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COMPLEXATION OF $\mathrm{Bi^{III}}$ BY NITROGEN DONOR LIGANDS. A POLAROGRAPHIC STUDY

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Abstract—Differential pulse polarography was used to determine the formation constants of $\mathrm{Bi^{3+}}$ at ionic strength 0.5 and 25°C with the ligands DIEN (1,4,7-triazaheptane), TETREN (1,4,7,10,13-pentaazatridecane), DPA [bis(2-pyridyl)amine], AMPY [2-(aminomethyl)pyridine], and THPED [N,N,N′,N′-tetrakis(2-hydroxypropyl)-1,2-diaminoethane]. The equilibria between $\mathrm{Bi^{3+}}$ and these ligands were mostly established slowly on the polarographic timescale, so that separate peaks occurred in the differential pulse polarograms for the free metal ion and complexes, simplifying calculation of the formation constants. Values obtained for $\mathrm{Bi^{3+}}$ were: DIEN, $\log K_1 = 17.4$; $\log K(\mathrm{ML+H = MLH}) = 3.9$; $\log K(\mathrm{ML+OH = MLOH}) = 8.1$; TETREN, $\log K_1 = 23.9$; $\log K(\mathrm{ML+OH = MLOH}) = 6.9$; AMPY, $\log K_1 = 9.6$; THPED, $\log K_1 = 12.0$; $\log K(\mathrm{ML+OH = MLOH}) = 12.0$; DPA, $\log K_1 = 9.0$, $\log K_2 = 7.4$. These results are shown to be reasonable in terms of the formation constant $\log K_1(\mathrm{NH_3}) = 5.0$ for $\mathrm{Bi^{3+}}$ predicted by a dual basicity equation developed previously. A good linear free energy relationship between $\log K_1$ values for $\mathrm{Bi^{III}}$ complexes and $\log K_1$ for analogous complexes of the isoelectronic $\mathrm{Pb^{II}}$ ion was found, which may be useful in predicting $\mathrm{Bi^{III}}$ solution chemistry.

The large number of formation constants reported for amine ligands[1] has focused on a few metal ions, which are $\mathrm{Cu^{II}}$, $\mathrm{Ni^{II}}$, $\mathrm{Co^{II}}$, $\mathrm{Zn^{II}}$, $\mathrm{Cd^{II}}$, $\mathrm{Ag^{I}}$, $\mathrm{Hg^{II}}$ and $\mathrm{Pb^{II}}$. This largely reflects the difficulty of studying amine complexes of other metal ions by glass electrode techniques, rather than intrinsic interest. Solution chemistry of neglected metal ions such as $\mathrm{In^{III}}$, $\mathrm{Ga^{III}}$, $\mathrm{Bi^{III}}$, $\mathrm{Gd^{III}}$ and $\mathrm{Y^{III}}$ is relevant[2] in biomedical applications in radiography,[3] positron emission tomography,[4] magnetic resonance imaging[5] and cancer therapy,[6] apart from its intrinsic theoretical interest.

Bismuth, as $^{212}\mathrm{Bi}$, shows potential in cancer therapy,[6] but not much is known[1] of its solution chemistry to assist in ligand design.[2] In fact, very little is known about the chemistry of $\mathrm{Bi^{III}}$ in general. In the seven volume *Comprehensive Coordination Chemistry*,[7] bismuth receives a mere 15 pages, compared to over 100 for copper. Recently, Rogers and coworkers[8,9] have determined crystal structures of complexes of $\mathrm{Bi^{III}}$ with polyethylene glycols, and structures of complexes of $\mathrm{Bi^{3+}}$ with crown ethers have been reported.[8,10,11] However, almost nothing is known about complexes of $\mathrm{Bi^{3+}}$ with nitrogen donor ligands. What affinity does $\mathrm{Bi^{III}}$ have for polyamine ligands? That $\mathrm{Bi^{III}}$ may have high affinity for the saturated nitrogen donor is suggested by two types of prediction. Firstly, an empirical model,[12] similar to the 'E and C' approach of Drago,[13] allows prediction of $\log K_1(\mathrm{NH_3}) = 5.0$ for $\mathrm{Bi^{III}}$. A second approach[14] that allows estimation of $\log K_1(\mathrm{NH_3})$ for metal ions from the $\log K_1$ values of ligands such as EDTA (see Fig. 1 for key to ligands) that contain nitrogen donors, also yields $\log K_1(\mathrm{NH_3}) = 5.0$ for $\mathrm{Bi^{III}}$. This can be contrasted with $\mathrm{Cu^{II}}$, which has[1] $\log K_1(\mathrm{NH_3}) = 4.1$, and which has a very extensive chemistry with nitrogen donor ligands.

