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Spectrophotometric Study of Mercury(II)–Azide Ion Equilibria[1]

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A study of solution equilibria involving Hg^{2+} and N_3^- ions is complicated by factors which limit the applicability of many of the direct techniques. Mercury(II) azide in the solid state is explosive, hydrazoic acid is only slightly dissociated, and the mercury(II) ion is a relatively strong acid in aqueous solution. In this study the highly colored FeN_3^{2+} ion is utilized in an indirect spectrophotometric determination of the stability constants of mercury(II) azide in aqueous solution. Combination of pH data and spectrophotometric measurements of the concentration of FeN_3^{2+} in solutions containing Fe^{3+}, Hg^{2+}, and N_3^- permits calculating $[N_3^-]$ and $\bar{n}$. By graphical analyses of these data values of the stoichiometric stability constants at molar ionic strengths 0.05, 0.15, and 0.25 are obtained. Extrapolation of the results to zero ionic strength yields the following thermodynamic stepwise stability constants at 28°: HgN_3^+, $K_1^0 = 5.6 \times 10^7$; $Hg(N_3)_2$, $K_2^0 = 3.1 \times 10^7$.

Introduction

In recent years there has been considerable interest in aqueous solution equilibria of metal ion–azide complexes. Among the species which have been studied are complexes of iron(III),[4–6] cobalt(II),[7] copper(II),[8] ruthenium(III),[9] zinc(II),[10] cadmium(II),[10] chromium(III),[11] and palladium(II).[12] The present paper describes studies of mercury(II)–azide ion equilibria in aqueous solution.

It has long been recognized that the mercuric halides dissociate only slightly in aqueous solution, existing primarily as the species HgX^+ and HgX_2. This phenomenon has also been shown to be characteristic of the mercuric "pseudo-halides," cyanide and thiocyanate. The stability constants of these mercury(II) salts have been the subject of several papers.[13] The azide ion has been classified as a "pseudo-halide"[14]; hence, it would be expected that mercuric azide would dissociate slightly in aqueous solution.

In 1904 Dennis and Browne[15] noted that mercuric chloride discharged the color of iron(III) thiocyanate and iron(III) azide solutions. It has been established that the red color of iron(III) thiocyanate solutions is due primarily to the complex ion, $FeNCS^{2+}$, and that discoloration of such solutions by mercury(II) is a result of the formation of highly associated $HgSCN^+$ and $Hg(SCN)_2$ species. The red color of iron(III) azide solutions is attributed to the ion, FeN_3^{2+},[4–6] and by analogy the discoloration of iron(III) azide solutions by mercury(II) is indicative of the formation of slightly ionized HgN_3^+ and $Hg(N_3)_2$. In spite of such qualitative evidence for the high degree of association of mercuric azide, no quantitative study of mercury(II)–azide ion equilibria has yet been reported.

The choice of a method for studying these equilibria is complicated by several factors. The explosive instability of pure dry mercuric azide, the acidity of the mercuric ion in aqueous solution, and the slight dissociation of aqueous hydrazoic acid are factors which severely limit the applicability of many of the direct techniques of studying solution equilibria. The method which is described here involves utilization of the highly colored FeN_3^{2+} complex as an indicator in an indirect spectrophotometric determination of the stepwise stability constants of $Hg(N_3)_2$. The iron(III) azide complex has a predominant absorption band in the visible region of the spectrum, with a maximum at 465 mμ. If the appropriate equilibrium quotients and molar extinction coefficients of FeN_3^{2+} are known, it is possible to follow the concentration of FeN_3^{2+}, and hence of N_3^-, in solutions containing Hg^{2+}, Fe^{3+}, and N_3^-. From knowledge of the stoichiometry of the solutions and of the free azide ion concentrations, it is possible to determine the stability quotients of HgN_3^+ and $Hg(N_3)_2$ at any particular ionic strength.

Experimental

Materials.—Mercuric perchlorate solutions were prepared from G. Frederick Smith reagent grade $Hg(ClO_4)_2 \cdot 9H_2O$ and were standardized by titration with standard thiocyanate to ferric ion end points.

