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Electrochemical behaviour of some organotin(IV) compounds by rotating disc voltammetry in non-aqueous solvents

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The electrochemical behaviour of three series of organotin(IV) compounds having the general formula R_ySnX_{4-y} (R = Me, nBu or Ph, $y = 2$ or 3, X = Cl; R = Me or Ph, $y = 3$, X = NO_3, N_3, NCS, NCO, OAc or OH) have been examined in the non-aqueous solvents dimethylformamide and acetonitrile, at rotating disc electrodes of glassy carbon and gold electrodes. The reduction of tin(IV) in the above series gave a single wave and obeyed the Levich plots at both electrodes in the two solvents. The electrode kinetic parameters and half-wave potentials have been determined, and the effect of solvents and substituents on these parameters have been explored.

Keywords: Organotin determination, rotating disc voltammetry, dimethylformamide, acetonitrile

INTRODUCTION

We mentioned in our previous work[1] the extensive applications of organotin compounds. Very few electrochemical studies[1] have been made on the important organotin(IV) compounds in non-aqueous solvents, and to the best of our knowledge there have been no studies involving rotating disc electrodes. A full investigation was therefore undertaken of the voltammetry and cyclic voltammetry at rotating disc electrodes (r.d.e.) of gold (Au) and glassy carbon (GC) in non-aqueous solvents, i.e. dimethylformamide (DMF) and acetonitrile (ACN), including the electrode kinetics and the reaction mechanisms. Cyclic voltammetry was used to check reversibility. Details of its role in calculating kinetic parameters will be reported elsewhere.

EXPERIMENTAL

Chemicals and reagents

Acetonitrile was purified for electrochemical measurements by distillation over phosphorus pentoxide as described by Donnell *et al.*[2] Dimethylformamide was purified as described by the literature.[3]

Organotin(IV) compounds

The compounds Me_4Sn, nBu_3SnCl, Ph_3SnCl and nBu_2SnCl_2 were commercial products (Fluka). The compounds Me_3SnCl and R_2SnCl_2 (R = Me, Ph) were prepared by a standard method.[4,5] The compounds R_3SnX with R = Me or Ph and X = OH, OAc, NO_3, N_3, NCS were prepared from R_3SnCl by reaction with NaOH,[6] AgOAc, $AgNO_3$,[7] NaN_3 and NaNCS,[8] respectively, and R_3SnNCO was made from R_3SnOH and NH_2CONH_2 (urea).[9] All the compounds prepared were purified, and were characterized by their melting points, IR spectra, and ^1H and ^{13}C NMR spectra.[10]

Apparatus

All electrochemical measurements were carried out using a potentiostat (Gerhard Bank Electronik, Model ST72). A type R.B.2 waveform generator, supplied by Chemical Electronics, was used. The voltammograms were recorded using a Bryans 29000 *X–Y* recorder. A three-electrode cell was used; the working electrode was a Bruker ER51 rotating disc with gold and glassy carbon electrodes (electrode area = 0.28 cm^2), the reference electrode was a saturated calomel electrode (s.c.e.) and the counter was a platinum plate. All measurements were carried out at room temperature (20 °C). Half-wave potentials were

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determined from current potential curves. Tables in this paper clarify the effects of half-wave potentials on the electrode reaction when going from one solvent to another.

RESULTS AND DISCUSSION

Voltammetry

(i) In ACN

Current–potential curves for the reduction of 5×10^{-3} mol dm^{-3} organotin(IV) compounds were recorded as a function of rotation speed at gold and glassy carbon electrodes. Figure 1 illustrates typical examples of the cathodic voltammograms obtained. For the phenyl series, i.e. Ph_2SnCl_2 and Ph_3SnX, clearly defined limiting currents were obtained for the compounds where X = Cl, N_3, NO_3, OH or NCS, whereas these were less defined for the methyl series, i.e. Me_2SnCl_2 and Me_3SnX, and the butyl series, i.e. nBu_2SnCl_2 and nBu_3SnCl. At lower rotation speeds where limiting current plateaus are less well defined, limiting current values were obtained by extrapolation. The Levich euqation was found to be valid here over

