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A New Approach to Measurement of the Donor Strength and Co-ordination Chemistry of Various Solvents by Oxidation of Metal Amalgam Electrodes in Dichloromethane

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Electrochemical oxidation of thallium, lead, and cadmium amalgam electrodes in dichloromethane containing 0.2 mol dm^{-3} $[NBu_4][PF_6]$ produces highly activated metal cations. The cations generated in this non-co-ordinating medium react rapidly with added donor solvents (solv) such as dimethyl sulphoxide, dimethylformamide, tetrahydrofuran, methanol, ethanol, and acetonitrile but not benzene to produce solvated metal ions. The kinetics of solvation are more rapid than precipitation of the metal salts which occurs in longer-time-scale bulk electrolysis experiments. The co-ordination number and equilibrium constants have been calculated for many of the solvated metal complexes, and the equilibrium constants compared with the solvent donor strengths. In the case of the dropping thallium amalgam electrode, the oxidation process is a well defined, strictly reversible one-electron step. From the data obtained for the thallium oxidation process, the value of the equilibrium constant, β_1, may be calculated for the reaction $Tl^+ + \text{solv} \xrightleftharpoons{\beta_1} [Tl(\text{solv})]^+$ and correlated with the Gutmann donor number. Measurement of β_1 values calculated in this way is proposed as a simple method of estimating the donor strengths of co-ordinating solvents.

In many inorganic reactions the nature of the solvent is of central importance. Important physical properties of the solvent include the dielectric constant, viscosity, boiling and freezing point. However, one of the most important properties is often the donor ability of the solvent. For this reason a substantial quantity of data is available on the relative donor properties of solvents.[1] There have been numerous methods proposed to measure the donor strength of solvents. However, the Gutmann method has generally found the widest acceptance. This method involves the reaction of a solvent with antimony pentachloride and measurement of the enthalpy of reaction.[2]

Recently we have demonstrated that it is possible to oxidise metal amalgam electrodes electrochemically in dichloromethane and benzene.[3] The product of this reaction is a highly activated soluble metal cation, M^{n+}. Whilst precipitation of the normal metal salt occurs on the synthetic time-scale (controlled-potential electrolysis), the soluble highly active cation is formed on the polarographic and voltammetric time-scales. The highly activated M^{n+} cation forms extremely stable complexes with $[ClO_4]^-$ and $[BF_4]^-$ as ligands, *e.g.* $[Cd(ClO_4)_4]^{2-}$ (log β_4 = 9.1), $[Cd(BF_4)_3]^-$ (log β_3 = 7.3), $[Pb(ClO_4)_3]^-$ (log β_3 = 8.3), $Pb[BF_4]_2$ (log β_2 = 7.5), $Tl[ClO_4]$ (log β_1 = 3.3), and $Tl[BF_4]$ (log β_1 = 2.9).

The ready generation of a highly activated metal cation suggests that a simple method may be available for determining the relative donor strength of co-ordinating solvents. Electrochemical data obtained at amalgam electrodes readily enable $E_{\frac{1}{2}}^{\text{rev}}$ values (reversible half-wave potential) to be determined.[4] This is essentially a measure of the standard redox potential. If a co-ordinating solvent is added to the solution, then the difference in $E_{\frac{1}{2}}^{\text{rev}}$, between that obtained in the presence and the absence of the solvent, provides a direct measure of the free-energy change associated with solvent co-ordination. Both the co-ordination number (p) and the equilibrium constant (ln β) may be obtained from the expression[5] (1) provided only one complex is formed over the ligand (solvent) concentration range and that the ligand is in a considerable excess. It is also assumed that junction-potential effects are minimal on addition of the ligand; D and D^* are the diffusion coefficients of the free and complex cation respectively and other symbols have their usual electrochemical meanings.

$$E_{\frac{1}{2}}^{\text{rev}}(\text{solvent complex}) - E_{\frac{1}{2}}^{\text{rev}}(\text{free}) = \frac{RT}{nF}\ln\frac{D}{D^*} - \frac{RT}{nF}\ln\beta - \frac{RT}{nF}\ln[\text{solvent}]^p \quad (1)$$

