Electrochemically Generated Copper(II), Tin(II), Bismuth(III) and Zinc(II) Complexes in Dichloromethane containing Tetrabutylammonium Perchlorate, Tetrafluoroborate or Hexafluorophosphate as the Electrolyte

Alan M. Bond,* Andrzej Bobrowski and Fritz Scholz
Department of Chemical and Analytical Sciences, Deakin University, Geelong, Victoria 3217, Australia

Oxidation of M(amalgam) (M = Cu, Sn, Bi or Zn) electrodes under direct current and differential pulse polarographic or cyclic voltammetric conditions in dichloromethane containing 0.2 mol dm^{-3} $[NBu_4][PF_6]$, $[NBu_4][BF_4]$ or $[NBu_4][ClO_4]$ as an electrolyte generates weakly solvated and therefore very reactive Cu^{2+}, Sn^{2+}, Bi^{3+} and Zn^{2+} cations. Since the kinetics of nucleation and precipitation of the usually formed insoluble salts is slow on the voltammetric time-scale, data on the formation of complexes with the electrolyte anions can be obtained. A general order of stability, $[PF_6]^- \ll [BF_4]^- < [ClO_4]^-$, was found for all metals. However, since the Zn (amalgam) $\longrightarrow Zn^{2+}$ oxidation process is completely irreversible, quantitative stability constant data on the complexes formed with Zn^{2+} could not be obtained. From these and other data it is concluded that $[PF_6]^-$ generally seems to represent an example of a very weak ligand for metal cations in relatively non-co-ordinating solvents such as dichloromethane. Mechanical transfer of small amounts of metallic Sn and Pb onto a platinum electrode and use of the method of abrasive stripping voltammetry also enabled stability constant data to be obtained. Data for $[BF_4]^-$ complexes with Sn^{2+} and Pb^{2+} thus obtained are in excellent agreement with those derived from the use of amalgam electrodes.

Most studies concerning the electrochemical determination of stability constants of simple inorganic metal complexes have been undertaken in aqueous solution or other protic solvents,[1,2] although in the last decade a range of data has become available[3] from electrochemical studies in aprotic media. In almost all of these studies the complexes have been soluble in the media in which the electrode process has been examined. However, recently[4–6] it has been shown that reactive metal cations may be generated in a transiently soluble form as a result of electrochemical oxidation of electrodes of Cd, Pb and Tl (amalgam) in solvents such as dichloromethane or benzene where the simple metal salts are normally found to be completely insoluble. This novel procedure enables the complexation[5] or solvation[6] of the electrochemically generated cations to be investigated under circumstances where insolubility of complexes normally precludes this possibility.

In dichloromethane, anions such as $[PF_6]^-$, $[ClO_4]^-$ and $[BF_4]^-$ as well as the solvent itself traditionally have been regarded as non-co-ordinating or weakly co-ordinating.[7–9] However, application of the proposed voltammetric procedure[4–6] applied at the dropping amalgam electrode has suggested that non- or weakly solvated Tl^+, Cd^{2+} and Pb^{2+} cations, generated in dichloromethane *via* electrochemical oxidation of amalgam electrodes, form extremely strong complexes with $[ClO_4]^-$ or $[BF_4]^-$ anions[5] prior to precipitation of their insoluble metal salts.

In the present work, voltammetric studies aimed at elucidating the behaviour of the electrochemically generated Cu^{2+}, Sn^{2+}, Bi^{3+} and Zn^{2+} ions in dichloromethane have been performed in the presence of $[ClO_4]^-$, $[BF_4]^-$ and $[PF_6]^-$ electrolytes to ascertain the strength of complexes formed by these metal cations relative to those formed with Tl^+, Pb^{2+} and Cd^{2+}. In addition to using the oxidation of amalgam electrodes, some data were obtained *via* the use of a new technique called abrasive stripping voltammetry. The total data available from a range of metals now enables the systematic chemical behaviour of this field of investigation to be presented.

Experimental

All polarographic experiments were undertaken with a Princeton Applied Research (PAR) model 174A polarographic analyzer while abrasive stripping voltammetric measurements were performed with a BAS 100 electrochemical analyzer.

The reference electrode was Ag–AgCl (dichloromethane saturated with LiCl and containing 0.1 mol dm^{-3} $[NBu_4][ClO_4]$). However, the potential in the polarographic studies was measured relative to the cobaltocene–cobaltocenium $[Co(cp)_2]$–$[Co(cp)_2]^+$ or ferrocene–ferrocenium $[Fe(cp)_2]$–$[Fe(cp)_2]^+$ couples (cp = cyclopentadienyl) using the following procedure. To all solutions, 10^{-3} mol dm^{-3} $[Fe(cp)_2]$ or $[Co(cp)_2]$ was added at the end of each experiment, and the polarograms for the above reversible couples were recorded. The reversible half-wave potentials, $E^r_{\frac{1}{2}}$, of these couples were used as the internal standard to minimise junction-potential effects. Shifts in $E_{\frac{1}{2}}$ *versus* Ag–AgCl for a given series of experiments are essentially the same as those quoted *versus* $[Co(cp)_2]$–$[Co(cp)_2]^+$, although the absolute value of each potential, is of course considerably different. Ferrocene, which is a more common internal standard,[10] could not be employed in all studies, because for example the tin oxidation process interfered with the ferrocene–ferrocenium process.