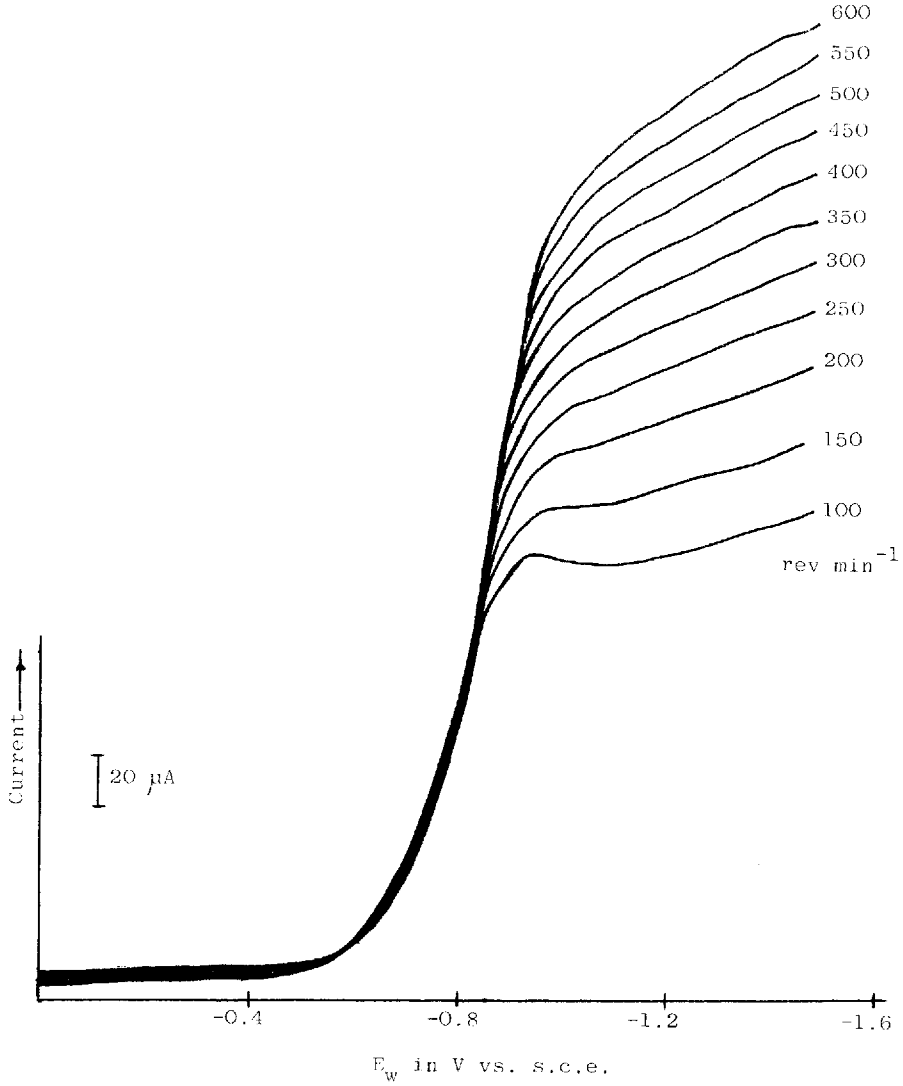

Figure 1 Cathodic reduction of 10^{-3} mol dm^{-3} Ph_3SnNCO in DMF at a glassy carbon electrode. Scan speed = 5 mV s^{-1}. Tetraethylammonium perchlorate (TEAP) = 0.1 mol dm^{-3}.

a wide range of rotation speeds. The Levich plots displayed an excellent linearity with zero or near-zero intercepts. From this, it is clear that the electrode process is controlled by diffusion. Figure 2 shows examples of Levich plots.[11] A similar behaviour was found for the dependence of the limiting current on tin(IV) concentration ($10^{-3}-10^{-6}$ mol dm^{-3}). This is also further evidence that the observed limiting current is a diffusion-controlled limiting current.