Sodium azide solutions were prepared from twice recrystallized Fisher "Purified" sodium azide. Standard solutions were prepared by weighing out appropriate portions of the carefully dried material and dissolving these in the desired amount of distilled water. The titer of these solutions was checked by titration with standard silver nitrate to chromate ion end points.

Standard iron(III) perchlorate solutions were prepared according to the method of Anton, Dodd, and Harvey.[16] By this

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method iron(III) solutions free of iron(II) and chloride ions can be prepared.

Sodium perchlorate solutions were prepared from G. Frederick Smith reagent grade hydrated sodium perchlorate. These were standardized by evaporation of an aliquot to dryness, dissolution of the solid sodium perchlorate in absolute ethyl alcohol, and addition of excess ethanolic potassium acetate to the solution. The precipitated potassium perchlorate was then aged, filtered, dried, and weighed.

Apparatus.—Absorbance measurements were made with a Beckman DB spectrophotometer, operated manually and equipped with matched 1.0-cm. silica cells. The temperature was maintained at 28 ± 1° throughout the study. In order to prevent temperature changes within the spectrophotometer, absorbance measurements were made immediately after insertion of the sample and reference cells into the instrument. The reference cell contained distilled water.

A Beckman Zeromatic pH Meter was used for pH measurements. Standardization of the instrument was accomplished with Coleman buffers.

Procedure.—In order to determine the molar extinction coefficient (at 460 mμ) and stability quotient of the monoazido iron(III) complex, the following titration procedures were adopted. Solutions to be titrated contained ferric perchlorate, sodium azide, perchloric acid, and, if necessary for ionic strength adjustment, sodium perchlorate. Care was taken to ensure that the stoichiometries were such that the total iron(III) concentrations were in excess of the total azide ion concentrations. The ionic strengths of these starting solutions were adjusted to the desired value, *e.g.*, 0.25 *M*. (Hereafter, all ionic strength dimensions are understood to be moles per liter.) The titrant consisted of either a solution of perchloric acid and sodium perchlorate of the same pH and ionic strength as the solution to be titrated or of a solution of sodium perchlorate, perchloric acid, and hydrazoic acid of identical pH and ionic strength as the solution to be titrated. The titrations simply involved incremental additions of the titrant to the starting solution. Total solution volumes varied from 100 to 1000 ml. After each addition of titrant, the absorption of the solution was measured at 460 mμ. Temperature and pH were checked periodically during the course of any given titration. Studies were made at ionic strengths 0.05, 0.15, and 0.25 at 28 ± 1°.

For the determination of the stability quotients of mercuric azide, the conditions and procedures were exactly the same as described above, except for the fact that the starting solutions or solutions to be titrated contained known amounts of mercuric perchlorate in addition to ferric perchlorate, sodium azide, perchloric acid, and sodium perchlorate.

Treatment of Data.—For the iron(III)-azide systems, it may be assumed that stoichiometric concentrations, $C_{\text{Fe(III)}}$ and C_{N_3}, are equal to

$$C_{\text{Fe(III)}} = [\text{Fe}^{3+}] + [\text{FeN}_3{}^{2+}]$$

and

$$C_{\text{N}_3} = [\text{HN}_3] + [\text{N}_3{}^-] + [\text{FeN}_3{}^{2+}]$$

From the expression for Q (stability quotient of $\text{FeN}_3{}^{2+}$) and for Q_a (dissociation quotient of HN_3), it may be shown that

$$\frac{Q}{1 + \dfrac{[\text{H}^+]}{Q_a}} = \frac{[\text{FeN}_3{}^{2+}]}{[\text{Fe}^{3+}]([\text{HN}_3] + [\text{N}_3{}^-])} \qquad (1)$$