The high acidity[1] of $\mathrm{Bi^{III}}$, with log

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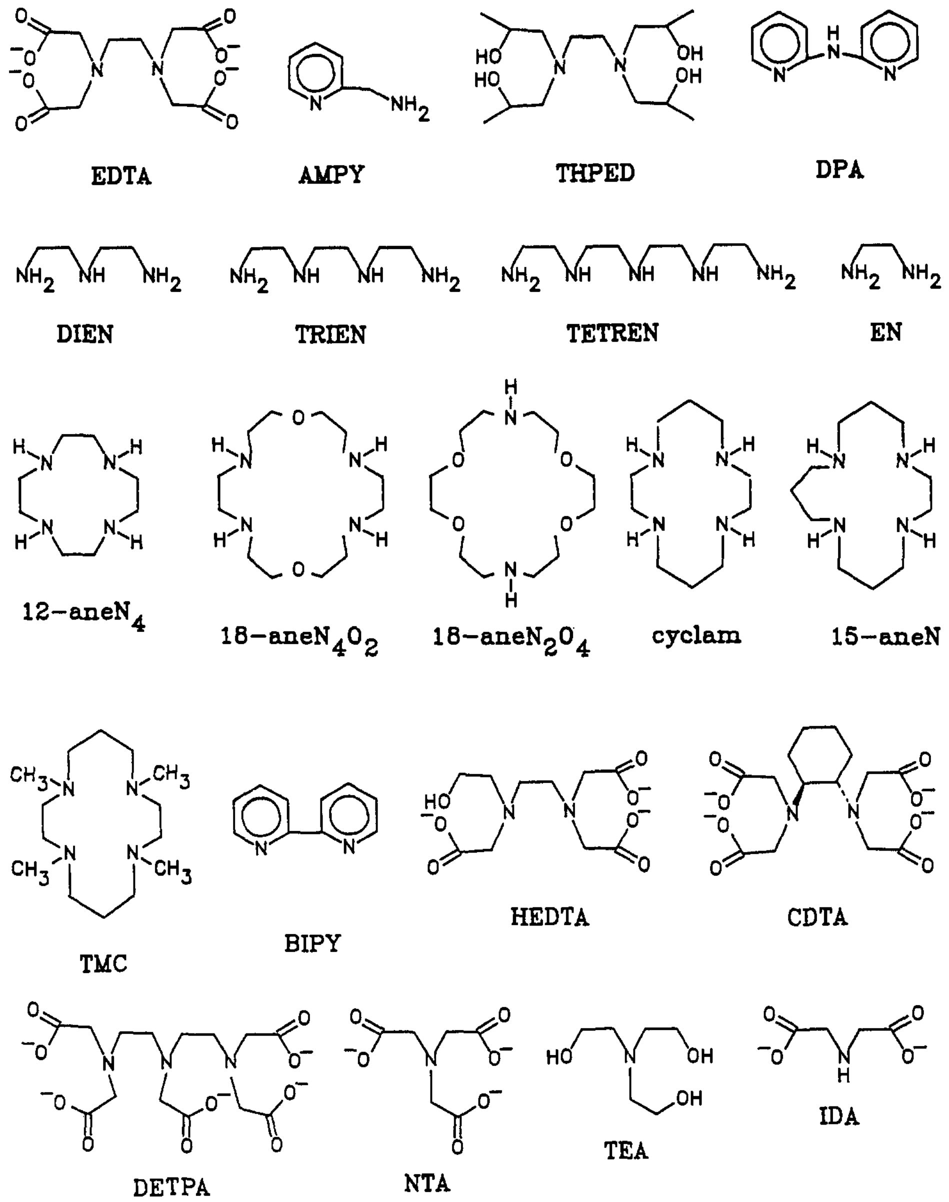

Fig. 1. Ligands discussed in this paper.

$K_1(OH^-) = 12.36$ (ionic strength 0.5) and K_{SO} for $Bi(OH)_3(s)$ that we estimate here as at most 10^{-40}, means that Bi^{III} remains in solution only at acid concentrations of 0.5 M and above, and low Bi^{3+} concentrations. Any ligand that forms a stable complex with Bi^{III} must be able to do so well below pH 2, which eliminates glass electrodes for determining stability constants. Polarography has not been widely used in stability constant studies. Inczédy[15] has pointed out a useful aspect of polarography. Where equilibration of the metal ion with the ligand is slower than the rate of reduction of the complex at the mercury electrode, separate peaks are obtained for the free metal ion and its complexes, greatly simplifying analysis of speciation. Polarography needs careful interpretation, which accounts for some less reliable formation constants reported by this technique. Equilibria that involve protonation or deprotonation of complex species to give MLH or MLOH type species from ML species are often fast. A single peak representing the concentration of one or more species is observed, which shifts to more negative potentials as free ligand concentration rises. If the possibility of a single peak representing more than one species is not recognized, errors of interpretation can arise.