(ii) In DMF

The current–potential curves for the reduction of 5×10^{-3} mol dm^{-3} organotin(IV) compounds were recorded at gold and glassy carbon electrodes at different rotation speeds. Figure 3 shows typical voltammograms obtained. A very well defined limiting current was obtained for all series at gold and glassy carbon. The Levich plots, shown in Fig. 4, are straight lines with near-zero intercept, which indicate a simple mass-transfer electrode process.

It should be noted that the reduction of all tin compounds used in this work showed a single wave in both solvents, i.e. ACN and DMF. Furthermore, scan rates higher than that used in this work (5 mV s^{-1}) did not affect the results.

Coulometric determination of *n*-values

Amperostatic coulometry[12] gives a decrease in the limiting current of 50% per electron equivalent of charge passed for the reduction process of each compound studied, identifying a two-electron reaction, which is confirmed by cyclic voltammetry.

Substituent and solvent effects on half-wave potentials

The effects of substituents and solvents on the electrochemical reactivity were examined for all the series of organotin(IV) compounds. The corresponding half-wave potentials are given in Table 1. The half-wave potentials are almost similar when measured at gold or at glassy carbon electrodes. The phenyl series showed well-defined cathodic waves, with half-wave potentials ranging from −0.75 to 0.78 V vs s.c.e. in DMF and from −0.77 to −0.81 V vs s.c.e. in ACN. The values are slightly higher for the methyl and n-butyl series in both solvents, which indicates that the reduction becomes more difficult as the donating effect of R in R_ySnX_{4-y} increases, i.e. from Ph to Me and nBu. Similar observations have been found

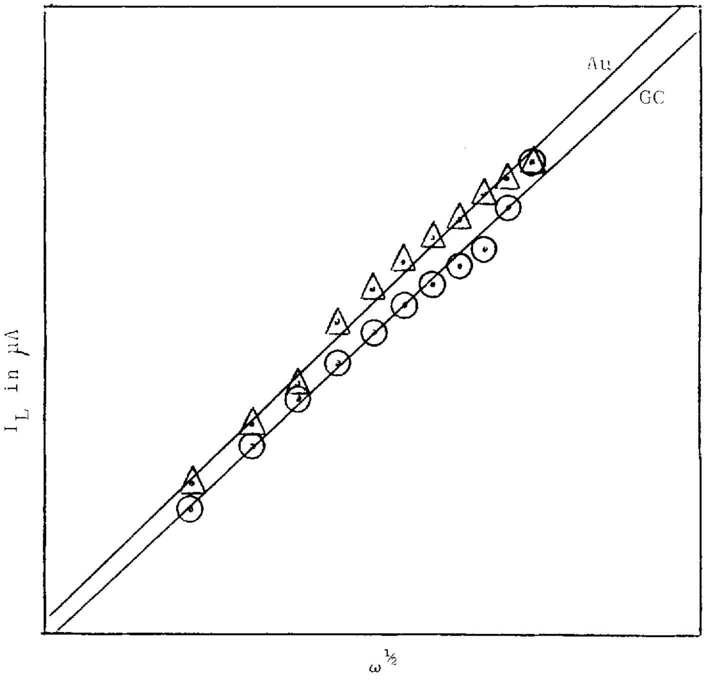

Figure 2 Levich plots for reduction of Ph_3SnNO_3 in DMF. I_L = limiting current.