The dropping amalgam electrode (DAE), applied as a working electrode, was filled with the amalgam of the metal being investigated. Amalgams (*ca.* 0.5–1 mmol dm^{-3}) of Cu, Sn, Bi and Zn were prepared by dissolving an appropriate amount of weighed metal in mercury. The metal surfaces were cleaned with nitric acid prior to use. The amalgams were kept under an argon atmosphere during the preparation of the electrode and in the course of polarographic studies. The oxidation process associated with each amalgam electrode was studied by direct current (DC), sampled DC (SDC), and differential pulse polarography (DPP) at a DAE with a drop time of 0.5 s, as well as by cyclic voltammetry (CV) at a slowly growing DAE. In the DPP experiments the pulse amplitude was 50 mV. The auxiliary electrode was platinum wire. The oxidation of the amalgam

Table 1 Oxidation half-wave potential and characteristics of reversibility of amalgam electrodes of Cu, Sn and Bi in dichloromethane[a]

		DC polarography (drop time 0.5 s)		Cyclic voltammetry (scan rate 500 mV s^{-1})			Differential-pulse polarography (pulse width 50 ms)	
Metal	Electrolyte[b]	$E_{\frac{1}{2}}$/V	$(E_{\frac{3}{4}} - E_{\frac{1}{4}})$/V	E_p^{ox}/V	ΔE_p/V	$E_{\frac{1}{2}}^{c,d}$	$E_{\frac{1}{2}}^{c,e}$/V	$W_{\frac{1}{2}}$/V
Copper ($Cu \longrightarrow Cu^{2+}$)	$[NBu_4][PF_6]$	1.590	0.025	1.62	0.085	1.580	1.600	0.060
	$[NBu_4][ClO_4]$	1.430	0.040	1.49	0.070	1.440	1.430	0.065
	$[NBu_4][BF_4]$	1.450	0.040	1.50	0.080	1.460	1.460	0.080
Tin ($Sn \longrightarrow Sn^{2+}$)	$[NBu_4][PF_6]$	1.120	0.035	1.170	0.120	1.110	1.120	0.070
	$[NBu_4][ClO_4]$	0.920	0.035	0.960	0.100	0.920	0.910	0.075
	$[NBu_4][BF_4]$	0.955	0.035	0.985	0.080	0.950	0.940	0.075
Bismuth ($Bi \longrightarrow Bi^{3+}$)	$[NBu_4][PF_6]$	1.560	0.050	1.620	0.110	1.560	1.570	0.090
	$[NBu_4][ClO_4]$	1.370	0.035	1.420	0.090	1.370	1.380	0.075
	$[NBu_4][BF_4]$	1.430	0.030	1.480	0.080	1.440	1.440	0.070

[a] $E_{\frac{1}{2}}$ = Half-wave potential, $E_{\frac{3}{4}}$ and $E_{\frac{1}{4}}$ = potentials at three-fourths and one-fourth of wave height, respectively, E_p^{ox} = oxidation peak potential, E_p^{red} = reduction peak potential, ΔE_p = separation in peak potential, and $W_{\frac{1}{2}}$ = width at half-wave height. [b] Electrolyte concentration 0.2 mol dm^{-3}. [c] Potential quoted with respect to $[Co(cp)_2]$–$[Co(cp)_2]^+$ couple which has a value of −0.79 V *vs.* Ag–AgCl. [d] Calculated from the relationship $(E_p^{ox} + E_p^{red})/2$. [e] Calculated from the relationship $(E_p + \Delta E/2)$, where ΔE_p = pulse amplitude.

electrodes in dichloromethane was undertaken in the presence of 0.2 mol dm^{-3} $[NBu_4][ClO_4]$, $[NBu_4][BF_4]$, or $[NBu_4][PF_6]$ electrolyte and in constant concentration (0.2 mol dm^{-3}) solutions of $[NBu_4][PF_6]$–$[NBu_4][ClO_4]$ and $[NBu_4][PF_6]$–$[NBu_4][BF_4]$ mixed electrolytes.

In the abrasive stripping voltammetric studies the working electrode was prepared in the following manner. Initially, a clean surface of the metal was prepared by cutting the metal with a knife. A thick platinum wire was then rubbed over the clean metal surface in order to transfer small amounts of the metal on to the platinum. Cyclic voltammograms obtained in the abrasive stripping method were recorded with a scan rate of 100 mV s^{-1} with the first cycle being used for data evaluation. After each experiment the metal which had been mechanically transferred to the platinum electrode was removed by placing it in a mixture of warm hydrochloric and nitric acids. The electrode was then rinsed with distilled water and dried with tissue paper.

Dichloromethane was dried over 4A molecular sieves and distilled from calcium hydride prior to use[11] under an inert atmosphere of nitrogen keeping the middle 70% fraction. After distillation, dichloromethane was stored over CaH_2. In order to minimise contamination by water, freshly activated alumina was maintained in the voltammetric cell during the course of the experiments. Electrolytes were obtained from Southwestern Analytical Chemicals and dried *in vacuo*. Ferrocene (Riedel-de-Haën), cobaltocene (ICN Biomedicals), and triply distilled mercury (Engelhard Industries) were used as received. All solutions were purged with solvent-saturated argon to remove oxygen prior to electrochemical experiments. Data are reported at 20 ± 1 °C.

