Journal of Physical and Theoretical Chemistry
of Islamic Azad University of Iran, 5 (2) 73-78: Summer 2008
(J.Phys.Theor.Chem.IAU Iran Summer 2008)
ISSN: 1735-2126

Hydrolysis of cadmium cation in different ionic strength

Farahnaz Soleimani[1], Hossein Aghaie[1*], and Farrokh Gharib[2]

1. Chemistry Department, Islamic Azad University, Science and Research Campus, Tehran, Iran
2. Chemistry Department, Shahid Beheshti University, Tehran, Evin, Iran

---

ABSTRACT

The hydrolysis of cadmium nitrate was studied spectrophotometrically at different ionic strengths of sodium perchlorate in a wide pH range, 1-12, and at 25 C. Least squares calculations are consistent with the formation of M(OH)+, M(OH)2, M(OH)3- and M(OH)42- species, which M is Cd2+. The dependency on ionic strength in the background electrolyte solutions was taken into account by using a Debye-Huckel type equation, and finally the results have been compared with data previously reported and interpreted.

Keywords: Hydrolysis; Ionic strength; Formation Constant; Formation

---

INTRODUCTION

Among the toxic heavy metals in the environment, cadmium is of particular significance due to its ecotoxicity [1]. It has a pronounced tendency to be accumulated by marine organisms and therefore constitutes a certain hazard for man consuming sea food. The direct uptake of cadmium occurs predominantly from the dissolved state. Commonly over 97 % of Cd exists in the open sea as chloro complexes [2-3]. Yet in regions of higher phytoplankton abundance, complexing components of dissolved organic matter might affect and alter the usual inorganic Cd speciation.

Ecotoxic trace metals are present in various parts of the aquatic environment. They are partly dissolved, partly bound by the suspended particulate matter, and partly taken up by aquatic organisms, especially phytoplankton.

The distribution of the ecotoxic metals among various parts of the aquatic environment and their transfer to and from the suspended particular matter, the sediments and aquatic organisms, however, are greatly affected by the respective chemical forms or speciation of the metals. Therefore, elucidation of the speciation of ecotoxic trace metals constitutes one of the significant tasks in environmental research [4-5]. Owing to the toxicity of this metal ion, we have recently begun to investigate several reaction equilibria of cadmium species with some ligands, particularly those of biological interests, such as amino acids, peptides, nucleotides and some aqueous soluble porphyrins. The main objectives of the researches are to establish the stoichiometries, structures, and stability constants of the reactions of cadmium ions with a range of ligands having a variety of donor atoms.

---

[*] Corresponding author: hn_Aghaie@yahoo.com

The effect of varying reaction media, such as ionic strength, ionic media, and using different aqueous-organic solvents on the stability and hydrolysis constants are also investigated.
Cadmium cations show a strong tendency to hydrolysis in aqueous solution, as demonstrated by several authors [6-7]. The formed hydrolytic species are very different and a variety species are reported in the literature to date [RRR]. Hydrolysis of this metal ion becomes significant above pH 7 usually in concentrated solutions, where polynuclear species are formed in small amounts before precipitation of cadmium hydroxide. Mononuclear hydrolysis products appear above pH 8, but the low solubility of the hydroxide limits the concentration of cadmium. In this work hydrolysis of cadmium cation are studied in aqueous solution at 25 C and different ionic strength ranging from 0.1 to 0.7 mol dm-3 sodium perchlorate, using a combination of potentiometric and spectrophotometric techniques. The parameters which define this dependency were analyzed with the aim of obtaining further information with regard to their variation as a function of charges involved in the hydrolysis reaction. Moreover, a general equation was established for the dependence of hydrolysis constant on ionic strength. This equation gives the possibility of estimating a hydrolysis constant at a fixed ionic strength when its value is known at another ionic strength in the range 0.1 < ionic strength < 0.7 mol dm-3, and therefore may make a significant contribution to solving many analytical and speciation problems.