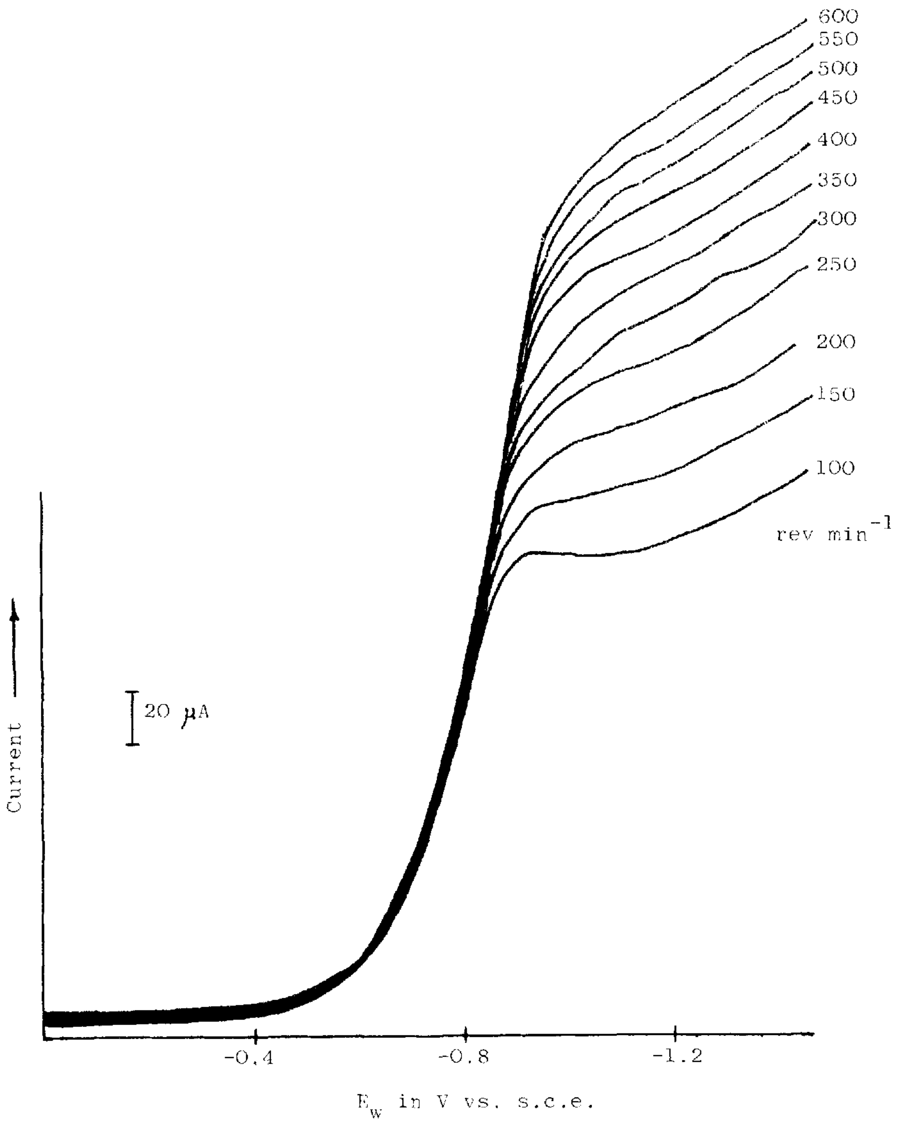

Figure 3 Cathodic reduction of 10^{-3} mol dm^{-3} Ph_3SnN_3 in DMF at a gold electrode. Scan speed = 5 mV s^{-1}. TEAP = 0.1 mol dm^{-3}.

previously[13] that these substituents possess the same effects. Furthermore, in all series the values of half-wave potentials are not much influenced by changing the anion (X) attached to tin, and the reversibility of the reaction did not change. The small difference in half-wave potential on going from X = Cl to X = OH for the same series could be reasonably explained on the basis of solvation energy. The standard electrode potential $E^{\ominus}$ in various solvents is determined by the corresponding free energy of solvation ($\Delta G^{\ominus}_{\mathrm{solv}}$) which can be divided into two species; the electrostatic solvation energy ($\Delta G^{\ominus}_{\mathrm{el}}$) and the neutral solvation energy ($\Delta G^{\ominus}_{\mathrm{neut}}$) as given by Eqn [1]:[14,15]

$$\Delta G^{\ominus}_{\mathrm{solv}} = \Delta G^{\ominus}_{\mathrm{el}} + \Delta G^{\ominus}_{\mathrm{neut}} \qquad [1]$$