Results and Discussion

The oxidation processes of interest in this work occur according to the reactions (1)–(3) and are reversible or quasi-reversible.

$$Cu(Hg) \rightleftharpoons Cu^{2+} + Hg + 2e^- \quad (1)$$

$$Sn(Hg) \rightleftharpoons Sn^{2+} + Hg + 2e^- \quad (2)$$

$$Bi(Hg) \rightleftharpoons Bi^{3+} + Hg + 3e^- \quad (3)$$

In spite of the proximity of the mercury electrode oxidation process, well defined DC, SDC, DPP and CV curves were obtained (Figs. 1–3), provided the metal amalgam concentration was less than 1 mmol dm^{-3}. Above this concentration maxima and erratic drop behaviour were observed. In the case of the zinc (amalgam) electrode the oxidation wave is ill defined and very drawn out. Since the zinc oxidation is completely irreversible ($E_{\frac{3}{4}} - E_{\frac{1}{4}}$ = 120 mV) the half-wave potential may not be used for quantitative calculations of thermodynamic terms. In all cases, insoluble salts are formed on long-term oxidative bulk electrolysis experiments, confirming that precipitation reactions occur on the longer time-scale electrochemical experiments.

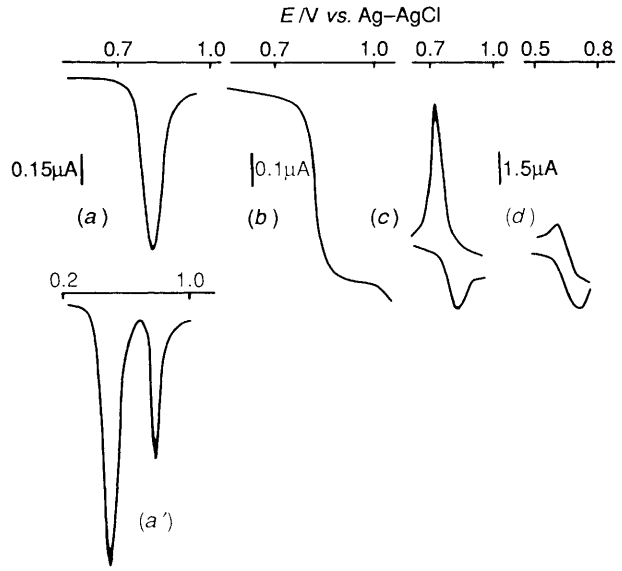

Fig. 1 Voltammetric curves obtained for the oxidation of a copper (amalgam) electrode in dichloromethane containing [(*a*)–(*c*)] 0.2 mol dm^{-3} $[NBu_4][PF_6]$, or [(*d*)] 0.2 mol dm^{-3} $[NBu_4][ClO_4]$. (*a*) DPP polarogram; (*b*) SDC polarogram; (*c*), (*d*) cyclic voltammograms; (*a′*) as for (*a*) but in the presence of 1 × 10^{-3} mol dm^{-3} ferrocene

Table 1 contains half-wave potentials in the different electrolytes examined, as well as an estimate of the degree of reversibility, as assessed by the Tomes criteria ($E_{\frac{3}{4}} - E_{\frac{1}{4}}$), half width of DPP waves, and the difference of oxidation and reduction peak potentials on the CV curves. In all cases the half-wave potential measured with 0.2 mol dm^{-3} $[Bu_4N][PF_6]$ as the electrolyte is considerably more positive than when 0.2 mol dm^{-3} $[NBu_4][ClO_4]$ or $[NBu_4][BF_4]$ is used as the electrolyte. These data suggest that $[PF_6]^-$ forms a much weaker complex with M^{n+} than does $[ClO_4]^-$ or $[BF_4]^-$ as previously observed for Tl^+, Cd^{2+} and Pb^{2+}.[5]

The DC polarographic wave for oxidation of copper is particularly close to that of the mercury electrode dissolution

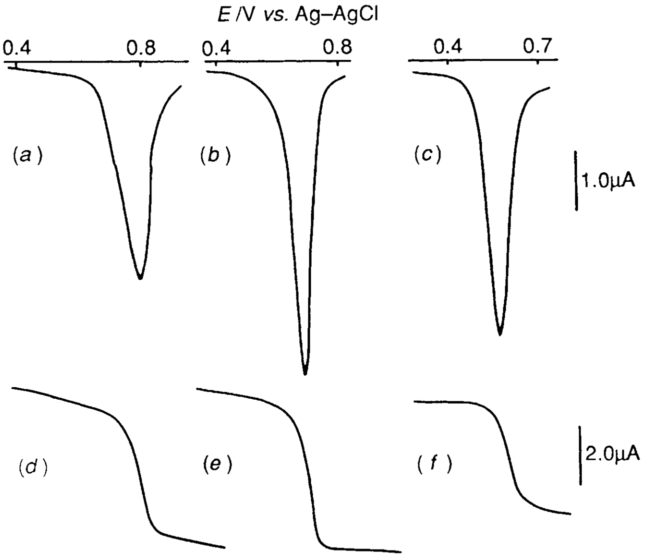

Fig. 2 DP [(*a*)–(*c*)] and SDC [(*d*)–(*f*)] polarograms obtained at a dropping bismuth (amalgam) electrode in dichloromethane containing [(*a*),(*d*)] 0.2 mol dm^{-3} $[NBu_4][PF_6]$, [(*b*),(*e*)] 0.025 mol dm^{-3} $[NBu_4][BF_4]$ and 0.175 mol dm^{-3} $[NBu_4][PF_6]$, and [(*c*),(*f*)] 0.2 mol dm^{-3} $[NBu_4][ClO_4]$