For acidic metal ions such as Bi^{III} polarography has particular advantages. It is well suited to studies in the strong acid needed to suppress hydrolysis of acidic metal ions, and can easily be used at low metal ion concentrations of 10^{-4} to 10^{-6} M, so limiting hydroxide precipitation. Polarography is used here to determine the formation constants of the amines DPA [bis(2-pyridyl)amine], AMPY [2-(aminomethyl)pyridine], THPED (N,N,N′,N′-tetrakis(2-hydroxypropyl)-1,2-diaminoethane], DIEN (1,4,7-triazaheptane) and TETREN (1,4,7,10,13-pentaazatridecane) with Bi^{III}. Various theoretical approaches[12,14] allow for prediction of the formation constants for Bi^{III} with these ligands. This study, and future studies to be reported in this area, thus also become a test of theories of complex formation proposed[2,12,14] earlier, in addition to opening up a largely unexplored area of chemistry.

EXPERIMENTAL

Materials

The free ligands DPA, AMPY, THPED, DIEN and TETREN were obtained from Aldrich, and used as received. Stock solutions approximately 0.01 M in free ligand in 0.5 M HNO_3, were prepared, and used with the stock solution of bismuth, which was 0.001 M $Bi(NO_3)_3$ in 0.5 M HNO_3, to make up solutions used in the polarography. The pH values of the solutions in the cell were adjusted upwards with a solution of, typically, 0.5 M NaOH to get to about pH 2, and then 0.1 M NaOH in 0.4 M $NaNO_3$ to get to higher pH values.

Instrumentation

Polarograms were recorded on a Metrohm 626 Polarecord fitted with a 626 VA stand in differential pulse mode. A multi-mode electrode (Metrohm) was employed as working electrode, and used in the dropping mercury electrode mode with a drop time of 1 s and a pulse amplitude of 50 mV. Experiments were carried out in a three-electrode system with a saturated calomel electrode and a glassy carbon electrode (both Metrohm) used as reference and auxiliary electrodes respectively. The pH of the solutions was measured to within 0.002 pH units with a PHI 72 pH meter (Beckman). The temperature of the cell was controlled to 25.0 ± 0.1°C.

Polarography

In a typical run, the cell would contain Bi^{3+} (5×10^{-5} to 5×10^{-6} M) with ligand added to give ligand : bismuth ratios from 1 : 1 to 2200 : 1, all in 0.5 M HNO_3. For each ligand, a minimum of three widely differing ligand : bismuth ratios was used to aid in establishing the correct species model. After recording a polarogram, the pH of the solution would be adjusted upwards in steps of about 0.1–0.2 pH units, by addition of NaOH solution from a microburette graduated to 0.01 cm^3, and a new polarogram recorded. For each ligand with Bi^{III}, between 10 and 20 polarograms were obtained at a range of pH values for each different ligand : metal ratio. Polarograms of the ligand alone as a function of pH, to identify any ligand peaks on the polarogram, were also run for each ligand.

Calculation of formation constants

A computer program METSPEC[16] was used, which runs on the IBM PC and allows for correction for the hydrolysis of Bi^{3+} to give species such as $BiOH^{2+}$ or $[Bi_6(OH)_{12}]^{6+}$ reported[1] in solutions of Bi^{III}. The program essentially solves the appropriate mass-balance equations, incorporating the estimated formation constants for the Bi^{III}/ligand complexes thought to be present in solution. The predicted species distribution and concentrations were then compared with those indicated by the polarograms, and the formation constants adjusted to give as close a fit as possible. One criterion for which species were present was, as is usual in stability constant studies, which model fitted the peak size data best. A second was the slopes of potentials of the peaks versus pH, which should also agree with the numbers of protons released by the postulated complex species in the reduction process. Types of model tried incorporated species such as BiL, BiL_2, BiL(OH) and BiLH.

RESULTS AND DISCUSSION

In Table 1 are seen the formation constants for the Bi^{3+} complexes of DPA, THPED, AMPY, DIEN and TETREN, determined here, as well as constants for Bi^{3+} with some other amine ligands determined previously.[1,16]

The Bi^{III}/DIEN system

This system is discussed in some detail to illustrate how the variation of the polarograms as a function of pH is analysed. As discussed above, slow and fast polarographic behaviour can be observed for Bi^{III} complexes. Our experience[16] shows that when two or more Bi—N bonds are formed in complex formation, then slow polarographic behaviour usually occurs, with separate peaks for different species. Equilibria involving deprotonation of a coordinated water molecule are fast, with single peaks shifting according to the Nernst equation. Deprotonation of $BiLH^{4+}$ species

Table 1. Formation constants for Bi^{III} with some amine ligands[a]