$\Delta G^{\ominus}_{\mathrm{el}}$ can be calculated using the modified Born equation (Eqn [2]):[16]

$$\Delta G^{\ominus}_{\mathrm{el}} = \frac{Ne^2}{2}\left(1 - \frac{1}{\epsilon}\,\frac{(Z^+)^2}{(r^+ + R^+)}\right) \qquad [2]$$

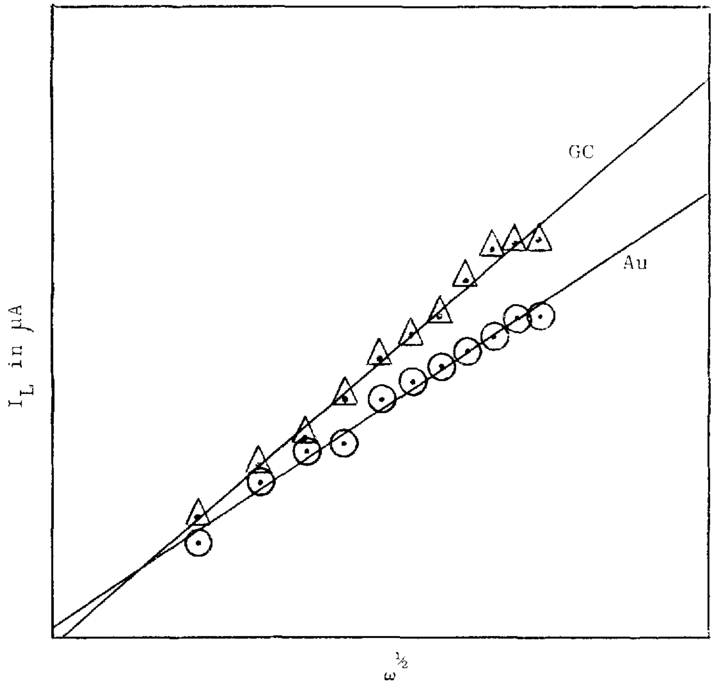

Figure 4 Levich plots for reduction of Me_3SnNO_3 in DMF. Limiting currents were measured at *ca* −0.9 V (s.c.e.) potential.

Table 1 Half-wave potentials for the organotin compounds in DMF and ACN

	$E_{1/2}$ in DMF		$E_{1/2}$ in ACN	
Compound	Au	GC	Au	GC
nBu_2SnCl_2	−0.82	−0.81	−0.83	−0.83
Me_2SnCl_2	−0.77	−0.78	−0.80	−0.81
Ph_2SnCl_2	−0.75	−0.76	−0.78	−0.78
nBu_3SnCl	−0.82	−0.82	−0.83	−0.83
Me_3SnCl	−0.78	−0.79	−0.81	−0.80
Ph_3SnCl	−0.77	−0.76	−0.77	−0.78
Me_3SnNCS	−0.78	−0.77	−0.80	−0.79
Me_3SnN_3	−0.79	−0.78	−0.82	−0.81
Me_3SnNO_3	−0.78	−0.79	−0.81	−0.81
Ph_3SnNCO	−0.75	−0.75	−0.77	−0.77
Ph_3SnNCS	−0.75	−0.75	−0.76	−0.77
Ph_3SnOAc	−0.76	−0.75	−0.77	−0.77
Ph_3SnN_3	−0.76	−0.76	−0.78	−0.79
Ph_3SnOH	−0.77	−0.78	−0.81	−0.81
Ph_3SnNO_3	−0.76	−0.77	−0.81	−0.80

where ϵ and r^+ are the permittivity of the solvent and crystallographic radius of the cation respectively and Z^+ is the charge of the cation. R^+ is a correction term in the Born equation which is a function of the donor number of the solvent (DN).[17] The R^+ values are 0.68 Å (0.068 nm), and 0.8 Å (0.080 nm) for DMF and ACN respectively, and the ϵ values are 36.0 and 36.7.