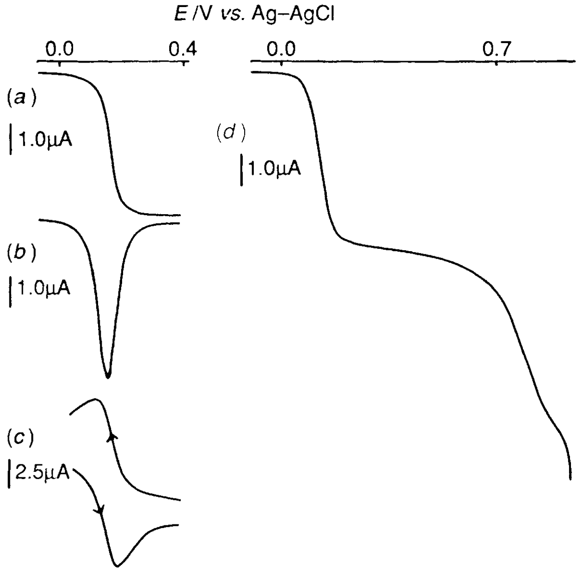

Fig. 3 Voltammetric curves for the oxidation of a tin (amalgam) electrode in dichloromethane containing [(*a*)–(*c*)] 0.2 mol dm^{-3} $[NBu_4][BF_4]$ or [(*d*)] 0.2 mol dm^{-3} $[NBu_4][PF_6]$. (*a*), (*d*) SDC polarograms; (*b*) DPP polarogram; (*c*) cyclic

process but DPP curves are well resolved (Fig. 1). The shape of the reduction peak on the CV curve [Fig. 1(*c*)] indicates precipitation effects are present with 0.2 mol dm^{-3} $[NBu_4][PF_6]$ as the electrolyte. The salt $Cu(PF_6)_2$ is completely insoluble in dichloromethane and can be presumed to precipitate on the time-scale of the 0.5 s drop time of the mercury (amalgam) electrode. However, with $[ClO_4]^-$ or $[BF_4]^-$ as the anion [Fig. 1(*d*)] essentially reversible processes are observed without evidence of precipitation. Presumably the kinetics of formation of insoluble $Cu(ClO_4)_2$ and $Cu(BF_4)_2$ salts is slower than for $Cu(PF_6)_2$. The excellent agreement of $E_{\frac{1}{2}}$ values calculated *via* various methods indicates this is close to the reversible value, $E^r_{\frac{1}{2}}$, required for calculation of stability constants.

The oxidation potential of a bismuth (amalgam) electrode in dichloromethane is similar to that of copper and well defined DC and DPP waves (Fig. 2) and cyclic voltammograms also have been obtained. Polarographic characteristics such as the logarithmic analysis or the slope of a linear plot of $E_{d.a.e.}$ *vs.* $\log(i_d - i)/i$ which equals 48 mV in 0.2 mol dm^{-3} $[NBu_4][PF_6]$ and 35 mV in 0.2 mol dm^{-3} $[NBu_4][BF_4]$ suggest that the electrode process for Bi is not completely reversible. However, the ohmic *iR* drop for the bismuth process is more severe than is the case for Cu and Sn because of the larger current per unit concentration associated with the three- relative to a two-electron process. Reference of potentials to the cobaltocene process at a concentration producing a similar current minimises the *iR* drop effect with respect to the $E_{\frac{1}{2}}$ value and values in Table 1 were calculated this way. Importantly, the excellent agreement between $E_{\frac{1}{2}}$ values calculated in this way from three techniques suggests that the values obtained are closely related to $E^r_{\frac{1}{2}}$ and have thermodynamic significance. In particular the value calculated from the average of the oxidation and reduction peak potentials *via* cyclic voltammetry should only be minimally influenced by kinetic terms arising from slow electron transfer or *iR* drop terms and the values obtained by this technique was used in calculation of stability constant data. In the presence of $[ClO_4]^-$ or $[BF_4]^-$ anions, the half-wave potentials of the bismuth (amalgam) oxidation wave shift towards more negative values relative to that obtained with $[PF_6]^-$ media. Addition of these anions to the solution also appears to increase the rate of the oxidation of Bi although complete reversibility is not achieved with any electrolyte (Fig. 2, Table 1).

The oxidation of a tin (amalgam) electrode in dichloromethane occurs in two steps [Figs. 3(*a*)–(*c*)]. In the first step, Sn(Hg) is oxidised to Sn^{II} at a less positive potential than for oxidation of Cu(Hg) or Bi(Hg). A second oxidation step corresponding to the oxidation of Sn^{II} to Sn^{IV} occurs at 0.5 V more positive potentials than the oxidation of Sn to Sn^{II} [Fig. 3(*d*)]. The second oxidation wave is partially masked by oxidation of electrode mercury and is completely irreversible.

The shift of the half-wave potential towards more negative values as the $[ClO_4]^-$ or $[BF_4]^-$ anion concentration is increased, while keeping the total ionic strength nominally constant at 0.2 mol dm^{-3} with $[PF_6]^-$, is consistent with the formation of very strong perchlorate or tetrafluoroborate complexes of Cu^{2+}, Bi^{3+}, Sn^{2+} and Zn^{2+} as is the case of Tl^+, Cd^{2+} and Pb^{2+}.[5] Data for zinc were not considered quantitatively, because the process is fully irreversible.