For conditions of constant pH and ionic strength, the left side of eq. 1 is constant and, for convenience, may be designated by the symbol q. Applying Beer's law and with a light path of 1.0 cm., eq. 1 may be written as

$$q = \frac{A/\epsilon}{(C_{\text{Fe(III)}} - A/\epsilon)(C_{\text{N}_3} - A/\epsilon)} \qquad (2)$$

where A is the absorbance due to $\text{FeN}_3{}^{2+}$ and ϵ is the molar extinction coefficient of the complex (at a particular wave length). If the multiplication indicated in the denominator of eq. 2 is carried out, and the squared term $(A/\epsilon)^2$ is neglected (which introduces no appreciable error), eq. 2 may be rearranged to give

$$\frac{C_{\text{Fe(III)}}C_{\text{N}_3}}{A} = \frac{1}{q\epsilon} + \frac{1}{\epsilon}(C_{\text{Fe(III)}} + C_{\text{N}_3}) \qquad (3)$$

A plot of values of the left side of eq. 3 *vs.* $(C_{\text{Fe(III)}} + C_{\text{N}_3})$ should be linear with a slope of $1/\epsilon$ and an intercept of $1/q\epsilon$. The value of Q may then be obtained from q when $[\text{H}^+]$ and Q_a are known. At each of the indicated ionic strengths Q_a was determined from the relationship

$$\log Q_a = \log K_a{}^0 + \frac{1.0\sqrt{I}}{1 + 2.6\sqrt{I}}$$

where $K_a{}^0$ is the thermodynamic dissociation constant of hydrazoic acid (1.95×10^{-5})[17] and I is the ionic strength.

For systems containing mercury(II), iron(III), and $\text{N}_3{}^-$, the parameter $\bar{n}$ may be defined in the usual manner

$$\bar{n} = \frac{C'_{\text{N}_3} - (\text{total azide not bound to Hg(II)})}{C_{\text{Hg(II)}}}$$

where

$$C_{\text{(HgII)}} = [\text{Hg}^{2+}] + [\text{HgN}_3{}^+) + [\text{Hg(N}_3)_2]$$

and

$$C'_{\text{N}_3} = [\text{N}_3{}^-] + [\text{HN}_3] + [\text{FeN}_3{}^{2+}] + [\text{HgN}_3{}^+] + 2[\text{Hg(N}_3)_2]$$

The stability quotients Q_1 and Q_2 are defined as

$$Q_1 = \frac{[\text{HgN}_3{}^+]}{[\text{Hg}^{2+}][\text{N}_3{}^-]}; \qquad Q_2 = \frac{[\text{Hg(N}_3)_2]}{[\text{HgN}_3{}^+][\text{N}_3{}^-]}$$

Assuming no complexes of mercury(II) of coordination number greater than two exist, $\bar{n}$ can be written

$$\bar{n} = \frac{[\text{HgN}_3{}^+] + 2[\text{Hg(N}_3)_2]}{[\text{Hg}^{2+}] + [\text{HgN}_3{}^+] + [\text{Hg(N}_3)_2]}$$

or, in terms of Q_1, Q_2, and $[\text{N}_3{}^-]$

$$n = \frac{1 + 2Q_2[\text{N}_3{}^-]}{1 + 1/Q_1[\text{N}_3{}^-] + Q_2[\text{N}_3{}^-]} \qquad (4)$$

Equation 4 may be rearranged to give

$$\left([\text{N}_3{}^-] - \frac{[\text{N}_3{}^-]}{\bar{n}}\right) = -\frac{1}{Q_1} + \left(\frac{2}{\bar{n}} - 1\right)[\text{N}_3{}^-]^2Q_2 \qquad (5)$$

If values of the left side of this equation are plotted *vs.* $((2/\bar{n}) - 1)[\text{N}_3{}^-]^2$, a straight line of slope Q_2 and intercept $-1/Q_1$ should be obtained.

Results and Discussion

Table I lists some typical data pertaining to the determination of ϵ (460 mμ) and Q for $\text{FeN}_3{}^{2+}$. Figure 1 shows plots of the variables of eq. 3 at ionic strengths 0.05, 0.15, and 0.25. From the slopes of these linear plots the best average value of the molar extinction coefficient of $\text{FeN}_3{}^{2+}$ at 460 mμ was found to be $3.10 \pm 0.05 \times 10^3$ cm.$^{-1}$ mole^{-1} l.$^{-1}$. The values of q obtained were 54.0, 10.0, and 6.32 at ionic strengths 0.05, 0.15, and 0.25, respectively.

