16884-55-2; $[FeL_6][ClO_4]_2$, 16742-95-3; $[NiL_6][ClO_4]_2$, 16742-94-2.

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Kinetics of the Disproportionation Reaction of Mercury(I) with Hydrogen Cyanide in Acidic Solutions

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The kinetics of the disproportionation reaction of mercury(I) with HCN in perchloric acid solutions have been measured by the stopped-flow method. The rate law is given by $-d[Hg(I)]/dt = 2.2 \times 10^3[Hg(I)][HCN][H^+]^{-1}$ M s^{-1} at 25 °C. The activation parameters are $\Delta H^* = 9.5 \pm 0.2$ kcal mol^{-1}, $\Delta S^* = -11.6 \pm 0.6$ cal mol^{-1} deg^{-1}. The rate constant, k_1, for the possible rate-determining reaction $Hg_2OH^+ + HCN = Hg^0 + HgCN^+ + H_2O$ is calculated to be 2.2×10^8 M^{-1} s^{-1}. The breaking of the Hg–Hg bond is considered to be the rate-determining step in the disproportionation reaction with HCN. Discussions on some possible mechanisms are made.

Introduction

It is generally accepted that the rate of disproportionation of Hg_2^{2+} into Hg^{2+} and dissolved mercury atoms is rapid and is readily reversible[1]

$$Hg_2^{2+} \rightleftharpoons Hg^0 + Hg^{2+} \qquad (1)$$

The equilibrium constant, K_d, measured by many workers,[2,3] more recently by Moser and Voigt[4] who gave 5.5×10^{-9} M at 25 °C, shows Hg_2^{2+} is sufficiently stable in acidic solutions.

Many texts describe Hg_2^{2+} as unstable toward disproportionation with ligands which form strong covalent bonds such as ammonia, many amines, cyanide ion, hydroxide ion, thiocyanide ion, sulfide, and acetylacetone.[5] However, no data concerning the kinetics have been reported to the best of our knowledge. The disproportionation reaction of Hg_2^{2+} in the presence of ligands which form stable mercuric complexes has been believed to proceed via eq 1. That is, decreasing the concentration of free mercuric ions with concomitant formation of metallic mercury shifts the equilibrium to the right. However, little information is available to discuss the mechanism in further detail. It is an interesting question whether ligands induce the spontaneous disproportionation as mentioned above or they take part in direct interaction to break the Hg–Hg bond.

This paper describes the kinetics of the disproportionation reaction of Hg_2^{2+} with HCN. The reasons that HCN was chosen were (1) simple interpretation of the kinetic results, i.e., kinetic contribution from the CN^- may be neglected owing to the sufficiently high pK value of HCN, and (2) formation of a very stable mercuric cyanide complex even in acidic solutions.

Experimental Section

Materials. Doubly distilled water was used throughout this work. All the chemicals were of analytical reagent grade unless otherwise specified. Metallic mercury was purified in the usual manner.[6] Stock solution (0.01 M) of mercuric perchlorate was prepared by dissolving the required amount of mercuric oxide (red) in perchloric acid in 0.05 molar excess of this acid. Mercurous perchlorate solutions (10^{-2}–10^{-4} M) were prepared from the mercuric perchlorate solution by dilution with 0.05 M $HClO_4$ and shaking with a few drops of metallic mercury. These solutions were kept over the metallic mercury. The solutions (10^{-2}, 10^{-3} M) thus prepared were standardized by oxidizing the Hg(I) with $KMnO_4$ and titrating the resulting Hg(II) against KSCN with ferric alum indicator. More dilute mercurous sample solutions used in the kinetic measurements were prepared from the 10^{-3} M stock solution by dilution with $HClO_4$ and were not kept in contact with metallic mercury; their concentrations were determined spectrophotometrically based on calibration curves made by the 10^{-4} M stock solution.[6] The acid concentrations of the sample solutions were determined titrimetrically by Na_2CO_3 against methyl red indicator. A KCN stock solution (0.1 M) was prepared. More dilute solutions, 2×10^{-3}–10^{-2} M, were prepared by dilution with water and their concentrations were standardized against $AgNO_3$ with KI indicator. Merck grade $NaClO_4$ was used to examine the effect of ionic strength.