It is proposed that the overall oxidation of the metal amalgam and complexation reactions of its cations consists of a number of elementary steps. The first step involves removal of the mercury sheath.[12] The second step is the metal-expulsion step (4) followed by solvation by solvent (solv) molecules,

$$M(Hg) \rightleftharpoons M^{n+} + ne^- + Hg \qquad (4)$$

equation (5), and/or co-ordination by other ligands such as

$$M^{n+} + y\text{solv} \rightleftharpoons [M(\text{solv})_y]^{n+} \qquad (5)$$

X^-, equations (6) and (7).

$$M^{n+} + y\text{solv} + gX^- \rightleftharpoons [M(\text{solv})_yX_g]^{(n-g)+} \qquad (6)$$

$$M^{n+} + gX^- \rightleftharpoons [MX_g]^{(n-g)+} \qquad (7)$$

For simplification, the amalgam oxidation process is usually represented only by equations (4) and (7) and the stability constant β_g and composition of the complex formed according to equation (7) may be determined from the Lingane equation (8). In the present case, $[X^-]$ is a $[ClO_4]^-$ or $[BF_4]^-$

$$\Delta E^r_{\frac{1}{2}(\text{complex})} = E^r_{\frac{1}{2}(\text{complex})} - E^r_{\frac{1}{2}(\text{free})} = -(RT/nF \ln \beta_g) - (RT/nF \ln [X^-]^g) \qquad (8)$$

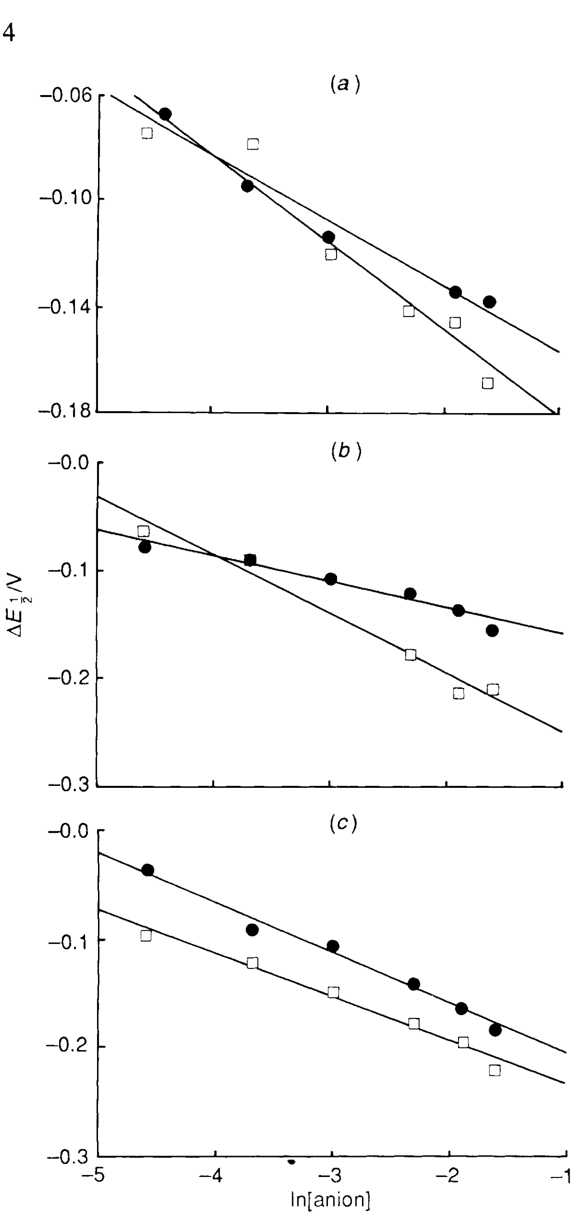

Fig. 4 Plots of the variation of $\Delta E_{\frac{1}{2}} = E_{\frac{1}{2}(\text{complex})} - E_{\frac{1}{2}(\text{free})}$ obtained at an amalgam electrode in dichloromethane with ln[anion] {anion = $[BF_4]^-$ (●) or $[ClO_4]^-$ (□)} for (*a*) copper, (*b*) bismuth and (*c*) tin. Lines drawn are linear least-squares fits of the data

anion, M^{n+} is the electrochemically generated metal cation, *g* is the co-ordination number of the complex, and β_g is the equilibrium constant for the reaction shown in equation (7). From the slope of a plot of $(E_{\frac{1}{2}})_{\text{complex}}$ *vs.* ln $[X^-]$, which should be a straight line, the co-ordination number can be calculated and from the intercept at ln $[X^-] = 0$ the stability constant β_g can be calculated.

The calculation of the co-ordination number and stability constant for a complex *via* use of equation (8) involves the following assumptions. (*i*) The diffusion coefficient of the cation is approximately equal to that of free metal in mercury. Additionally, the diffusion coefficients of free and complexed ions are assumed to be equal. (*ii*) The ion $[PF_6]^-$ is a non-co-ordinating ligand for all the investigated cations. (*iii*) The ionic strength is constant (nominally = 0.2 mol dm^{-3}) in all experiments. (*iv*) The analytical concentration of the ligand is $[X^-]$. (*v*) The metal is oxidised reversibly in the presence and absence of ligand so that $E_{\frac{1}{2}}^{r}$ can be measured directly or else calculated for a non-reversible process. Alternatively, equation (5) is still valid for electrode processes that are not completely reversible provided that the irreversible value of $(\Delta E_{\frac{1}{2}})_{\text{complex}} = (E_{\frac{1}{2}})_{\text{complex}} - (E_{\frac{1}{2}})_{\text{free}}$ is equal to the reversible value of $(\Delta E_{\frac{1}{2}})^{r}$. This requires that non-reversibility of the electrode reaction is due to the charge-transfer step and that the rate constant for the latter is independent of complex formation.[13] (*vi*) The half-wave potential of the oxidation wave is not influenced by changes in junction potential as the concentration and nature of the electrolyte change. (*vii*) The complexes $[MX_g]^{(n-g)+}$ and uncomplexed M^{n+} species are the only species present in solution and they are in rapid equilibrium with each other as represented by equation (7). This implies that ion pairs, triple ions, and oligomers can be neglected and that the electrode process is not perturbed by reactions such as adsorption or precipitation. That is, equations (4) and (7) occur at a diffusion-controlled rate, and the rate constant for precipitation k_1 in equation (9) is slower than the electrochemical time-scale.

$$[MX_g]^{(n-g)+} \xrightarrow{k_1} MX_n\downarrow + (g - n)X^- \qquad (9)$$

(*viii*) One particular complex predominates over the ligand concentration range studied and to a good approximation other species can be neglected.