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TABLE I

DATA PERTAINING TO THE DETERMINATION OF ϵ (460 mμ) AND Q FOR THE COMPLEX ION, FeN_3^{2+}

A	$C_{N_3} \times 10^3$	$C_{Fe(III)} \times 10^3$
	Ionic Strength 0.05 M; pH 1.60	
0.206	0.40	3.80
0.172	0.40	3.04
0.128	0.40	2.22
0.097	0.40	1.60
0.067	0.40	1.09
0.045	0.40	0.72
	Ionic Strength 0.15 M; pH 1.00	
0.661	2.66	9.00
0.432	2.12	7.20
0.225	1.52	5.14
0.139	1.18	4.00
0.079	0.89	3.00
0.029	0.53	1.80
	Ionic Strength 0.25 M; pH 0.80	
1.35	5.30	14.40
0.359	2.66	7.20
0.162	1.77	4.80
0.092	1.33	3.60
0.059	1.06	2.88
0.041	0.88	2.39

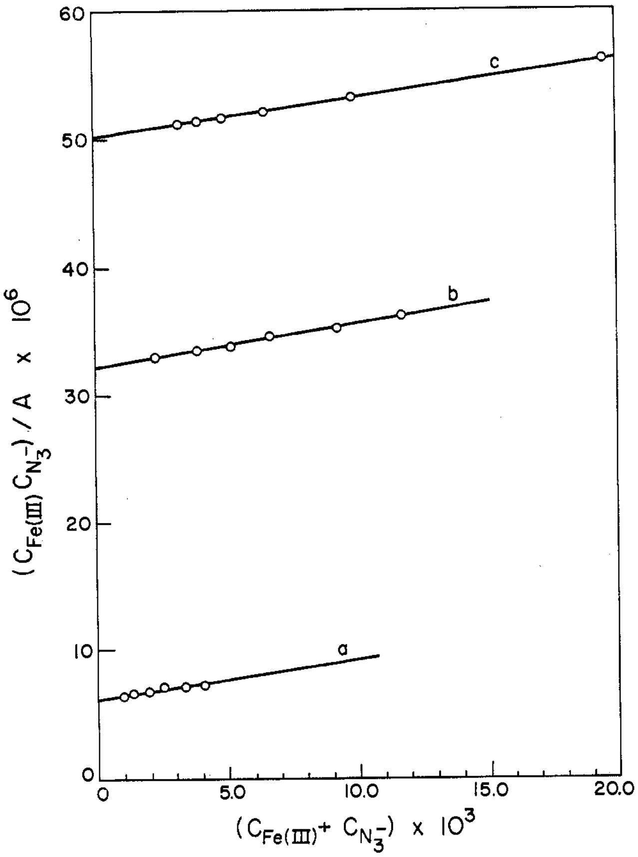

Figure 1.—Plots of determination of ϵ (at 460 mμ) and Q for FeN_3^{2+} at ionic strengths 0.05 (a), 0.15 (b), and 0.25 (c).

TABLE II

DATA PERTAINING TO THE DETERMINATION OF THE STABILITY QUOTIENTS OF MERCURY(II) AZIDE

$C_{Fe(III)} \times 10^3$	$C'_{N_3} \times 10^3$	$C_{Hg(II)} \times 10^4$	A	$\bar{n}$
		Ionic Strength 0.05 M; pH 1.60		
3.96	1.78	8.38	0.155	1.78
3.96	1.78	8.92	0.127	1.73
2.64	1.18	5.89	0.072	1.68
1.98	0.89	4.42	0.048	1.64
1.58	0.71	3.54	0.034	1.60
		Ionic Strength 0.15 M; pH 1.00		
8.49	2.49	9.39	0.219	1.68
6.54	1.84	7.26	0.130	1.59
4.37	1.29	4.83	0.072	1.51
2.94	0.87	3.25	0.038	1.37
2.22	0.66	2.45	0.023	1.28
1.94	0.55	2.18	0.017	1.20
		Ionic Strength 0.25 M; pH 0.80		
13.50	6.86	27.2	0.518	1.73
12.01	5.34	24.1	0.319	1.61
10.52	4.12	21.3	0.194	1.46
9.03	3.06	18.2	0.119	1.29
6.75	1.98	13.6	0.064	1.08