Stoichiometric Measurements. The stoichiometry of the overall reaction of Hg_2^{2+} with HCN was measured by spectrophotometry at 236.5 nm in a stopped-flow apparatus. Stoichiometry with regard to elemental mercury was measured by the atomic absorption method. In the flameless atomic absorption method, the mercury compounds in the solution are reduced with tin(II) chloride, and resulting elemental mercury is driven as a vapor by an air stream into an acidic permanganate absorption solution[7] or a measuring cuvette.[8] In the absence of the reductant, only mercury presented in the elemental state in the solution is driven.[9] This method is, therefore, suitable for the determination of stoichiometry regarding elemental mercury. The apparatus and procedure were essentially similar to those employed by many workers[7,10,11] to concentrate trace amounts of mercury. Two gas-washing type cylindrical vessels of 3-cm diameter and 100-ml capacity, each with a glass-sintered inlet tube, were used. One was used as a reduction–aeration vessel and the other as an absorbing vessel. These vessels were connected to each other and further connected to a nitrogen cylinder through a regulator with polyethylene tubes. The procedure for the stoichiometric measurements of mercury consisted of two steps. In the first step, the sample solution in the reduction–aeration vessel was treated with and without the reductant and was aerated for 30 min by nitrogen gas at constant flow rate, 1.5 l./min, into the absorbing vessel in which 20 ml of a permanganate–sulfuric acid solution was placed. This solution was then decolorized by the dropwise addition of hydroxammonium chloride solution (1.44 M). In the second step, the decolorized solution was diluted to 100 ml with water, a suitable aliquot of which was treated with the reductant, and the resulting mercury was further aerated into the measuring cuvette. The reductant used was a 0.44 M tin(II) chloride solution in 1 M HCl. In the first step, each 1 ml of tin(II) chloride and 18 N sulfuric acid was used as the reductant, whereas each 2 ml of these solutions was used in the second step. The solution used for absorbing mercury was prepared by mixing equal volumes of 0.13 M potassium permanganate and 18 N sulfuric acid. The sample solution was prepared

Table I. Stoichiometry of the Reaction of Hg_2^{2+} with HCN (25 °C)

				Calcd				
$[Hg_2^{2+}]_0$, 10^{-5} M	$[HCN]_0$, 10^{-5} M	$[Hg_2^{2+}]$, 10^{-5} M	Stoichiometric ratio	$[Hg_2^{2+}]$, 10^{-5} M	[HCN], 10^{-7} M	$[HgCN^+]$, 10^{-6} M	$[Hg(CN)_2]$, 10^{-6} M	Stoichiometric ratio
				$[H^+] = 0.309$ M				
1.00	0.50	0.68	1.6	0.665	0.696	1.75	1.59	1.49
1.00	0.99	0.36	1.6	0.406	1.38	2.12	3.82	1.67
1.00	1.24	0.34	1.9	0.287	1.89	2.06	5.08	1.74
1.00	1.74	0.15	2.0	0.0832	4.36	1.37	7.80	1.90
				$[H^+] = 0.510$ M				
2.52	0.99	1.82	1.4	1.83	0.940	3.95	2.93	1.43
2.52	1.24	1.70	1.5	1.69	1.14	4.39	3.95	1.49
2.52	1.74	1.48	1.7	1.40	1.55	4.99	6.13	1.55
2.52	2.48	1.12	1.8	1.02	2.28	5.34	9.62	1.65
2.52	3.72	0.68	1.9	0.453	4.43	4.59	16.1	1.80

by mixing 1 ml of 10^{-5} M Hg_2^{2+} in 0.1 M $HClO_4$ and 5 ml of 10^{-4} M KCN solutions and diluting to 30 ml with 0.1 M $HClO_4$. The sample mixture preparation was made just before the nitrogen gas inducing. All the work in the first step must be done in the draft chamber.

Kinetic Measurement. Rates of reaction were followed by measuring the decrease in absorbance of Hg(I) at 236.5 nm, λ_{max}, using an Aminco-Morrow stopped-flow apparatus attached to an Aminco DW-2 uv–visible spectrophotometer which was operated in the dual-wavelength mode: one monochrometer was set at 236.5 nm and the other, used as a reference, was set at 290 nm where any absorptions were not observed before and after the mixing. The output from the photomultiplier was monitored by a Nihon-Koden Model VC-8 oscilloscope, traces from which were photographed by a camera. The temperatures around the cuvette, valve block, and drive syringes in the apparatus were held constant to within ± 0.05 °C by circulating water from a constant-temperature bath. The temperature of the room where the apparatus was placed was controlled within ± 0.5 °C.