The assumption of equal diffusion coefficients for the free and complexed metal ions appears to be a reasonable approximation. The limiting currents of the DC polarograms for all metals, with the exception of copper, were almost independent of both the complexing electrolyte used and its concentration. For copper the limiting currents varied by 20% on changing from 0.2 mol dm^{-3} $[NBu_4][PF_6]$ to $[NBu_4][ClO_4]$ or $[NBu_4][BF_4]$. However, evidence (see above) is available that precipitation of $Cu(PF_6)_2$ occurs in the $[PF_6]^-$ media and this rather than a change in diffusion coefficients may explain this particular situation.

All data were obtained at a nominal ionic strength of 0.2 mol dm^{-3}. Assuming that the electrolytes are completely dissociated, then the anion concentrations are more than two orders of magnitude higher than the amalgam concentration. Thus, the approximation that the concentration of complexing anion, $[X^-]$, is the analytical concentration is valid. The use of ferrocene–ferrocenium or cobaltocene–cobaltocenium as a reference redox couple allows shifts of potential to be made which are less likely to contain errors due to changes in junction potentials than would those based upon the assumption of a constant potential for the reference electrode. The half-wave potentials $E_{\frac{1}{2}}$, obtained from the three distinctly different techniques of DC polarography (drop time 0.5 s), cyclic voltammetry (scan rate 500 mV s^{-1}), and differential pulse polarography (pulse width 50 ms), having distinctly different time domains are in excellent agreement. If the processes had been completely irreversible this would not have occurred. Furthermore, the cyclic voltammetric calculation based on the average of $(E_p^{ox} + E_p^{red})/2$ minimises errors associated with slow electron transfer or *iR* drop. Finally, systematic errors are likely to be minimised because a $\Delta E_{\frac{1}{2}}$ value is used in calculations. In summary, the use of equation (8) should be valid to a good approximation for the $Cu(Hg) \rightleftharpoons Cu^{2+} + 2e^-$ and the $Sn(Hg) \rightleftharpoons Sn^{2+} + 2e^-$ systems whereas a small degree of uncertainty is attached to the $Bi(Hg) \rightleftharpoons Bi^{3+} + 3e^-$ process.

Finally, it has been previously noted[5] that the nucleation and precipitation reactions may distort polarographic curves.[5,14,15] However, for most of the systems studied in this work complex formation is rapid, and precipitation reactions, which probably occur on the seconds time-scale, do not influence the results of complexation studies under conditions when the amalgam is dilute. Evidence of significant precipitation (adsorption) on the voltammetric time-scale in $[PF_6]^-$ media is found only in the case of the copper oxidation process.

Recognising the limitations placed by the above assumptions, equation (8) was used to determine the co-ordination number and stability constant β_g. Plots of $E_{\frac{1}{2}(\text{complex})} - E_{\frac{1}{2}(\text{free})}$ *vs.* ln [ligand] are shown in Fig. 4(*a*)–(*c*), and in Table 2 the co-ordination numbers and equilibrium (overall stability) constants are collected.

Table 2 Co-ordination numbers[a] and equilibrium constants for complexes of Cu^{2+}, Sn^{2+}, Bi^{3+} and Pb^{2+} with weak ligands

Metal	Anion	Solvent	Co-ordination no. (g)	log β_g	Ref.
Cu^{2+}	$[ClO_4]^-$	CH_2Cl_2	3	7.2 ± 0.4	This work
	$[BF_4]^-$	CH_2Cl_2	2	6.1 ± 0.3	This work
	Cl^-	Water	1	0.09	16
	Br^-	Water	1	−0.08	16
	$[NO_3]^-$	Water	2	−0.06	16
Sn^{2+}	$[ClO_4]^-$	CH_2Cl_2	3[b]	9.3 ± 0.3	This work
	$[BF_4]^-$	CH_2Cl_2	3[b]	8.5 ± 0.2	This work
		CH_2Cl_2	3	9.0 ± 0.5	This work[c]
	Cl^-	Water	4	1.5	16
			3	1.5	16
	Br^-	Water	4	0.4	16
			3	1.2	16
	I^-	Water	6	2.6	16
			4	2.3	16
Bi^{3+}	$[ClO_4]^-$	CH_2Cl_2	6	14.9 ± 0.5	This work
	$[BF_4]^-$	CH_2Cl_2	3	9.4 ± 0.6	This work
	Cl^-	Water	6	6.6	16
			5	6.7	16
	Br^-	Water	6	9.5	16
	I^-	Water	6	18.8	16
	$[NO_3]^-$	Water	4	0.6	16
			3	0.7	16
			2	0.8	16
Pb^{2+}	$[BF_4]^-$	CH_2Cl_2	3	8.3 ± 0.4	This work[c]
		CH_2Cl_2	3[b]	7.5	5

[a] Co-ordination numbers obtained in this work have been rounded off to the nearest integer and have an error of ±0.2. The designated complex is the predominant species over the anion concentration range of 0.001–0.2 mol dm^{-3}. [b] Co-ordination number is four at higher anion concentrations. [c] Data obtained by abrasive stripping voltammetry.