In our initial studies on the oxidation of amalgam electrodes in CH_2Cl_2 containing $[NBu_4][PF_6]$ (0.2 mol dm^{-3}) it has been shown that $[PF_6]^-$ ligation provides a convenient reference point for $E_{\frac{1}{2}}^{\text{rev}}$(free)[3] in the sense that $[PF_6]^-$ is a far weaker ligand than $[ClO_4]^-$ or $[BF_4]^-$. It is thus proposed that as a co-ordinating solvent is added to a solution of CH_2Cl_2–$[NBu_4][PF_6]$ large shifts in the metal amalgam oxidation potential will occur and that the value of $E_{\frac{1}{2}}^{\text{rev}}$(solvent complex) − $E_{\frac{1}{2}}^{\text{rev}}$(free) will provide a direct measure of the donor strength of the solvent molecule. In the present study, the electrochemical oxidation of lead, thallium, and cadmium in the form of dropping amalgam electrodes (d.a.e.s) has been examined in the presence of CH_2Cl_2–$[NBu_4][PF_6]$ containing low concentrations (0.01—0.13 mol dm^{-3}) of dimethyl sulphoxide (dmso), dimethylformamide (dmf), acetonitrile (MeCN), tetrahydrofuran (thf), methanol (MeOH), ethanol (EtOH), and benzene. Concentrations of the co-ordinating solvent greater than 0.01 mol dm^{-3} are required to satisfy the condition that the ligand concentration should be in a considerable excess over the concentration of the metal amalgam, which is 5×10^{-4} mol dm^{-3}. The data obtained from these experiments are thus examined with respect to the different metals and with respect to Gutmann donor number to determine whether this experimentally simple method can be used as a measure of the donor ability of various solvents. The proposed method uses reaction with metal ions, whereas the Gutmann method uses reaction with neutral species, thus the two techniques may be expected to be complementary.

Experimental

Voltammetric electrochemical experiments were undertaken using a Princeton Applied Research (PAR) 174A polarographic analyser. Controlled-potential electrolysis (c.p.e.) experiments were performed using a PAR 173 potentiostat and PAR 179 digital coulometer. The reference electrode was Ag–AgCl with dichloromethane saturated with LiCl and containing 0.1 mol dm^3 [NBu_4][ClO_4]. However, potentials from voltammetric studies are reported relative to the cobaltocene–cobaltocenium couple [$Co(cp)_2$]–[$Co(cp)_2$]$^+$ (cp = η-C_5H_5) which was used as an internal standard to minimise junction-potential effects; 10^{-3} mol dm^{-3} [$Co(cp)_2$] was added to all solutions at the end of each experiment and the voltammogram for the above redox couple recorded. 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 values of both potentials are considerably different. Ferrocene, which is a more common internal standard, was not employed[6] as the metal oxidation interfered with the ferrocene–ferrocenium couple. The auxiliary electrode was a platinum wire in the case of the voltammetric studies and platinum gauze separated from the solution by a Vycor frit in the case of c.p.e. Mercury amalgams (*ca.* 0.5 mmol dm^{-3}) of cadmium, lead, and thallium were prepared by dissolving weighed amounts of the respective metal in triply distilled mercury. The metal surfaces were cleaned with nitric acid prior to use. The oxidation of cadmium, lead, and thallium amalgams was examined by d.c. polarography at a d.a.e. (drop time 0.5 s) and by cyclic voltammetry at a slowly growing single amalgam drop. C.p.e. oxidations were carried out using a mercury pool to which a concentrated metal amalgam was slowly added.

Dichloromethane was dried over CaH_2 and distilled prior to use.[7] Tetrabutylammonium hexafluorophosphate, [NBu_4][PF_6], was obtained from South-Western Analytical Chemicals Inc. and dried by dissolving in CH_2Cl_2, stirring over Na_2SO_4, filtering, and evaporating the solution to dryness. The resulting electrolyte was dried *in vacuo*.