Results

Stoichiometry. The stoichiometry of the overall reaction of Hg_2^{2+} with HCN was determined. In this paper, a cyanide species not combined with Hg(II) is written as HCN because the concentration of free CN^- ion in solution is negligibly small under the present acidic conditions. The results are given in Table I. When initial molar concentration ratios of Hg_2^{2+} to HCN were close to 1/2, stoichiometric ratios, $[HCN]_0/[Hg_2^{2+}]_{consumed}$, were obtained to be 2. These calculations were based on the assumption that $[Hg_2^{2+}]_{consumed} = C_{Hg^{2+}}$, and $[HCN]_{after\ mixing} = 0$, where $C_{Hg^{2+}}$ represents the concentration of total mercuric species. With increasing the $[Hg_2^{2+}]_0/[HCN]_0$ ratio, the stoichiometric ratios deviate from 2, which can be ascribed to the formation of $HgCN^+$ species. The concentrations of the species in the equilibrium can be predicted together with those of $Hg(CN)_2$, Hg_2^{2+}, and HCN based upon the reported complex formation constants,[12] $\log K_1 = 17.0$ for $HgCN^+$ and $\log K_2 = 15.8$ for $Hg(CN)_2$ at 25 °C, the acid dissociation constant for HCN, K_a, and the disproportionation constant, K_d.[13] The results are listed in Table I. The discrepancies between the observed and calculated stoichiometric ratios may be due, in part, to the effect of ionic strength on the various equilibrium constants. As long as $[HCN]_0$ is somewhat greater than twice $[Hg_2^{2+}]_0$, the stoichiometry is in reasonable agreement with eq 2. The

$$Hg_2^{2+} + 2HCN \rightarrow Hg^0 + Hg(CN)_2 + 2H^+ \qquad (2)$$

results of stoichiometric study with respect to metallic mercury are given in Table II. In the presence of the reductant, the total amount of mercury species was obtained, whereas only elemental mercury formed according to eq 2 was determined in the absence of the reductant.

Kinetics. All the kinetic runs were carried out in the presence of excess HCN. Plots of ln $(A_t - A_\infty)$ where A_t and A_∞ represent the absorbance at time t and infinity time, respectively, were linear for over 4 half-lives for reactions at $[H^+] = 0.51$ *M*. This linearity was taken as evidence that the reaction is first order with respect to Hg(I)

$$-d[Hg(I)]/dt = k'[Hg(I)] \qquad (3)$$

where k' is the pseudo-first-order rate constant.

The ionic strength in the solution is of limited significance in the rate as shown in Table III. Therefore no attempt was made to maintain a constant ionic strength.

The data in Table IV clearly indicate that the reaction was also first order with respect to HCN concentration. Therefore, the data were treated according to the second-order rate law

$$-d[Hg(I)]/dt = k_{obsd}[Hg(I)][HCN] \qquad (4)$$

where k_{obsd} is the observed second-order rate constant.

Hydrogen Ion and Temperature Dependence. The effects of hydrogen ion concentration and temperature on the observed

Table II. Amount of Metallic Mercury Found with and without Reductant[a] ($[HCN]_0 = 1.67 \times 10^{-5}$ M)

	Amt × 10^8, mol	
Run no.[b]	Hg^0	Hg^0_{red}
1	0.97	
2	1.12	
3	0.99	
4	1.02	
5		1.86
6		1.96
7		1.76

[a] In all runs, the amount of Hg_2^{2+} taken is 1.01×10^{-8} mol.
[b] Runs no. 1–4 were performed without reductant and runs no. 5–7 were with reductant.