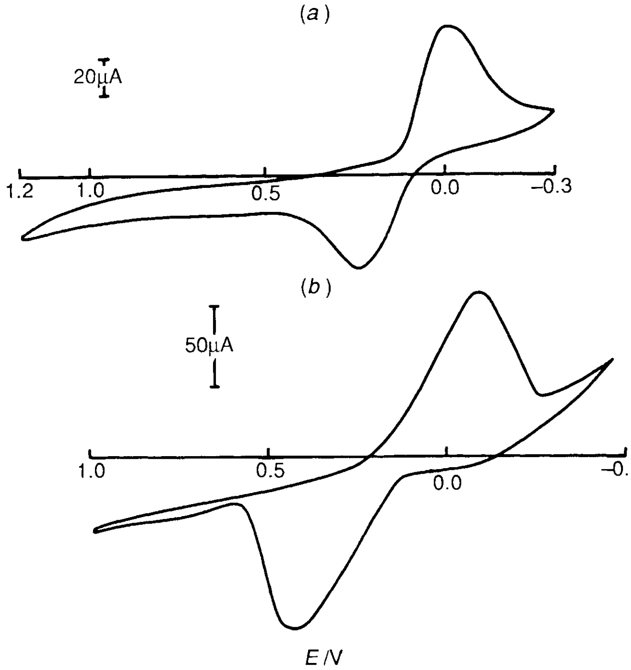

Fig. 5 Abrasive stripping voltammograms: (*a*) for tin in dichloromethane containing 0.1 mol dm^{-3} $[NBu_4][PF_6]$ and 0.1 mol dm^{-3} $[NBu_4][BF_4]$; (*b*) for lead in dichloromethane containing 0.05 mol dm^{-3} $[NBu_4][PF_6]$ and 0.15 mol dm^{-3} $[NBu_4][BF_4]$

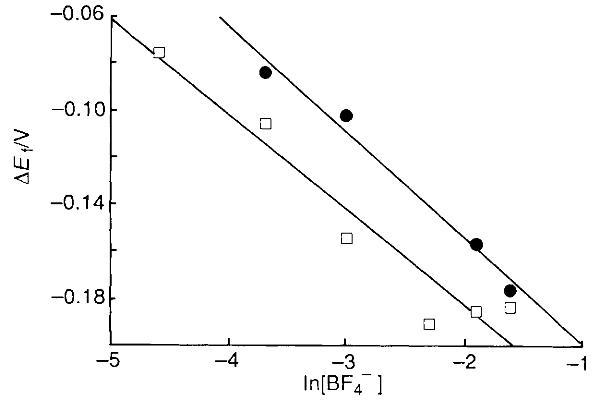

Fig. 6 Plot the variation of $\Delta E_f = E_{f(complex)} - E_{f(free)}$ with $\ln[BF_4^-]$ for tin (□) and lead (●) using the technique of abrasive stripping voltammetry in dichloromethane

As indicated previously,[5] certain small deviations from the reversible model are evident and consequently $E_{\frac{1}{2}}$ does not exactly represent the thermodynamic $E^r_{\frac{1}{2}}$ value, although errors are believed to be small. Unfortunately, other methods are not available to determine comparative values as they demand soluble bulk solutions that cannot be obtained with these systems.

Employing the assumption that $[PF_6]^-$ is a non-co-ordinating ligand leads to the conclusion that the composition of copper complexes formed with $[ClO_4]^-$ and $[BF_4]^-$ ligands is $[Cu(ClO_4)_3]^-$ (log $\beta_3 = 7.2$) and $[Cu(BF_4)_2]$ (log $\beta_2 = 6.1$). Some indirect evidence that indicates the possibility of forming copper(II) perchlorate complexes appears in ref. 17 where the discrepancy between the diffusion coefficients for copper in two different reduction states was tentatively attributed to the interaction between Cu^{2+} and $[ClO_4]^-$ ions.

In the case of tin the data are consistent with a co-ordination number of three at low concentrations and four at higher concentrations of $[ClO_4]^-$ or $[BF_4]^-$ ligands. The data obtained for the complex of bismuth with $[ClO_4]^-$ indicate the formation of $[Bi(ClO_4)_6]^{3-}$ (log $\beta_6 = 14.9$). In this case, the determined co-ordination number $g = 6$ is the same as highest ligand number for complexes of Bi with Cl^-, Br^- and I^- anions.[16] The complex of Bi^{3+} with $[BF_4]^-$ only has a co-ordination number of three and log $\beta_3 = 9.4$.