The oxidation of the metal amalgam electrodes was examined in CH_2Cl_2 containing 0.2 mol dm^{-3} [NBu_4][PF_6] which was progressively titrated with either dried dmso, dmf, thf, MeOH, EtOH, MeCN, or benzene.[7] The concentration range examined for these solvents was 0.01—0.13 mol dm^{-3}. All reactions were examined at 22 ± 1 °C and the solutions were purged with solvent-saturated argon gas prior to electrochemical experiments.

Cadmium-113 n.m.r. spectra were recorded on a JEOL JNM GX-270 MHz Fourier-transform n.m.r. spectrometer in tubes of 10-mm outside diameter at −60 °C. N.m.r. spectra were referenced to 4.5 mol dm^{-3} $Cd(NO_3)_2$ in D_2O.[8]

Results and Discussion

Figure 1 shows an example of d.c. polarograms at the dropping cadmium amalgam electrode as acetonitrile was added to the

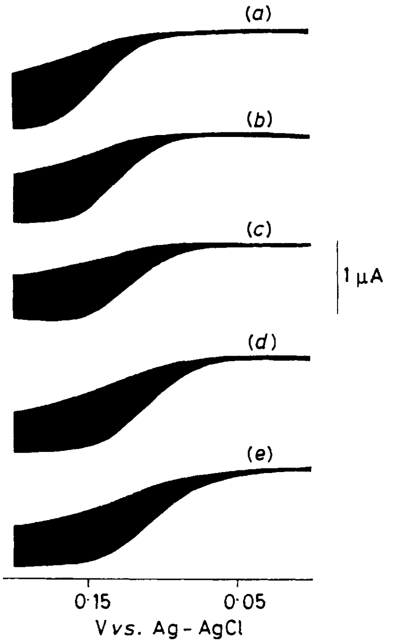

Figure 1. D.c. polarograms obtained at a dropping cadmium amalgam electrode in dichloromethane containing 0.2 mol dm^{-3} [NBu_4][PF_6] and acetonitrile concentrations of (*a*) 0.025, (*b*) 0.050, (*c*) 0.075, (*d*) 0.100, and (*e*) 0.125 mol dm^{-3}

Table. Representative data obtained from the oxidation of cadmium, lead, and thallium amalgam electrodes in CH_2Cl_2 and 0.2 mol dm^{-3} [NBu_4][PF_6]

		D.c. polarography[a]						
Metal	Solvent	$E_{\frac{1}{2}}$[b]	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$[b]	$E_{\frac{1}{2}}$[c]	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$[c]	Co-ordination number, *n*	log β_n	Gutmann donor number
Cadmium[d]	dmso	0.760	0.055	0.590	0.050	6[e]	23.4	29.8
	dmf	0.880	0.055	0.720	0.045	6	17.6	24
	thf	1.050	0.040	1.020	0.040	1	2.4	20
	MeOH	1.085	0.040	1.015	0.040	2[e]	4.2	20
	EtOH	1.025	0.035	0.985	0.035	2	5.0	19
	MeCN	1.055	0.030	1.020	0.035	1[e]	3.4	14.1
Lead[f]	dmso	0.870	0.040	0.730	0.050	5	18.8	29.8
	dmf	0.980	0.030	0.820	0.050	5[e]	16.6	24
	thf	1.185	0.040	1.130	0.040	2	3.5	20
	MeOH	1.170	0.030	1.090	0.040	3	7.1	20
	EtOH	1.140	0.030	1.065	0.035	3	6.2	19
	MeCN	1.185	0.035	1.075	0.035	2[e]	5.0	14.1
Thallium[g]	dmso	0.850	0.055	0.745	0.050	2[e,h]	4.3	29.8
	dmf	0.875	0.060	0.815	0.065	1[e]	3.0	24
	thf	0.905	0.065	0.845	0.065	1	2.2	20
	MeOH	0.895	0.060	0.865	0.065	1	1.4	20
	EtOH	0.865	0.055	0.835	0.055	1	1.7	19
	MeCN	0.875	0.050	0.865	0.055	1[e]	1.0	14.1