EXPERIMENTAL SECTION

Chemicals

Analytical reagent grade sodium perchlorate (Fluka) was dried under vacuum at room temperature for at least 72 hours before use. The NaOH solution was prepared from a titrisol solution (Merck) and its concentration was determined by several titrations with standard HCl solution. Analytical reagent grade perchloric acid (Merck) and cadmium nitrate (Merck) were used as supplied. Dilute acid solutions were standardized against standard NaOH solutions. All dilute solutions were prepared from double-distilled water with specific conductance equal to 1.3 ±0.1 μΩ-1cm-1.

Apparatus

A Metrohm research pH-meter, model 744 (with a precision of 0.01 units), was used for the pH measurements. The pH was measured with a combination electrode (metrohm). Spectrophotometric titrations were performed with a UV-Vis Carry 300 spectrophotometer (with a precision of 0.0002 absorbance units) combined to a Pentium 4 computer and using thermostated matched 10 mm quartz cells.

Measurements

All measurements were carried out at 25 C. The ionic strength was maintained at 0.1 to 0.7 mol dm-3 with sodium perchlorate. The pH-meter was calibrated with the relevant H+ concentration with a 0.01 mol dm-3 HClO4, containing 0.09 mol dm-3 NaClO4 solution (for adjusting the ionic strength to 0.1 mol dm-3). The same procedure was performed for the other ionic strengths. For these standard solutions, we have - log10[H+] = 2.00 [8]. Junction potential corrections were calculated from eq 1

-log10[H+]real = -log10[H+]measured + a + b[H+]measured (1)

where a and b were determined by measuring pH values for two different solutions of perchloric acid with sufficient sodium perchlorate to adjust the ionic strength.

Procedure

50 mL acidic solution of cadmium nitrate, (1.0 to 2.0) $\times10^{-4}$ mol dm-3, was titrated with an alkali solution, 0.10 mol dm-3 NaOH with the same ionic strength. The pH and absorbance were measured after addition of a few drops of titrant, and this procedure was extended up to the required pH. To exclude carbon dioxide from the system, a stream of purified nitrogen was passed through a sodium hydroxide solution and then bubbled slowly through the reaction solution. In all cases, the procedure was repeated at least three times and the resulting average values and corresponding standard deviation are shown in the text and Tables.

RESULTS & DISCUSSION

On the basis of literature data [6-7] , the formation of the following hydrolytic species have been hypothesized: $Cd(OH)^+$, Cd(OH)2, $Cd(OH)^-_3$, $Cd(OH)_4^{2-}$,$Cd_2(OH)^+_3$, and $Cd_4(OH)_4^{4+}$ Our results in this work are consistent with the formation of the first four mononuclear species, i.e. $Cd(OH)_{(1+q)}^{(1-q)}$ (where q = 0, 1, 2, 3). The hydrolysis reactions and their formation constants are defined as:

$Cd^{2+} + OH^- \rightleftharpoons M(OH)^+ K_{11} = [M(OH)^+]/[Cd^{2+}][OH^-]$ (2)

$Cd^{2+} + 2OH^- \rightleftharpoons M(OH)_2 K_{12} = [M(OH)_2]/[Cd^{2+}][OH^-]^2$(3)

$Cd^{2+} + 3OH^- \rightleftharpoons M(OH)_3^- K_{13} = [M(OH)_3^-]/[Cd^{2+}][OH^-]^3$(4)

$Cd^{2+} + 4OH^- \rightleftharpoons M(OH)_4^{2-} K_{14} = [M(OH)_4^{2-}/[Cd^{2+}][OH^-]^4$(5)

According to equation 2-5, the stability constant of hydrolytic species, β_{pq}, are expressed as,

$$\beta_{11} = K_{11}\,Kw$$

$$\beta_{12} = \beta_{11}\,K_{12}\,Kw$$

$$\beta_{13} = \beta_{12}\,K_{13}\,Kw$$

$$\beta_{14} = \beta_{13}\,K_{14}\,Kw$$

where Kw is the autoprotolysis constant of water at 25 °C [9].