Despite the high acidities employed in these studies, it was necessary to correct the data for the hydrolysis of iron(III). The ratios of $FeOH^{2+}$ to Fe^{3+} at each pH and ionic strength were calculated from the relationship between ionic strength and the molar stability constant of $FeOH^{2+}$, as derived by Milburn and Vosburgh.[18] From such calculations it was possible to correct the value of q and, hence, of Q. The uncorrected values of Q were 5.01×10^4, 3.27×10^4, and 3.09×10^4 at ionic strengths 0.05, 0.15, and 0.25, respectively. The values of Q, corrected for the hydrolysis of Fe^{3+}, were found to be 5.70×10^4, 3.36×10^4, and 3.13×10^4, at the above ionic strengths. In order to utilize these values in an extrapolation of Q to zero ionic strength, it was necessary to evaluate $\mathring{a}$ in the Debye–Hückel expression

$$\log Q = \log K^0 - \frac{\Delta z^2 A\sqrt{I}}{1 + \mathring{a}B\sqrt{I}} \qquad (6)$$

For the reaction of Fe^{3+} and N_3^- to form FeN_3^{2+}, Δz^2 is -6. Plots of log Q vs. $A\sqrt{I}/(1 + \mathring{a}B\sqrt{I})$ gave lines approaching linearity with slopes of -6 for values of $\mathring{a}$ between 6.0 and 6.5. When $\mathring{a}$ was set equal to 6.3 and eq. 6 was solved using the stability quotients obtained at each ionic strength, K^0 (average) was found to be $1.7 \pm 0.1 \times 10^5$.

Table II lists typical data obtained for systems containing mercury(II), iron(III), and sodium azide. Figure 2 shows plots of the variable functions of eq. 5 for each ionic strength. For each point, the concentration of FeN_3^{2+} was calculated from A, the absorbance of the solution at 460 mμ, and from the molar extinction coefficient of the complex at that wave length. The free azide ion concentration was then calculated from the values of Q, uncorrected for hydrolysis of Fe^{3+}. Since ionic strength and pH were the same in these studies as in those of the ferric azide complex alone, the correction factors necessary to account for formation of $FeOH^{2+}$ cancel out and are not needed for these determinations.

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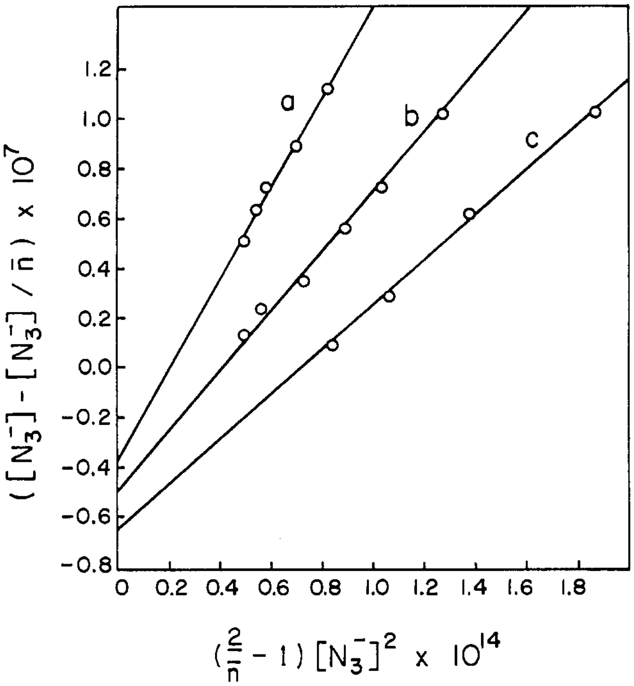

Figure 2.—Plots of $\bar{n}$ functions pertaining to the determination of the stability quotients of mercury(II) azide at ionic strengths 0.05 (a), 0.15 (b), and 0.25 (c).