Ligand[b]	Equilibrium	log *K*	Ref.
OH^-	$H^+ + OH^- = H_2O$	13.74	1
	$Bi^{3+} + OH^- = Bi(OH)^{2+}$	12.36[c]	1
	$Bi^{3+} + 3OH^- = Bi(OH)_3$	31.9[c]	1
	$Bi^{3+} + 4OH^- = Bi(OH)_4^-$	32.8[c]	1
	$6Bi^{3+} + 12OH^- = [Bi_6(OH)_{12}]^{6+}$	164.95[c]	1
AMPY	$L + H^+ = LH^+$	8.74	1
	$LH^+ + H^+ = LH_2^{2+}$	2.25	1
	$Bi^{3+} + L = BiL^{3+}$	9.6(1)	this work
THPED	$L + H^+ = LH^+$	8.84	1
	$LH^+ + H^+ = LH_2^{2+}$	4.35	1
	$Bi^{3+} + L = BiL^{3+}$	12.0(1)	this work
	$BiL^{3+} + OH^- = BiL(OH)^{2+}$	12.0(1)	this work
DIEN	$L + H^+ = LH^+$	9.88	1
	$LH^+ + H^+ = LH_2^{2+}$	9.09	1
	$LH_2^{2+} + H^+ = LH_3^{3+}$	4.47	1
	$Bi^{3+} + L = BiL^{3+}$	17.4(1)	this work
	$BiL^{3+} + OH^- = BiL(OH)^{2+}$	8.1(1)	this work
	$BiL^{3+} + H^+ = BiLH^{4+}$	3.9(1)	this work
TETREN	$L + H^+ = LH^+$	9.70	1
	$LH^+ + H^+ = LH_2^{2+}$	9.14	1
	$LH_2^{2+} + H^+ = LH_3^{3+}$	8.05	1
	$LH_3^{3+} + H^+ = LH_4^{4+}$	4.70	1
	$LH_4^{4+} + H^+ = LH_5^{5+}$	2.97	1
	$Bi^{3+} + L = BiL^{3+}$	23.9(1)	this work
	$BiL^{3+} + OH^- = BiL(OH)^{2+}$	6.9(1)	this work
DPA	$L + H^+ = LH^+$	8.74	1
	$Bi^{3+} + L = BiL^{3+}$	9.0(1)	this work
	$BiL^{3+} + L = BiL_2^{3+}$	7.4(1)	this work
glycine	$Bi^{3+} + L = BiL^{3+}$	10.0(1)	16
	$BiL^{3+} + OH^- = BiL(OH)^{2+}$	9.8(1)	16
bipy	$Bi^{3+} + L = BiL^{3+}$	4.5(1)	16
trien	$Bi^{3+} + L = BiL^{3+}$	21.9(1)	16
	$BiL^{3+} + OH^- = BiL(OH)^{2+}$	8.0(1)	16
	$BiL^{3+} + H^+ = BiLH^{4+}$	3.1(1)	16
triethanol amine	$Bi^{3+} + L = BiL^{3+}$	9.2(1)	16
	$BiL^{3+} + OH^- = BiL(OH)^{2+}$	10.3(1)	16
15-aneN_4	$Bi^{3+} + L = BiL^{3+}$	23.5(1)	16
	$BiL^{3+} + OH^- = BiL(OH)^{2+}$	8.5(1)	16
	$BiL^{3+} + H^+ = BiLH^{4+}$	3.5(1)	16

[a] At 25°C and ionic strength 0.5.

[b] For key to ligand abbreviations, see Fig. 1.

[c] These constants are actually reported at ionic strength 1.0, but have been used as a reasonable approximation, since none have been reported[1] at ionic strength 0.5 for Bi^{3+} hydroxide complexes.

may be fast, except when major reorganization of the complex occurs on deprotonation. Thus deprotonation of $[Bi(15\text{-ane}N_4H)]^{4+}$ is slow[16] suggesting that Bi—N bond formation occurs as part of the deprotonation process.

In Fig. 2 is shown a selection of polarograms for Bi^{3+} with DIEN at different pH values. The overall decrease in peak height apparent in A–H in Fig. 2 is due to dilution of the solution as base was added to raise the pH. It was assumed that species concentration was directly proportional to peak height. Where overlap of a small peak with a large peak was considerable, the height of the smaller peak was estimated by assuming the larger peak to be symmetrical, with the contribution of the larger peak to the observed current at the potential at which the maximum of the smaller peak occurred being subtracted.