The method of determination of pq based on the relation A = f(pH) [10]. Absorbance, A, and –log[H+] were measured for a solution containing Cd^{2+} with sufficient NaOH solution, as described before. Treatments of the spectrophotometric data in the wavelength range 210-225 nm (with an interval of 5 nm) obtained during the titrations as a function of the H+ concentration were conducted with the computer program [11]. The program allows calculation of hydrolysis constant for different stoichiometry models. The degree of refinement then guides to choice between the models. Using a suitable computer program [11] the data were fitted to the final equation for estimating the hydrolysis constant of eq 2-5. We used the Gauss-Newton nonlinear least-squares method in computer program to refine the absorbance by minimizing the error squares sum from eq 6

$$U = \sum(a_i - b_i)^2 \qquad (i = 1, 2, 3, \ldots) \qquad (6)$$

where ai is a quasi-experimental and bi is a calculated one. The computer program consisted of two different kinds of fitting, (a) graphical, (b) numerical. The final selection of the species was based on both graphical and numerical methods, considering in addition the various statistical criteria, i. e. sums of squared residuals and the differences of total concentration of Cd2+ used from those of calculated ones.

Different models including polynuclear species with various hydroxyl groups were tested by the program. The models finally chosen, formed by Cd(OH)+, Cd(OH)2, Cd(OH)3- and Cd(OH)42- resulted in a satisfactory of numerical and graphical fitting. The average values for various wavelengths calculated for the hydrolysis constant values of the species at different background salt are listed in Table 1 together with values reported in the literature for comparison and are shown in Figure 1 as a function of ionic strength [6-7].

Table 1. Average values of the hydrolysis constants for cadmium nitrate species in aqueous solution at 25 C and different ionic strengths of NaClO4 together with the values reported in the literature

ionic strength / mol dm^{-3}	*logβ_{11}*	*logβ_{12}*	*logβ_{13}*	*logβ_{14}*	ref.
0.1	3.88 ± 0.03	7.49 ± 0.04	9.81 ± 0.09	10.87 ± 0.05	this work
0.3	3.65 ± 0.02	7.14 ± 0.05	9.55 ± 0.11	10.71 ± 0.06	this work
0.5	3.60 ± 0.01	7.02 ± 0.06	9.49 ± 0.10	10.62 ± 0.05	this work
0.7	3.63 ± 0.04	7.03 ± 0.04	9.51 ± 0.11	10.64 ± 0.07	this work
0.1	4.0	7.7	10.3	12.0	6
0.1	3.7	7.21	8.04	7.77	7

In similar studies some poly-nuclear hydrolytic species of Cd2+ were reported in the literature [6-7]. So, we performed several experiments with different concentration of cadmium cations at the mentioned condition, but our results showed a participation of cadmium hydroxide and a scattering in absorbance when the concentration of Cd2+ exceeded from 0.01 mol dm-3 at pH > 10, because of low solubility of cadmium hydroxide in aqueous solution. In Figure 2 the equilibrium distribution of various hydrolytic species of cadmium cation are plotted versus –log[H+] where the ionic strength is 0.1 mol dm-3. The first and second species, Cd(OH)+ and Cd(OH)2, are predominant at pH

≅10 and 11, respectively. The third species, Cd(OH)3- becomes predominant at pH ≅12 and the last species, Cd(OH)42- is formed in fairly low percentage at pH > 11.

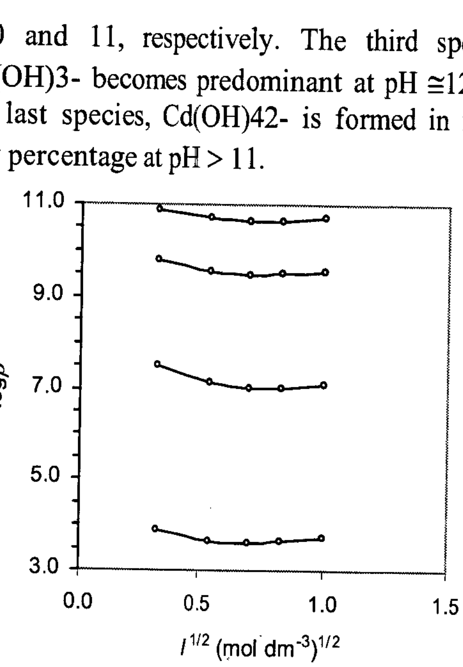

Fig. 1. Dependence of hydrolysis constant values species of cadmium cation with ionic strength at 25 °C.