From the slopes and intercepts of plots such as those shown in Figure 2, it is possible to determine Q_1 and Q_2 for $Hg(N_3)_2$ in aqueous solution. The results are: $Q_1 = 3.0 \pm 0.6 \times 10^7$, $Q_2 = 1.8 \pm 0.2 \times 10^7$ at ionic strength 0.05; $Q_1 = 2.0 \pm 0.4 \times 10^7$, $Q_2 = 1.2 \pm 0.2 \times 10^7$ at ionic strength 0.15; $Q_1 = 1.4 \pm 0.3 \times 10^7$, $Q_2 = 9.4 \pm 1.2 \times 10^6$ at ionic strength 0.25. The uncertainties listed are experimental deviations observed in several different experiments at each ionic strength. Plots of log Q_1 and log Q_2 *vs.* $\sqrt{I}$ give stability constants at zero ionic strength of: $K_1^0 = 5.6 \pm 1.1 \times 10^7$ and $K_2^0 = 3.1 \pm 0.4 \times 10^7$. More rigorous methods of extrapolation to zero ionic strength seemed unwarranted considering the probable limits of accuracy of the results as obtained by the method described.

It is of interest to compare the stability quotients of aqueous mercuric azide with stability quotients of the mercuric halides and other "pseudo-halides." The following published values[13] are listed in order of increasing magnitude: $HgCl_2$, $Q_1 = 5.5 \times 10^6$, $Q_2 = 3.0 \times 10^6$ (ionic strength 0.50, 25°, perchlorate media); $HgBr_2$, $Q_1 = 1.1 \times 10^9$, $Q_2 = 1.9 \times 10^8$ (ionic strength 0.50, 25°, perchlorate media); $Hg(SCN)_2$, $Q_1Q_2 \cong 3 \times 10^{17}$ (varied media, 25°); HgI_2, $Q_1 = 7.4 \times 10^{12}$, $Q_2 = 8.9 \times 10^{10}$ (ionic strength 0.50, 25°, perchlorate media); $Hg(CN)_2$, $Q_1 = 1 \times 10^{18}$, $Q_2 = 5 \times 10^{16}$ (ionic strength 0.10, 25°, nitrate media). Thus, it would seem that the azide ion with respect to its tendency to form HgX^+ and HgX_2 species in aqueous solution may be placed in the following series, where derivatives of CN^- are the most stable: $Cl^- < N_3^- < Br^- < SCN^- < I^- < CN^-$. The values which are available for formation constants for azido complexes make it clear that the above order is not necessarily a general one. For example, the FeN_3^{2+} ion is far more stable than either $FeCl^{2+}$ or $FeBr^{2+}$, whereas the formation constant for $CuCl^+$ is probably greater than that for CuN_3^+.[13]

CONTRIBUTION FROM CALLERY CHEMICAL COMPANY,
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Raman and Infrared Spectra of Nitronium Perchlorate

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The Raman spectrum of crystalline nitronium perchlorate exhibits ten well-resolved lines plus an additional tentative line appearing as a weak shoulder. The infrared spectrum, with sodium chloride optics, contains moderately intense absorptions at 940 and 2300 cm.$^{-1}$ and a strong broad absorption in the region of 1100 cm.$^{-1}$ which shows some tendency to resolve into three peaks. The spectra have been interpreted in terms of structural features shown by X-ray structure data. In addition, an interpretation is given correlating the bending mode of the nitronium ion with cation–anion interaction in crystalline nitronium salts.

Introduction

Nitronium perchlorate has classically been considered to be an ionic compound, with discrete nitronium ions and perchlorate ions. Evidence of its ionic character is well documented in the literature. Infrared data[2a] and Raman spectra[2b] are generally what should be expected of a linear NO_2^+ ion isoelectronic with CO_2 and a tetrahedral ClO_4^- ion. We have obtained a more highly resolved Raman spectrum of nitronium perchlorate which cannot be interpreted using a model of isolated linear nitronium ions and isolated tetrahedral perchlorate ions. Our infrared data and those of earlier workers[2a] are generally consistent with one another. The spectral data for solid nitro-

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