In order to compare the results with those obtained by means of another voltammetric technique, an attempt was made to find out if it is possible to apply the technique[18,19] of abrasive stripping voltammetry to determine the co-ordination number and stability constant of Sn^{2+} with the $[BF_4]^-$ ligand in dichloromethane. Additionally, the equilibrium constant for complexation of Pb^{2+} with $[BF_4]^-$ was also determined and compared with the value obtained previously[5] with an amalgam electrode. Fig. 5 shows the voltammograms obtained with this method in which small amounts of metal are mechanically transferred to a platinum electrode by rubbing the electrode against the metal and then the transferred metal is oxidised in the usual way. For data evaluation the formal potentials were calculated according to equation (10) where

$$E_f = (E_p^{ox} + E_p^{red})/2 \qquad (10)$$

E_p^{ox} and E_p^{red} are the oxidation and reduction peak potentials respectively. The number of ligands and overall stability constants were calculated from equation (8), in which the polarographic half-wave potential $E^r_{\frac{1}{2}}$ was replaced by the formal potential E_f. The calculations are valid using the same assumptions as in the amalgam method, if $\Delta E_f = E_{f(complex)} - E_{f(free)}$ is equal to $(\Delta E_{\frac{1}{2}})^r$. The co-ordination numbers were determined from plots of ΔE_f *vs.* $\ln[BF_4^-]$. In both investigated systems a linear plot was obtained (Fig. 6). The values obtained for the co-ordination number and stability constant are summarised in Table 2 and compared with results obtained with an

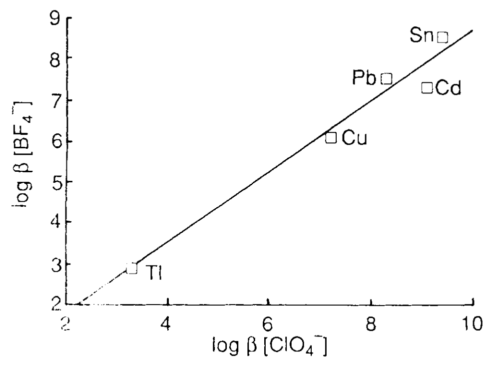

Fig. 7 Correlation between the logarithms of stability constants of metal complexes with $[BF_4]^-$ and $[ClO_4]^-$ for data obtained at a dropping amalgam electrode in dichloromethane. The straight-line plot was obtained from a linear least-squares fit of the data.

amalgam electrode. The data from both techniques are in good agreement, even though the peak separation for the oxidation and reduction peak potentials in the case of abrasive stripping voltammetry is about 200 mV (Fig. 5) suggesting a noticeable deviation from reversible behaviour. The described experiments demonstrate the applicability of abrasive stripping voltammetry for the study of complex formation of metal ions in aprotic solutions provided that the metals do not behave too irreversibly. The reproducibility of the determination of the formal potential E_f is usually poorer than the reproducibility of half-wave potentials $E_{\frac{1}{2}}$ obtained with a DAE. In case of tin the confidence interval for E_f was 7 mV (six determinations).

From the above data it has now been established that Cu^{2+}, Sn^{2+}, Bi^{3+} and probably Zn^{2+} as well as other metals[5] form complexes with $[ClO_4]^-$ and $[BF_4]^-$ in dichloromethane. The strength of the metal complexes formed with $[PF_6]^-$ cannot be determined but must be considerably weaker than those formed with $[BF_4]^-$ or $[ClO_4]^-$. As seen from comparisons presented in Table 2, the complexes of Cu^{2+}, Sn^{2+} and Bi^{3+} in CH_2Cl_2 are apparently significantly stronger than those formed with many other ligands in aqueous solutions.

From stability constant values for Tl^+, Cu^{2+}, Pb^{2+}, Cd^{2+} and Sn^{2+} contained in this and in a previous[5] paper, a reaction series[20,21] of the complexes may be composed, in which the constant structural features are $[ClO_4]^-$ and $[BF_4]^-$ ligands and the central metal ion M^{n+} is changed. As shown in Fig. 7 the two series of complexes of Tl^+, Cu^{2+}, Pb^{2+}, Cd^{2+} and Sn^{2+} with $[ClO_4]^-$ and $[BF_4]^-$ are very well correlated (correlation coefficient = 0.984). Bismuth data are not included in this plot since the vastly different co-ordination numbers in the two electrolytes cause other effects to be dominant.

The data obtained in this work confirm strongly the earlier conclusion that electrochemical oxidation of metals in relatively non-co-ordinating solvents has generated metal cations, which are able to form very strong complexes with $[BF_4]^-$ and $[ClO_4]^-$ which are commonly thought to be 'non-co-ordinating' ligands. The best way of obtaining such cations is by oxidation of their amalgam electrodes but as shown they might also be obtained in some cases directly by metal oxidation using the abrasive stripping voltammetric technique. This latter method is probably prone to a wide variety of mechanisms for the electrode process,[22] but at least for Sn and Pb may provide useful data. The reversibility of a metal ion–metal (amalgam) couple may vary considerably with the solvent,[23] but in dichloromethane, apart from the $Zn^{2+} \longrightarrow Zn(Hg)$ process, reversible or quasi-reversible data have been found. The anomaly of zinc is not understood, although it is conceivable that Zn and/or Zn^{2+} react directly with the solvent and that this is the cause of the irreversibility rather than slow electron transfer. The role of dichloromethane as a solvent may also be important as it has been found to be co-ordinating in some instances.[24,25] Additionally, the order of anion co-ordination which is $[PF_6]^- < [BF_4]^- < [ClO_4]^-$ has now been established for a wide range of metals. This result is in agreement with the observation made by Lever[26] that an electrochemical parameter is available for many ligands and that reversible redox potentials for a series of complexes can be related to each other by a simple increment equation. Recently, Honeychuck and Hersh[27,28] have examined the co-ordination of 'non-co-ordinating' anions to cationic transition-metal complexes and concluded that $[PF_6]^- < [BF_4]^- < [SbF_6]^-$, so that $[PF_6]^-$ is now being established as a relatively weak ligand in several areas of chemistry.

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