On substitution in Eqn [2], it can be shown that

$$\Delta G^{\ominus}_{\mathrm{el}}(\mathrm{ACN}) < \Delta G^{\ominus}_{\mathrm{el}}(\mathrm{DMF})$$

If the $\Delta G^{\ominus}_{\mathrm{neut}}$ is assumed to be constant for all ions and in all solvents (zero-energy assumption),[14] then

$$\Delta G^{\ominus}_{\mathrm{solv}}(\mathrm{ACN}) < \Delta G^{\ominus}_{\mathrm{solv}}(\mathrm{DMF})$$

or

$$-\Delta G^{\ominus}_{\mathrm{solv}}(\mathrm{ACN}) > -\Delta G^{\ominus}_{\mathrm{solv}}(\mathrm{DMF})$$

Since $\Delta G^{\ominus} = -nFE^{\ominus}$, therefore

$$nFE^{\ominus}(\mathrm{ACN}) > nFE^{\ominus}(\mathrm{DMF})$$

and

$$E(\mathrm{ACN}) > E(\mathrm{DMF})$$

or

$$E_{1/2}(\mathrm{ACN}) > E_{1/2}(\mathrm{DMF}).$$

From the above treatment, it is clear that the solvation energy in DMF is greater than that in ACN. This predicts a lower half-wave potential in DMF. This is indeed the case with the experimental results obtained here.

Kinetic parameters

The voltammograms obtained in the solvents studied can be described by simple mass-charge transfer theory.[18,19] The main equations are [3] and [4]:

$$\frac{1}{i} = \frac{1}{I} + \frac{K}{\omega^{1/2}} \qquad [3]$$

$$\log I = \log nFACK^{\circ} - \frac{\alpha nF}{RT}(E - E_{1/2}) \qquad [4]$$

where i (A) is the current for a particular electrode potential, ω (rad s^{-1}) is the r.d.e. rotational frequency, K is the potential-dependent constant, I (A) is the current corrected for diffusion, E (V) is the electrode potential vs s.c.e., K° is the charge-transfer rate constant, α is the charge-transfer coefficient, A (cm^2) is the electrode surface area, C (mol dm^{-3}) is the bulk concentration of organotin compounds, and n, F, R and T are defined as in the Nernst equation.