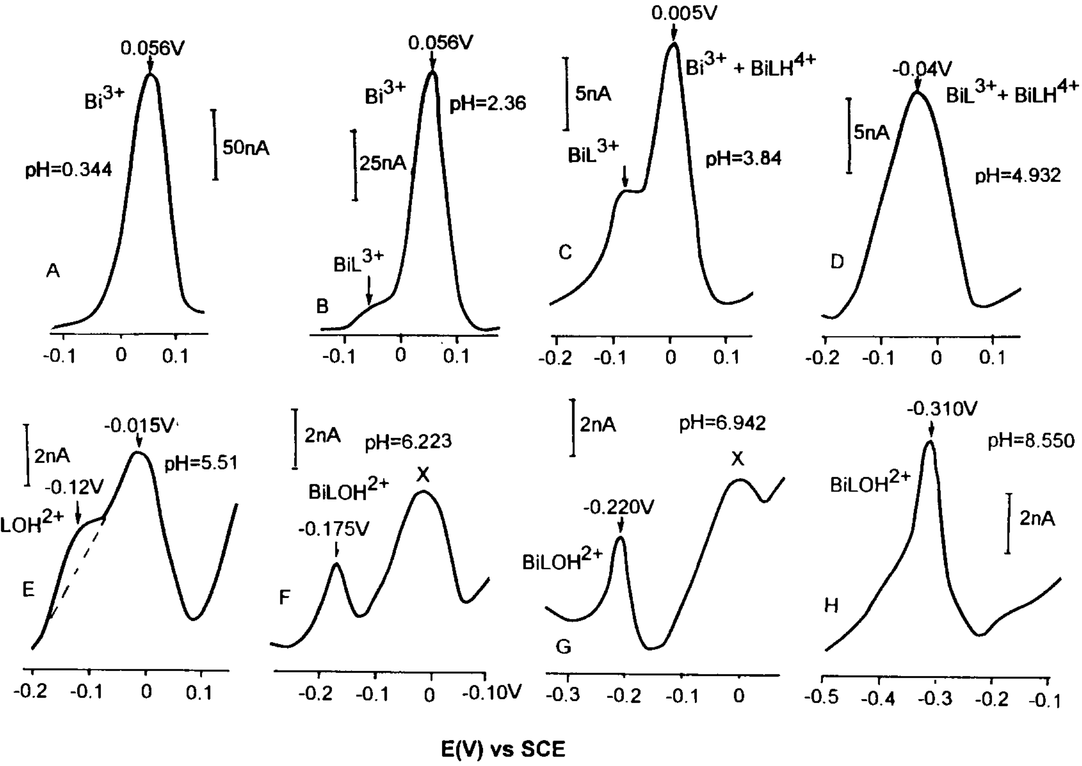

Fig. 2. Differential pulse polarograms (A–H) for the Bi^{3+}/DIEN system, as a function of pH. The vertical scale indicated by a bar on each polarogram corresponds to the current shown. The peaks correspond to the solution species Bi^{3+}, [Bi(DIEN)]$^{3+}$ and [Bi(DIEN)OH]$^{2+}$ as indicated, although, as discussed in the text, the Bi^{3+} peak represents Bi^{III} hydroxide species as well. Thus, above pH 2, the 'Bi^{3+}' peak refers exclusively to a mixture of bismuth hydroxy species. Below pH 4 the 'BiL^{3+}' peak also refers to some BiLH^{4+} present. The concentration of DIEN in solution A is 1.100×10^{-2} M, of Bi^{3+} is 9.57×10^{-6} M, and HNO$_3$ is 0.5018 M. The other polarograms B–H represent this same solution with 0.5 M NaOH or 0.1 M NaOH in 0.4 M NaNO$_3$ added to produce the pH values shown.

The interpretation of Fig. 2 here is that in polarogram A only Bi^{3+} plus hydroxy species are present. The single peak assigned as 'Bi^{3+}' in Fig. 2 is a composite peak, representing a mixture of Bi$_x$(OH)$_y^{(3x-y)+}$ species, which is corrected for by the program METSPEC.[16] In B a small peak due to BiL^{3+} begins to appear, and in C it has increased still further as the pH is raised. At the same time the peak assigned as Bi^{3+} begins to shift to more negative potentials. It appears that the equilibrium between Bi^{3+} and BiLH^{4+} is rapid on the polarographic timescale. A single peak is present for these two Bi^{III} species in solution, which shifts to more negative potential between pH 2.6 and 5.0 with a slope of 39 mV per pH unit (Fig. 3). This slope of potential versus pH is assigned to the following process, which involves two protons in this pH range:

$$\mathrm{BiLH^{3+} + 2H^+ + 3e = Bi(Hg) + LH_3^{3+}}.$$

In order to distinguish it from complex formation, we studied the polarographic behaviour associated with hydrolysis of Bi^{III}. In the absence of ligands, the 'Bi^{3+}' peak does not shift as the pH is raised, even though Bi^{III} hydroxy complexes are forming. Instead the peak becomes smaller, and asymmetrical peaks appear, with no precipitation up to a pH of 6. This is in spite of the fact that a K_{SO} for Bi(OH)$_3$ (s) of about 10^{-40} suggests that at this concentration, precipitation of Bi(OH)$_3$ (s) should occur. The non-precipitation of Bi(OH)$_3$ is due to slow kinetics of precipitation, and on standing, precipitation occurs. The polarograms then present typical flat asymmetrical peaks, which are a useful diagnostic tool where very low bismuth concentrations make the onset of precipitation difficult to detect by eye.