Table III. Effects of Ionic Strength[a] on the Rate Constants for the Reaction Between Hg_2^{2+} and HCN (25.0 °C, $[HClO_4] = 0.205$ M)

Ionic strength	10^5-$[Hg_2^{2+}]_0$, M	10^3-$[HCN]_0$, M	k', s^{-1}	10^{-3}-k_{obsd}, $M^{-1}\ s^{-1}$
0.205	2.50	0.995	11	11
0.306	2.46	0.995	11	11
0.404	2.47	0.995	11	11
0.505	2.45	0.995	10	10
0.604	2.46	0.995	10	10
0.934	2.45	0.995	9.0	9.0
0.204	2.50	1.97	20	10
0.306	2.46	1.97	20	10
0.404	2.47	1.96	20	10
0.505	2.45	1.97	20	10
0.604	2.46	1.97	18	9.0
0.934	2.45	1.97	16	8.0

[a] The medium used is $HClO_4$-$NaClO_4$.

Table IV. Dependence of Rate Constants on Initial HCN Concentration (25.0 °C, $[HClO_4] = 0.510$ M)

$10^5[Hg_2^{2+}]_0$, M	$10^3[HCN]_0$, M	k', s^{-1}	$10^{-3}k_{obsd}$, $M^{-1}\ s^{-1}$
2.55	0.995	4.2	4.2
2.55	1.97	8.2	4.2
2.55	2.93	12	4.2
2.55	3.94	16	4.0
2.55	4.95	19	3.9
4.97	0.995	4.1	4.1
4.97	1.97	8.1	4.1
4.97	2.93	11	3.8
4.97	3.94	16	4.0
4.97	4.95	19	3.9
0.98	0.995	4.1	4.1
0.98	1.97	8.2	4.2

Table V. Dependence of Rate Constants on Acid Concentration and Reaction Temperature ($[HCN] = 0.995 \times 10^{-3}$ M)

10^5-$[Hg_2^{2+}]_0$, M	$[H^+]_0$, M	$10^{-3}k_{obsd}$, $M^{-1}\ s^{-1}$				
		15 °C	20 °C	25 °C	30 °C	35 °C
2.55	0.510	2.0	3.2	4.2	5.8	7.7
2.53	0.409	3.2	4.3	5.5	7.7	9.4
2.53	0.308	4.1	5.8	7.5	10	14
2.54	0.204	6.3	8.7	11	15	20
2.48	0.155	8.2	12	15	20	25
2.48	0.104	12	17	21		
2.47	0.053	23				

second-order rate constant were determined. The results are given in Table V and are illustrated in Figure 1. A linear dependence of k_{obsd} on $[H^+]^{-1}$, at each temperature, with zero intercept was observed; thus it is convenient to define the rate constant $k'' = k_{obsd}[H^+]$. The activation parameters associated with k'' are calculated from Table V (excluding the discrepant value at 15 °C and 0.51 M acid), $\Delta H^* = 9.5 \pm 0.2$ kcal mol^{-1}, $\Delta S^* = -11.6 \pm 0.6$ cal mol^{-1} deg^{-1}. The ionic strength corrections were not made since the effects up to 0.5 were small.

Discussion

The form of the observed rate law indicates that the activated complex for the predominant path is formed from one Hg_2^{2+} and one HCN with the prior loss of one H^+ and the prior loss of an unknown number of Hg^0 (probably either zero or one). Many mechanisms are consisted with this, but the magnitude of the observed rate constant makes it possible to exclude some otherwise plausible mechanisms since it may safely be assumed that no second-order rate constant for an elementary reaction in aqueous solution near 25 °C can be greater than about 10^9 or 10^{10} $M^{-1}\ s^{-1}$, the diffusion-controlled limit. Some of the various possibilities can be summarized in tabular form:

No.	Reactants assumed	k''	k_i, $M^{-1}\ s^{-1}$
1	$Hg_2OH^+ + HCN$	k_1K_h	2.2×10^8
2	$Hg_2^{2+} + CN^-$	k_2K_a	3.5×10^{12}
3	$HgOH^+ + HCN$	$k_3K_dK_{h'}/S$	6×10^8
4	$Hg^{2+} + CN^-$	$k_4K_dK_a/S$	2×10^{14}