[a] Values of $E_{\frac{1}{2}}$ in volts *versus* [$Co(cp)_2$]–[$Co(cp)_2$]$^+$ and $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ in volts. [b] 0.01 mol dm^{-3} solvent. [c] 0.1 mol dm^{-3} solvent. [d] $E_{\frac{1}{2}}$ in CH_2Cl_2–0.2 mol dm^{-3} [NBu_4][PF_6] = 1.07. V[a]. [e] Data suggest more than one species present over the concentration range examined; co-ordination number given appropriate to β_n value quoted. [f] $E_{\frac{1}{2}}$ in CH_2Cl_2–0.2 mol dm^{-3} [NBu_4][PF_6] = 1.17 V[a]. [g] $E_{\frac{1}{2}}$ in CH_2Cl_2–0.2 mol dm^{-3} [NBu_4][PF_6] = 0.91 V[a]. [h] log $\beta_1 \approx 3.8$.

dichloromethane–0.2 mol dm^{-3} [NBu$_4$][PF$_6$] solution. The polarograms are extremely well defined at acetonitrile concentrations in the range 0.01—0.13 mol dm^{-3}. At higher concentrations of acetonitrile or metal (metal amalgam concentration recommended is 0.5 mol dm^{-3}) the d.c. polarograms become erratic and ill defined with maxima. At lower concentrations of solvent the approximation that the ligand concentration is considerably greater than that of the metal is no longer valid, thus equation (1) cannot be used. Data for other metals and solvents are of similar quality.

Figure 1 shows that chemical reversibility is retained throughout the concentration range examined, although as the data in the Table show some of the oxidation processes for cadmium and lead are quasi-reversible in the electrochemical sense when high concentrations of co-ordinating solvents are present. The value of $E_{\frac{1}{2}}$ in the presence of co-ordinating solvent is not equal to the reversible half-wave potential in these situations. The cyclic voltammetric average of the oxidation and reduction peak potentials ($E_p^{ox} + E_p^{red}$)/2 essentially reflects the thermodynamic value and can be used to provide a correction for the kinetic terms. More rigorous correction terms could be included.[9] However, these correction terms are insufficiently large to alter any of the conclusions presented herein. In the particular case of the thallium amalgam electrode, complete electrochemical reversibility was maintained for all measurements. In all calculations presented in this paper, $E_{\frac{1}{2}}$ values obtained at the d.a.e. from d.c. polarograms or cyclic voltammograms were used and assumed to have close to thermodynamic significance.

In order to demonstrate that solvated complexes were formed and not other species, the c.p.e. of a cadmium amalgam pool electrode in CH$_2$Cl$_2$–0.2 mol dm^{-3} [NBu$_4$][BF$_4$] was carried out in the absence and presence of dmf and the product of the electrolysis examined by ^{113}Cd n.m.r. spectroscopy. In the first instance the product was insoluble Cd[BF$_4$]$_2$ and in the second a soluble solvated cadmium(II) complex appeared to be formed since no precipitate resulted. Addition of dmf to solid Cd[BF$_4$]$_2$ prepared by c.p.e. produced a clear solution and ^{113}Cd n.m.r. examination indicated a resonance at −120 p.p.m. Cadmium-