For the Bi^{III}/DIEN system, the Bi^{3+}/BiLH^{4+} peak shifts right up to the point where it merges with the growing peak due to BiL^{3+} in polarogram D. The peak at about -20 mV which is present above pH 5.5, indicated with an X in polarograms F and G, is present in our NaOH solutions, and is clearly an impurity, so should be disregarded. The only important peak above pH 5.5 is that assigned to $BiL(OH)^{2+}$. This assignment is more reasonable than assigning the peak to $Bi(OH)_3$ (aq), since this peak does not appear in this pH range in solutions of Bi^{III} with no ligand added. The equilibration of $Bi(OH)_x$ with LH_2^{2+} species to give $BiL(OH)^{2+}$ appears to be fast. The $BiL(OH)^{2+}$ peak shifts with pH in polarograms E through H with a slope of 59 mV decade^{-1}, as shown in Fig. 3, right up to a pH of 8.55, after which precipitation of $Bi(OH)_3$ (s) occurs. This slope corresponds to a reduction process involving liberation of three protons, which is proposed in this pH range to be:

$$BiL(OH)^{2+} + 3H^{+} + 3e = Bi(Hg) + LH_2^{2+} + H_2O.$$

The formation constants calculated here for the Bi^{III}/DIEN system have been used to calculate a species distribution diagram at a concentration of 5×10^{-6} M Bi^{III} and 1.1×10^{-2} M DIEN as a function of pH, seen in Fig. 4. It is seen that the species distribution in Fig. 4 mirrors quite closely the discussion of the behaviour of the polarograms above. What is of interest is that, with a solubility product of[16] 10^{-40} for $Bi(OH)_3$ (s), which is estimated[16] to be the upper limit for this constant, precipitation is predicted to occur above pH 3.84. What is clear from the polarograms in Fig. 2 is that this is not happening. The species in Fig. 4 above a pH of 3.84 exist in solution for kinetic reasons. The very low concentrations of Bi^{III} hydroxy species at these higher pH values means that the rate of nucleation to form $Bi(OH)_3$ (s) is very low, and precipitation does not occur even though the solubility product has been greatly exceeded. The same occurs in solutions with no ligand added. The concentration of $Bi(OH)_3$ (aq) at pH 3.84 is calculated to be only 8×10^{-8} M, accounting for the slow rate of precipitation. Polarography thus allows for the study of complexes of highly hydrolysis-prone metal ions, even where precipitation is indicated by thermodynamic considerations, because the low total metal ion concentrations that can be used lead to slow rates of precipitation of hydroxides.

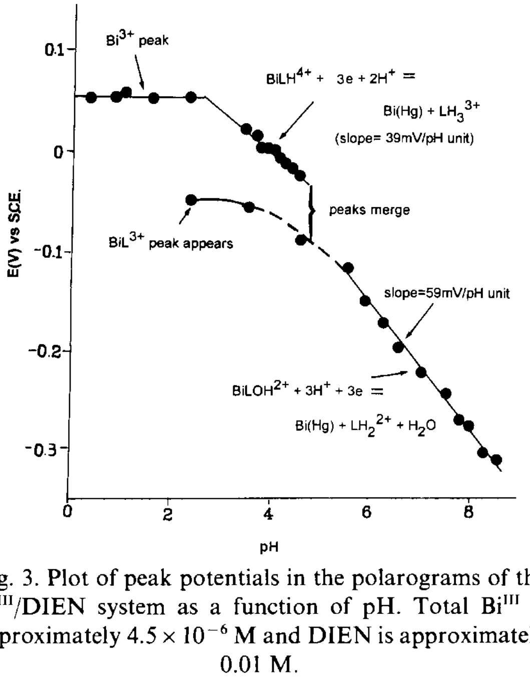

Fig. 3. Plot of peak potentials in the polarograms of the Bi^{III}/DIEN system as a function of pH. Total Bi^{III} is approximately 4.5×10^{-6} M and DIEN is approximately 0.01 M.

Other ligand systems with Bi^{III}

For the other systems studied, hydrolysis was not a problem so that more concentrated Bi^{III} solutions of about 5×10^{-5} M were used. Impurities at the 10^{-6} M level therefore did not interfere, as they did with the DIEN system. The Bi^{III} systems with AMPY and DPA showed the simplest type of behaviour, with the appearance of a single peak due to ML as the pH was raised. No shift in peak potential was observed with rising pH, indicating no formation of MLOH species. For DPA a second peak appeared at higher pH that could be satisfactorily assigned to the BiL_2 species. For the THPED/Bi^{III} system a peak appeared at low pH which then began to shift with a slope of 59 mV per pH unit as the pH was raised. The initial peak was assigned as the BiL complex, and its shift was attributed to a labile BiLOH complex, with the reduction corresponding to $BiL(OH)^{2+} + 3e + 3H^{+} = Bi(Hg) + LH_2^{2+} + H_2O$.

For the TETREN/Bi^{III} system an initial peak appeared, assigned to the BiL complex. This peak began to shift with a slope of 80 mV per pH unit, corresponding to a labile equilibrium between BiL and BiLOH, the latter being formed by loss of a proton from a coordinated water. The reduction process for the BiLOH complex would correspond to $BiL(OH)^{2+} + 3e + 4H^{+} = Bi(Hg) + LH_3^{3+} + H_2O$, accounting for the 80 mV slope.