where $k'' = 2.2 \times 10^3$ $M^{-1}\ s^{-1}$ at 25 °C, K_h, the hydrolysis constant for Hg_2^{2+}, $= 10^{-5}$ M,[2] K_a, the acid dissociation constant for HCN, $= 6.3 \times 10^{-10}$ M, K_d, the disproportionation constant, $= 5.5 \times 10^{-9}$ M, $K_{h'}$, the hydrolysis constant for Hg^{2+}, $= 2 \times 10^{-4}$ M,[14] and S, the solubility of Hg^0, $= 3 \times 10^{-7}$ M.[4,9,15] Since k_2 and k_4 are both considerably larger than 10^{10} $M^{-1}\ s^{-1}$, free CN^- cannot be an important reactant. The expression for k'' for the third assumption is an approximation; the complete expression is

$$k'' = (k_3K_dK_{h'}/S)/(1 + k_3K_{h'}[HCN]/(k_r[Hg^0][H^+]))$$

where k_r is the rate constant for the reproportionation reaction between Hg^0 and Hg^{2+}, and the hydrolysis equilibrium for Hg^{2+} is assumed to be maintained. If the slight decrease shown by k_{obsd} or k'' in Table IV with increasing HCN is due to the denominator in the above expression, the data can be used to set a lower limit for k_r. The expression requires that a plot for $1/k_{obsd}$ vs. [HCN] be linear and the ratio of slope to intercept will be $k_3K_{h'}/(k_r[Hg^0][H^+])$. The data in the table indicate that (slope)/(intercept) ≤ 20 M^{-1}. Thus $k_r \geq 6 \times 10^8 \times 2 \times 10^4/(20 \times 3 \times 10^{-7} \times 0.51) = 4 \times 10^{10}$ M^{-1} s^{-1}. Since this value is somewhat larger than the diffusion-controlled limit, the path for assumption 3 can probably be rejected. Thus neither path involving the prior disproportionation of Hg_2^{2+} can be accepted.[16]

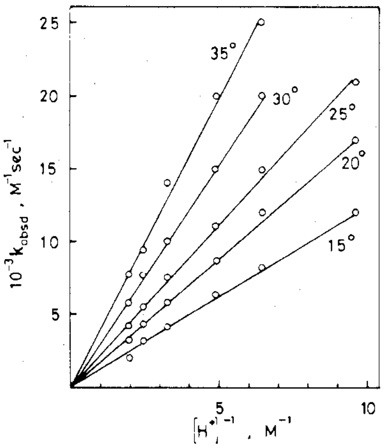

Figure 1. Hydrogen ion and temperature dependence of k_{obsd}.

From the x-ray results of interatomic distances in some mercurous compounds, Hg_2X_2 (X = F, Cl, Br, I, N_2Ac_2 (diacetylhydrazine)), Yamane and Davidson[17] advanced the hypothesis that the stronger the Hg–X bond, the longer and weaker the Hg–Hg bond. Cyanide ion forms a strong covalent complex with mercury even in acidic solution. Therefore, charges on the Hg–Hg ions are readily polarized and the bond lengthens to be broken. This process is considered to be the rate-determining step in the disproportionation reaction with HCN. A much greater reaction rate of Hg_2OH^+ than Hg_2^{2+} may be understood in terms of the basic nature of the hydroxo group which is favorable to HCN. The following mechanism is proposed:

$Hg_2OH^+ + HCN \rightleftharpoons Hg_2OH^+\cdots HCN$ rapid equilibrium

$Hg_2OH^+\cdots HCN \rightleftharpoons Hg_2CN^+ + H_2O$ rapid equilibrium

$(Hg\text{-}Hg\text{-}CN)^+ \rightarrow Hg^0 + HgCN^+$ rate determining

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Registry No. Hg_2^{2+}, 12596-26-8; HCN, 74-90-8.

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$2HgCN^+ + Hg^0 = Hg_2^{2+} + Hg(CN)_2$ ($K = K_2/K_dK_1 = 1.15 \times 10^7$) and the two stoichiometric equations $[HCN]_0 = [HCN] + [HgCN^+] + 2[Hg(CN)_2]$ and $[Hg_2^{2+}]_0 = [Hg_2^{2+}] + [HgCN^+] + [Hg(CN)_2]$.

