{2+}]$	
	DPASV	Amalgam	DPASV	Amalgam
k_{10}	3.19	2.95	2.99	2.83
k_{11}	1.89	0.98	1.01	-
k_{12}	12.40	2.86	4.22	32.40
k_{20}	4.36	4.15	4.12	4.00
k_{21}	6.58	1.67	4.88	4.58
k_{30}	5.48	5.30	5.19	5.14

Figure 3.1. % Distribution of hydroxo/fluoro Cd at 1.3×10^{-6} M in simulated lake water.

Figure 3.2. % Distribution of hydroxo/fluoro Cd/Hg at 1.3×10^{-6} M in simulated lake water.

Figure 3.3. % Distribution of hydroxo/fluoro Cd at 9.6×10^{-8} M in simulated lake water.
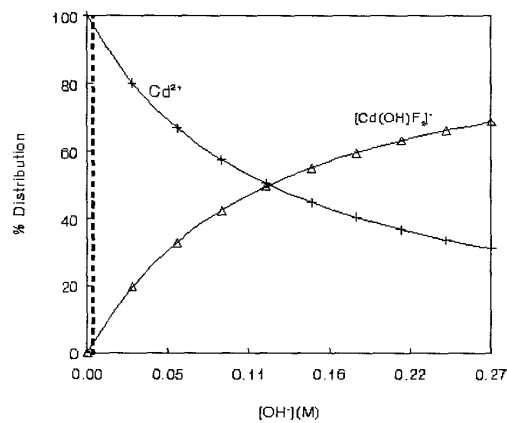
Figure 3.4. % Distribution of hydroxo/fluoro Cd/Hg at 9.6×10^{-8} M in simulated lake water.

CONCLUSIONS

In its natural state, the lake contains a high level of $[CO_3^{2-}]$ and so carbonato complexes are major contributors to the speciation of cadmium. Hydroxo complexes play an insignificant role since the $[OH^-]$ of the lake is very low. At the natural level of $[CO_3^{2-}] = 0.5$ M, the principal complexes are $[CdCO_3Cl_2]^{2-}$ and $[Cd(CO_3)_2Cl]^{3-}$. However, decrease in the $[CO_3^{2-}]$ of the lake leads to a consequential dominance of the free Cd^{2+} ions. Therefore, this system is potentially polluting and the aquatic life of the lake is indeed threatened.

ACKNOWLEDGMENTS

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