The formation constants obtained here for Bi^{III} with nitrogen donor ligands can be compared with the predictions[12,14] discussed in the introduction. The 'E and C' type equation[12] derived previously predicts $\log K_1(NH_3) = 5.0$ for Bi^{III}. This can be used in the chelate effect equation[14] (eq. 1) to predict $\log K_1$ for n-dentate polyamines, such as EN ($n = 2$) or TRIEN ($n = 4$).

$$\log K_1\,(\text{polyamine}) = 1.152 \log \beta_n(NH_3) + (n-1) \log 55.5. \quad (1)$$

In eq. (1), the factor 1.152 is the inductive effect factor that corrects for the greater basicity of the nitrogens

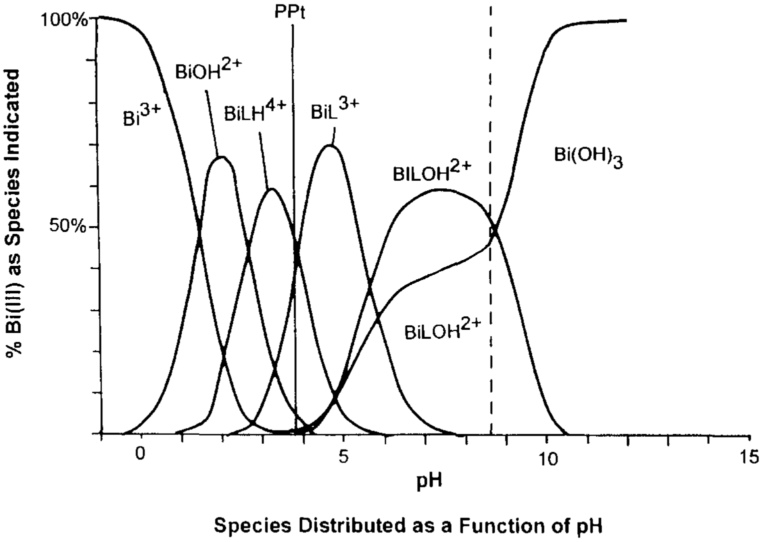

Fig. 4. Species distribution diagram calculated for 5×10^{-6} M total Bi^{III} and 1.1×10^{-2} M DIEN as a function of pH, using the appropriate protonation and formation constants in Table 1. The solid line labelled 'ppt' indicates where from a thermodynamic point of view $Bi(OH)_3$ (s) should precipitate with $\log K_{SO} = -39$ for Bi^{III} hydroxide. The broken line indicates approximately where precipitation does occur. The delay in precipitation of $Bi(OH)_3$ (s) is, as discussed in the text, considered to be a kinetic effect.

of, for example EN, as compared to the nitrogen of NH_3. The $(n-1)$ log 55.5 term is the entropy contribution to the chelate effect. Where only $\log K_1$ for the ammonia complexes of a metal ion is known, $\log \beta_n(NH_3)$ values for use in eq. (1) can be generated from L, the mean stepwise decrease from $\log K_n$ to $\log K_{(n+1)}$. L is about 0.5 for ammines,[14] which allows us to estimate from $\log K_1(NH_3) = 5.0$ and eq. (1) that for Bi^{III} $\log K_1$ for EN will be 12.1, or for TRIEN will be 24.8. The significance of L appears to be steric[18] and it is not unreasonable that L will be larger for trivalent than for divalent metal ions. It is found that the formation constants of the Bi^{III} polyamines are best correlated by eq. (1) using a larger value of $L = 1.0$. The values of $\log K_1$ obtained from eq. (1) for Bi^{III} with $L = 1.0$ are:

ligand:	EN	DIEN	TRIEN	TETREN
$\log K_1$(obs.):	—	17.4	21.9	23.9
$\log K_1$(calc.):	12.1	17.3	21.3	24.2

The value of $\log K_1$ for the polyamine complexes of Bi^{III} is very much in accord with the estimate of $\log K_1(NH_3)$ of 5.0, as can be seen by comparing $\log K_1$(TRIEN) and $\log K_1(NH_3)$ values[1] for other metal ions.

ions:	Mn^{II}	Pb^{II}	Zn^{II}	Ni^{II}	Cu^{II}	Bi^{III}	Hg^{II}	Pd^{II}
$\log K_1$ for NH_3:	1.0	1.6	2.1	2.7	4.1	5.0	8.8	9.6
TRIEN:	4.9	10.4	12.0	13.8	20.1	21.9	24.5	40.2
AMPY:	2.7	4.0	5.3	7.1	9.5	9.4	12.4	—

The $\log K_1$ value for the Bi^{III}/AMPY complex, in comparison with $\log K_1$ for AMPY with other metal ions, is also shown above to be in accordance with the high affinity of Bi^{III} for nitrogen donor ligands. The formation constants of polyamines with Bi^{III} here show that Bi^{III} has one of the highest affinities of any metal ion for polyamine ligands, exceeded only by metal ions such as Pd^{II} and Hg^{II}, and, as future papers will show, the Tl^{III} ion. However, no evidence can be found for NH_3 or EN complexes of Bi^{III} in aqueous solution. The larger polyamines are stabilized by the chelate effect. Even the DIEN complex can exist only with a 2200-fold excess of DIEN ligand, and total Bi^{III} of less than 5×10^{-5} M to prevent precipitation of $Bi(OH)_3$ (s).