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Formation of Chloro Complexes of Zinc and Cadmium in Acetic Acid

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Equilibria of zinc and cadmium perchlorates with lithium chloride in 0.1 mol kg^{-1} $LiClO_4$–acetic acid solution have been investigated potentiometrically with an Ag–AgCl electrode. The equilibria of zinc perchlorate with lithium chloride are found to be

$$Zn(ClO_4)_2 + LiCl \xrightleftharpoons{\beta_{11}} ZnCl(ClO_4) + LiClO_4$$

$$2Zn(ClO_4)_2 + 2LiCl \xrightleftharpoons{\beta_{22}} Zn_2Cl_2(ClO_4)_2 + 2LiClO_4$$

$$2Zn(ClO_4)_2 + 3LiCl \xrightleftharpoons{\beta_{23}} Zn_2Cl_3(ClO_4) + 3LiClO_4$$

$$2Zn(ClO_4)_2 + 4LiCl \xrightleftharpoons{\beta_{24}} Zn_2Cl_4 + 4LiClO_4$$

$$2Zn(ClO_4)_2 + 5LiCl \xrightleftharpoons{\beta_{25}} LiZn_2Cl_5 + 4LiClO_4$$

$$2Zn(ClO_4)_2 + 6LiCl \xrightleftharpoons{\beta_{26}} Li_2Zn_2Cl_6 + 4LiClO_4$$

with log β_{11} = 5.15, log β_{22} = 13.58, log β_{23} = 18.94, log β_{24} = 23.76, log β_{25} = 27.21, and log β_{26} = 30.09. The equilibria of cadmium perchlorate with lithium chloride are

$$Cd(ClO_4)_2 + LiCl \xrightleftharpoons{\beta_{11}} CdCl(ClO_4) + LiClO_4$$

$$Cd(ClO_4)_2 + 2LiCl \xrightleftharpoons{\beta_{12}} CdCl_2 + 2LiClO_4$$

$$Cd(ClO_4)_2 + 3LiCl \xrightleftharpoons{\beta_{13}} LiCdCl_3 + 2LiClO_4$$

$$2Cd(ClO_4)_2 + 2LiCl \xrightleftharpoons{\beta_{22}} Cd_2Cl_2(ClO_4)_2 + 2LiClO_4$$

with log β_{11} = 5.28, log β_{12} = 9.60, log β_{13} = 13.2, and log β_{22} = 13.1.

Introduction

The formation of halogeno complexes of group 2B elements in solution have been studied by potentiometry, polarography, solvent extraction, etc.[1] Mironov et al.[2] have also studied the ion-pair formation of the halogeno complexes with alkali metals with an amalgam electrode. Morris et al.[3] have investigated systematically the equilibria and structures of the halogeno complexes in solution by various methods. Gutmann et al.[4] have qualitatively studied the formation of halogeno complexes in various solvents. Crystal structures of the complexes have been reported by Brehler et al. and other authors.[5]

In addition to Raman spectra[6-10] and x-ray diffraction,[11-15] densimetry,[16] cryoscopy,[17] and vapor pressure measurements[18] have been used to study the equilibria and the structures of complexes in solution and gas phase. According to these results, it may generally be assumed that the configurations of the complexes in solution are similar to those in crystals. For example zinc ion is octahedrally surrounded by six water molecules in aqueous solution, and the monohalogeno complex is formed by the substitution of one water molecule of the hexaaqua complex by a halogenide ion. The structure of the dihalogeno complex is not unambiguously established as many authors have reported different structures in different solvents. However most of these results point to the tetrahedral dihalogenozinc complex, and the complex of a relatively large cation such as Hg^{2+} seems to have a linear X–M–X structure with the other sites of the octahedron occupied by four solvent molecules. Tri- and tetrahalogeno complexes of the metals are ordinarily of the tetrahedral configuration. Besides the monomeric species, the formation of dimeric complexes has been reported in gas-phase,[19,20] solution,[17] and crystal forms,[21] and polymeric structure, in the molten-salt form.[22,23]

Some qualitative aspects of the formation of the zinc–chloro complex in acetic acid have been reported.[24,25] In the present paper the equilibria of zinc and cadmium perchlorate with lithium chloride in acetic acid are investigated quantitatively by means of potentiometry.

Experimental Section

Zinc and cadmium perchlorates were prepared by dissolving pure metals (99.99%) in hot aqueous perchloric acid solution. After recrystallization from water, the crystals were recrystallized twice from anhydrous acetic acid containing some acetic anhydride. The other reagents were prepared by the same methods as described elsewhere.[26]

Potentiometric measurements were performed as described previously[26] with an Orion Research digital pH/mV meter, Model