DEPENDENCE ON IONIC STRENGTH

The dependence of the hydrolysis constants on ionic strength for the hydrolytic species of cadmium cation can be described by a semi-empirical equation [12-13].

logK(I) = log K(I*) – f(I) + CI (7)

where f(I) = Z*AI1/2/(1 +BI1/2), K(I) and K(I*) are the hydrolysis constants of the actual and the reference ionic media, respectively. A is the parameter of Debye-Hückel equation, (A=0.5115at 25°C), $Z^*= \sum (\text{charges})^2$ reactants ∑ (charges) 2 products, C is an empirical parameter that its value is considered, and B is set equal to1.5 [14] (a small error in fixing B is absorbed in the linear term C) [14]. Results of a series of investigations done by Daniele et al [12-13], De Stefano et al [15-16], and Gharib et al [17-25], showed that, when all the interactions occurring in the solution are considered, in the range 0 ≤ ionic strength ≤ 1, the empirical parameters are dependent on the stoichiometry of the formation reaction. If an approximate value of C is known, the hydrolysis constant can be determined for the variation of ionic strength from I* to I by the equation

logK(I) = logK(I*) – f(I,I*) + C(I - I*) (8)

where

f(I,I*) = Z*A[I1/2/(1 + 1.5I1/2) – I* 1/2/(1 + 1.5I* 1/2)] (9)

I and I* are the ionic strength of the solution by appropriate electrolyte. A preliminary analysis of the data showed that if a fixed value is assigned to C, the fit with eq 8 is not always good over the whole range of ionic strength from 0.1 to 0.7 mol dm-3. This equation may be useful for small changes of ionic strength, but a better fit is obtained by adding a further term of the from DI 3/2, (D is another adjustable parameter). Therefore the data were fitted to the eq 10.

logK(I) = logK(I*) – f(I,I*) + C(I – I*) + D(I3/2 – I* 3/2) (10)

It is noticeable that the introduction of the term D(I3/2 – I* 3/2) very often improves the goodness of the fit. For example, for the hydrolysis constant of Cd(OH)+ in sodium perchlorate media, from eq 10 we obtained two sets of values depending on whether or not we take into account the term in D:

$C = -0.28, U = 9.97 \times 10^{-3}$

$C = -1.08, D = 0.86, U = 3.03 \times 10^{-6}$

The squares sum, U, shows that there is a significant improvement in the fit when D term is introduced. We used the Gauss-Newton nonlinear least-squares method with the computer program [11] to refine the parameters C and D by minimizing the squares sum from eq 6. The parameters for the dependence on ionic strength (C and D) are calculated by the fitting method and reported in Table 2.

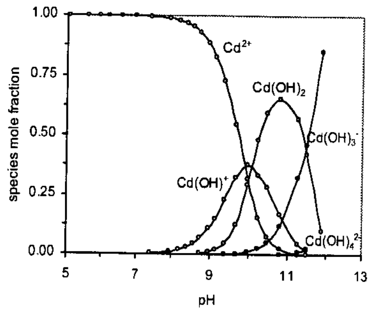

Fig. 2. Distribution diagram of different hydrolytic species of cadmium cation versus the pH of the aqueous solution at 25 °C and 0.1 mol dm^{-3} NaClO$_4$.