In general, it is found that the effect of 2-hydroxypropyl groups on the stability of complexes of THPED as compared to EN is to decrease $\log K_1$ slightly for small metal ions, and increase $\log K_1$ somewhat for large metal ions, as seen in Table 2. The ionic radius of Bi^{III} is[17] 1.03 Å, which makes it moderately large. Thus, for Bi^{III}, $\log K_1$ (THPED) = 12.0 is reasonable compared with $\log K_1$(EN) predicted as 12.1 from eq. (1).

What has been learned so far about the chemistry

Table 2. The effect on complex stability of adding 2-hydroxypropyl groups to ethylenediamine[a]

Metal ion	Ionic radius[b]	log K_1 (EN)	log K_1 (THPED)
Cu^{II}	0.57	10.7	9.8
Ni^{II}	0.69	7.5	7.5
Zn^{II}	0.74	5.9	6.1
Cd^{II}	0.95	5.6	7.8
Bi^{III}	1.03	(12.1)[c]	12.0
La^{III}	1.03	(1.6)[c]	2.9
Pb^{II}	1.18	5.0	7.6

[a] For key to ligand abbreviations see Fig. 1. Formation constants from ref. 1, except for log K_1 for (THPED), which was determined in this work.

[b] Ionic radii (Å) from ref. 17.

[c] For Bi^{III} and La^{III}, log K_1 (EN) was estimated as described in the text, using eq. (1).

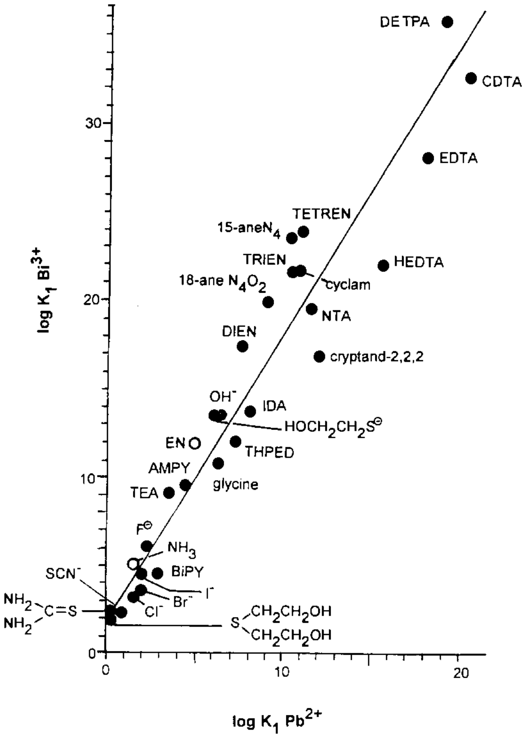

Fig. 5. Relationship between log K_1 for Bi^{III} complexes and log K_1 for the corresponding Pb^{II} complexes. Data from ref. 1, except for Bi^{III} with glycine, BIPY, TRIEN, 15-aneN_4, and triethanolamine (ref. 16), THPED, DIEN, TETREN, DPA, and AMPY (this work), and cyclam, 18-aneN_4O_2, iminodiacetate, and cryptand-2,2,2 (R. D. Hancock, I. Cukrowski, and J. Mashishi, to be published). The open circles are for Bi^{III} complexes where log K_1 has been predicted only theoretically, and not determined experimentally.

of Bi^{III}, apart from its high affinity for nitrogen donor ligands, is the considerable similarity of Bi^{III} to the isoelectronic Pb^{II} ion. In Fig. 5, log K_1 for Bi^{III} complexes has been plotted against log K_1 for the analogous Pb^{II} complexes. Figure 5 indicates a considerable similarity in chemistry between Bi^{III} and Pb^{II}. Very few metal ions show such similarity to each other as seen in Fig. 5—one of the few other examples that is as close is for Ni^{II} and Cu^{II}.

In this paper we have attempted to demonstrate the usefulness of differential pulse polarography as a tool for determining formation constants of the highly acidic metal ion Bi^{III}. In future papers the work will be extended to a wide variety of other ligands with Bi^{III}, and also Ga^{III} and In^{III}. The use of other electrochemical techniques to determine formation constants for Tl^{III}, some of which are remarkably large, will be reported. At the same time it will be demonstrated how well the results obtained agree with the models of complex formation proposed previously.[2,12,14]

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