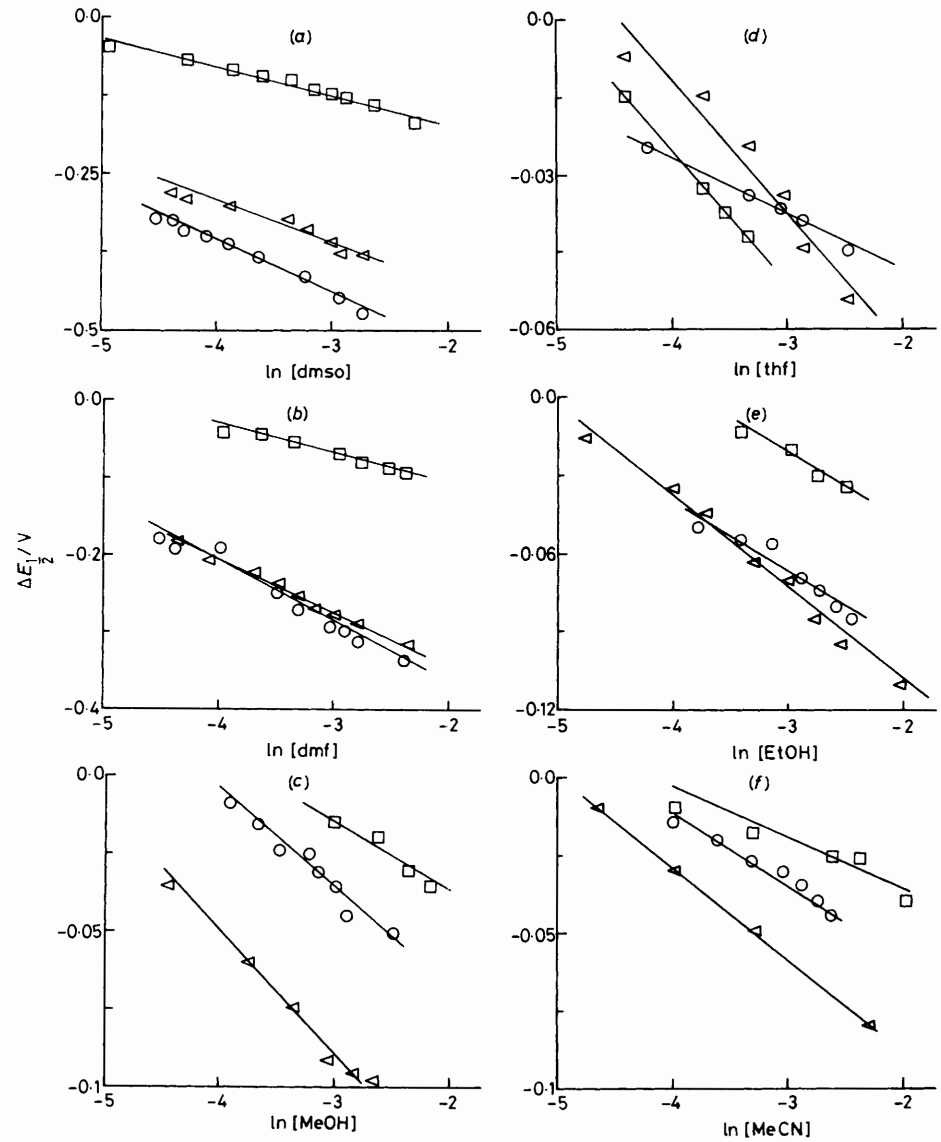

Figure 2. Variation of $\Delta E_{\frac{1}{2}}$ with ln [solvent] for data obtained at cadmium (○), lead (◁), and thallium (□) amalgam electrodes in the presence of (*a*) dmso, (*b*) dmf, (*c*) MeOH, (*d*) thf, (*e*) EtOH, and (*f*) MeCN. Straight-line plots were obtained from linear least-squares fits of the data

113 n.m.r. spectroscopy on the electrolysis product in the presence of dmf showed a resonance at −115 p.p.m. This suggests that the products were virtually identical with chemical shift differences being attributed to ionic strength effects.[10] This result clearly established the fact that cadmium ions co-ordinated by solvent species are formed on the c.p.e. time-scale. In order to establish that chloride ions leaking from the reference electrode were not responsible for the shifts in $E_{\frac{1}{2}}$, electrochemical oxidations of amalgam electrode were carried out in CH_2Cl_2 saturated with LiCl. Responses totally different to those reported in the absence of chloride were observed, thus establishing that the shifts in potential were not due to ligation by chloride ions.