Table 2. Parameters for the dependence on ionic strength (C and D) of hydrolysis constants for all species are calculated by the fitting method in the background electrolyte

empirical parameters	β_{11}	β_{12}	β_{13}	β_{14}
C	-1.08	-1.53	-0.99	-0.60
D	0.86	1.04	0.83	0.44

As can be seen from Table 2, the parameters which characterize the dependence of the hydrolysis constant on ionic strength show a regular trend and seem to be a function of Z* values. The dependence of hydrolysis constant values with ionic strength is shown in Figure 1. This Figure and Table 1 show that the hydrolysis constant have a larger values at lower ionic strength and a minimum when the ionic strength approaches 0.5 mol dm-3 sodium perchlorate, which are in good agreement with the results obtained for other species [12-27].

REFERENCES

1. Sugawara, M.; Valenta, P.; Numberg, H. W.; Kambara, T. J. Electroanal. Chem. 180 (1984) 343.
2. Simoes Goncalves, M. L. S.; Correia Dos Santos, M. M. J. Electroanal. Chem. 187 (1985) 333.
3. Valenta, p. Trace Metal Speciation in Surface Waters and Its Ecological Implications, Plenum Press, New York, (1983).
4. Numberg, H. W.; Fresenius, Z. Anal Chem. 316 (1983) 557.
5. Simoes Goncalves, M. L.; Abreu Vaz, M. C. T.; Frausto da Silva, J. J. Talanta, 28 (1981) 237.
6. Cukrowski, I.; Naseko, N. Electroanal. 15 (2003) 1377.
7. Charles F.Beas,Jr.Robert E. Mesmer ,The Hydrolysis of Cations, John Willey&New York . 1976.
8. Lagrange, P. ; Schneider, K. ; Zare.K ; Lagrange, J. Determination and Comparison of the Stability Constants of Uranium(VI) and Vanadium(V)Glycine Complexes. Polyhedrone.,13 (1994) 861.
9. Canel, E.; Gultepe, A.; Dogan, A.; Kihc, E., J. Solution Chem., 35(2006) 5.
10. M. T. Beck and I Nagypal, Chemistry of Complex Equilibria, Ellis Harwood, New York, (1990).
11. D. C. Harris, J. Chem. Educ., 75 (1998) 119.
12. P. G. Daniele, C. Rigano and S. sammartano, Talanta, 30 (1983) 81.
13. P. G. Daniele, C. Rigano and S. Sammartano, Anal. Chem. 57 (1986) 2956 .
14. F. Gharib, K. Zare, A. Taghvamanesh and M. Monajjemi, J. Chem. Eng. Data, 46 (2001) 1140.
15. C. De Stefano, C. Foti and A. Gianguzza, J. Chem. Res. 464 (1994).
16. A. De Robertis, C. De Stefano, S. Sammartano and C. Rigano, Talanta, 34 (1987) 933.
17. F. Gharib, K. Zare and K. Majlesi, J. Chem. Eng. Data, 45 (2000) 833.
18. F. Gharib, K. Zare and K. Majlesi, J. Chem. Res. 186 (2000).
19. Jabbari, M.; Gharib, F.; Mohammadpou Amini, M.; Azadmehr, A. Can. J. Chem. 86 (2008) 751.
20. F. Gharib and A. Shamel, Phys. Chem. Liq. 40 (2002) 637.
21. F. Gharib and A. Nouri, Russ. J. Inorg. Chem., 47 (2002) 1101.
22. F. Gharib, K. Zare, A. Taghvamanesh, A. Shamel and G. Shafiee, Main Group Met. Chem., 25 (2002) 647.
23. F. Gharib, A. Shamel, A. Taghvamanesh and G. Shafiee, Russ. J. Corrd. Chem., 29 (2003) 436 .
24. F. Gharib and L. Afrazeh, J. Chem. Eng. Data, 48 (2003) 999.
25. F. Gharib and M. Malekani, Revs. Inorg. Chem., 23 (2003) 97.
26. F. Gharib, F.; Sayadian, M.; shamel, A.; Mobasher-Moghadam, M.; J. Mol. Liq. 138 (2008) 9.
27. F.Gharib, F.; Farajtabar, A. J. Mol. Liq. 135 (2007)