Figure 2 includes a plot of $\Delta E_{\frac{1}{2}}$ [= $E_{\frac{1}{2}}$(solvent) − $E_{\frac{1}{2}}$(free)] *versus* ln [solvent] for data obtained with the thallium amalgam electrode. Use of equation (1) and assuming that the diffusion coefficients are equal for the 'free' and solvent-complexed metal ions enables the co-ordination number p and the equilibrium constant β to be evaluated. The diffusion-controlled limiting current is almost independent of the added solvent concentration suggesting that the diffusion coefficients of the free and complexed metal ion are in fact similar in magnitude. The data for thallium are consistent with the formation of two species, $[Tl(solv)_2]^+$ and $[Tl(solv)]^+$ for dmso and dmf. In contrast, a co-ordination number of one is found for thf, MeOH, and EtOH throughout the solvent concentration range examined and in the case of MeCN the data are consistent with the presence of $[Tl(MeCN)]^+$ and a non-solvated Tl^+ ion. No detectable complex was formed on addition of benzene and data for this solvent are not included in Figure 2. Figure 2 also shows equivalent plots for cadmium and lead respectively and the results, evaluated according to equation (1), are presented in the Table.

With all metals, dmso results in the highest co-ordination number and gives the largest shift in $E_{\frac{1}{2}}$ per unit concentration. Conversely, benzene shows no shift in $E_{\frac{1}{2}}$ with any metal, which is consistent with no complex formation. These results are predicted on the basis of solvating strengths derived from the Gutmann donor number.

It may be anticipated that the equilibrium constant for species having the same co-ordination number would correlate with the Gutmann donor number. Where such data are available this appears to hold.[11] A related correlation, which may readily be applied, is to plot $E_{\frac{1}{2}}$ at the 0.1 mol dm^{-3} solvent concentration *versus* the Gutmann donor number. As shown in Figure 3, a correlation exists for thallium and lead data where the co-ordination numbers are not highly solvent dependent. However when more than one complex is present, the complete equation assuming equal diffusion coefficients is (2) where β_n is

$$E_{\frac{1}{2}}(\text{solvent complex}) - E_{\frac{1}{2}}(\text{free}) = -\frac{RT}{nF}\ln(1 + \beta_1[\text{solv}] + \beta_2[\text{solv}]^2 + \cdots \beta_n[\text{solv}]^n) \quad (2)$$

the equilibrium constant for the nth complex formed and [solv] is the concentration of solvent. Other parameters and approximations are as specified in the description of equation (1). Thus, when more than one complex is present, $\Delta E_{\frac{1}{2}}$ is a complex function of β_n.

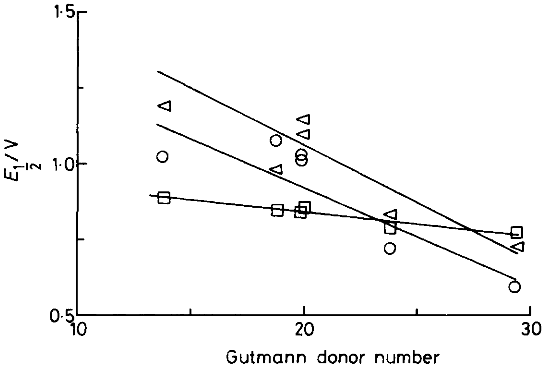

Figure 3. Variation of $E_{\frac{1}{2}}$ {V *versus* $[Co(cp)_2]$–$[Co(cp)_2]^+$} with the Gutmann donor number of the solvent at a solvent concentration of 0.1 mol dm^{-3} for data obtained at cadmium (○), lead (◁), and thallium (□) amalgam electrodes. Straight-line plots were obtained from linear least-squares fits of the data

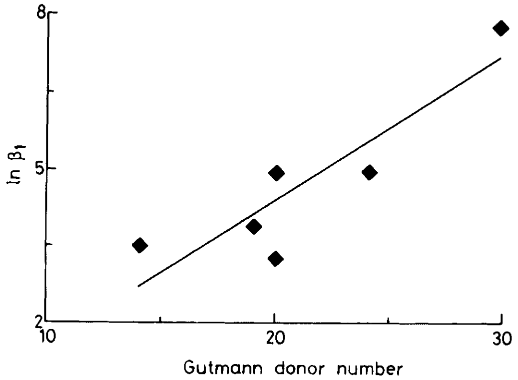

Figure 4. Variation of ln β_1 with Gutmann donor number for data obtained at a thallium amalgam electrode. The straight-line plot was obtained from a linear least-squares fit of the data

More realistically, the donor strength of a solvent (solv) could be expected to correlate with the equilibrium constants [equation (3)]. However, whilst higher-order complexes may reflect

$$M^{n+} + x(\text{solv}) \overset{\beta_n}{\rightleftharpoons} [M(\text{solv})_x]^{n+} \quad (3)$$

the donor strength, they will also reflect statistical, geometric, and steric factors. That is, when more than one ligand is bound, both $E_{\frac{1}{2}}$(solvent) − $E_{\frac{1}{2}}$(free) and $\beta_n(n \geqslant 2)$ may contain terms additional to donor strength. The most likely parameter to correlate with the donating strength is therefore β_1 which is a measure of the stability constant for addition of a single solvent molecule. In the case of the three metal ions examined in this work only the thallium data provide the possibility of calculating β_1. Whilst addition of dmso produces a mixture of $[Tl(dmso)]^+$ and $[Tl(dmso)_2]^+$, the data at low solvent concentration can be used to calculate the equilibrium constant for reaction (4). A similar situation applies to the addition of dmf.

$$Tl^+ + \text{dmso} \rightleftharpoons [Tl(\text{dmso})]^+ \quad (4)$$

Acetonitrile complexes are in general weak for all metals. In the particular case of thallium, a high proportion of unligated Tl^+ exists at the lower end of the concentration range examined. However at the higher concentrations $[Tl(MeCN)]^+$ is formed in significant concentrations and thus data obtained at high acetonitrile concentration can be used to calculate β_1. A plot of ln β_1 for thallium complexes *versus* the Gutmann donor number provides a reasonable correlation as shown in Figure 4. The fact that β_1 is readily measured, and that the thallium electrode process retains complete reversibility in all solvents, also makes this the preferred metal from a theoretical viewpoint. In principle, the cadmium and lead amalgam electrode processes could also be used. However, the formation of higher-order complexes is heavily favoured and calculation of β_1 is precluded, *e.g.* $[Cd(dmso)_6]^{2+}$, $[Cd(dmf)_6]^{2+}$, $[Pb(dmso)_5]^{2+}$, and $[Pb(dmf)_4]^{2+}$ are dominant species in the appropriate solvents.

Alternative electrochemical methods for measuring donor strength have concentrated on measuring the reduction of a metal complex in a neat solution of the donor solvent.[11] Disadvantages of this method are that the metal ions are usually co-ordinated by more than one solvent molecule so $E_{\frac{1}{2}}$ contains more than just donor-strength terms and the data are restricted to situations where the metal salts are soluble.

Conclusions

The data presented herein show that the oxidation of a thallium amalgam electrode and the subsequent co-ordination of the electrochemically generated thallium cation by a single solvent molecule may be used as a measure of the donor strength of that solvent molecule. The Gutmann donor number uses ΔH values as a measure of solvent donor strength. In contrast, the amalgam electrode method enables ΔG values to be derived. Since $\Delta G = \Delta H - T\Delta S = -RT \ln \beta$ the expected linear correlation of the Gutmann donor number with β_1 is observed at constant temperature and under conditions where ΔS terms, as in the case of formation of $[\mathrm{Tl(solv)}]^+$, are not influenced within a series of measurements by variable statistical and geometric terms.

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