During the calculation of kinetic parameters we used

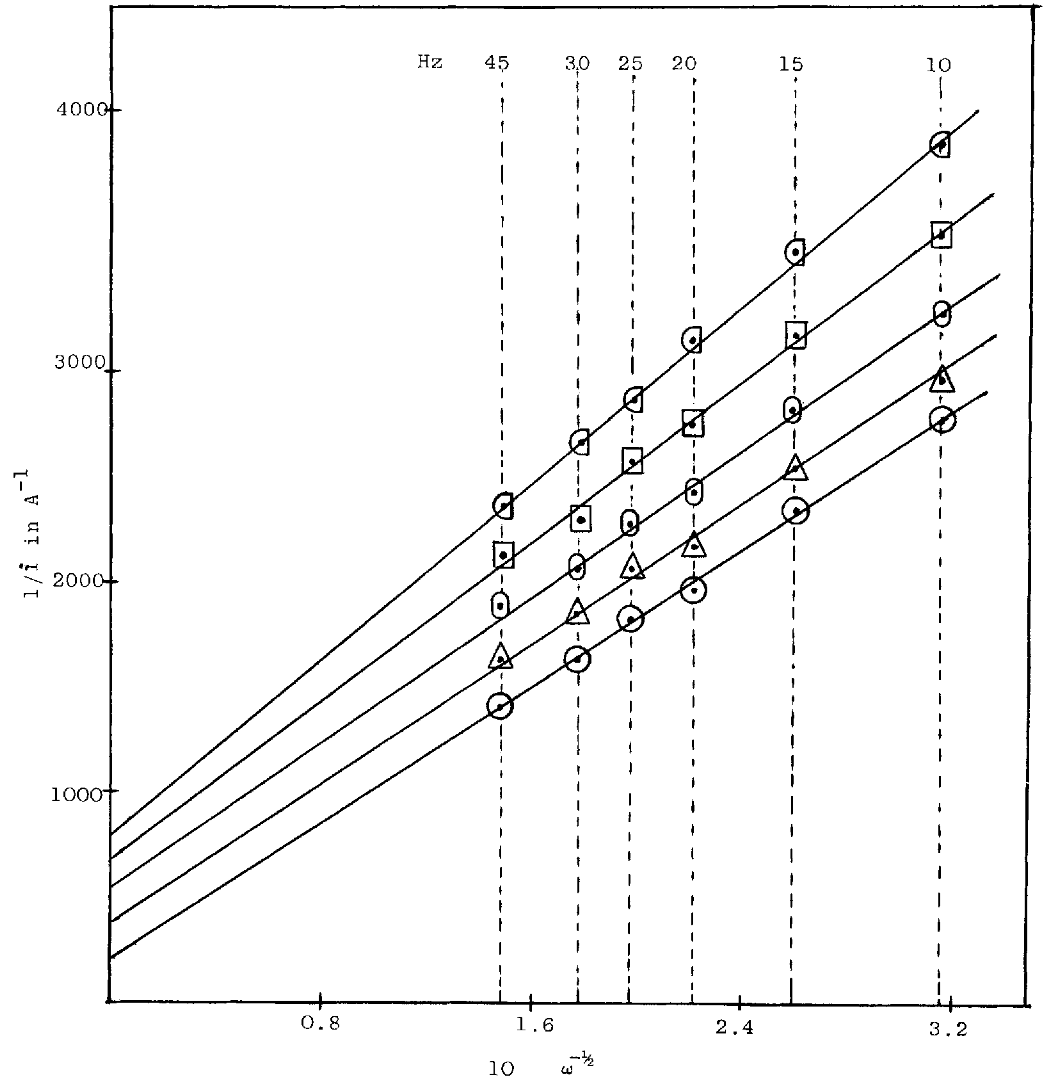

Figure 5 Extrapolation of diffusion method for calculation of kinetic parameters for reduction of 10^{-3} mol dm^{-3} Ph_3SnNCO in DMF at a glassy electrode. From Eqns [3] and [4] the limiting current was obtained at different potentials (from −0.7 to −0.85 V) and graphs of log I versus $E-E_{1/2}$ were obtained. K and α can be obtained by plotting log I versus $E-E_{1/2}$ (Eqn [4]). Curves from Fig. 1 were used to construct this figure.

the half-wave potentials ($E_{1/2}$) as a reference point instead of conditional potentials, because the latter are difficult to obtain for these systems. If Eqn [3] is applied to the set of voltammograms in Fig. 1, the plot of $1/i$ versus $1/\omega^{1/2}$ gives I from the intercept. A different value of I can be obtained for each electrode potential (E), as illustrated in Fig. 5.

A graph of I versus ($E - E_{1/2}$) using Eqn [4] gives a straight line. The charge-transfer kinetic parameters K° and α are obtained from the intercept and the slope respectively and are given in Table 2. The variation in charge-transfer coefficients from gold to glassy carbon and from one compound to another is small, ranging between 0.29 and 0.32 in ACN and DMF. The electrode material has a significant effect on the reaction rate: the K° sequence is gold > glassy carbon in both solvents. This difference may be attributed to the nature of the electrode material. On the other hand, the values obtained for methyl and butyl compounds are slightly higher than those obtained for phenyl compounds. This variation might be explained on the basis of the bulk of the substituent and the electron-withdrawal inductive effect, which in turn affects the structure of the double layer existing at the electrode solution interface. Furthermore, it was found that the anion has no significant effect on the organotin reduction rate. The charge-transfer reaction rate proceeds faster in DMF than in ACN. This could be attributed to the change in solvation sphere or the structure of the double layer of the solvent.[20,21] This indicates a higher activation free energy of the reaction in ACN and consequently the reaction proceeds faster in DMF.

Reaction mechanisms

The proposed reduction mechanism may well be due to the following two steps, the first one being the slow step (rate determining step) (Eqns [5]–[7]):

$$R_2SnCl_2 + e^- \xrightarrow{\text{slow}} R_2SnCl^{\cdot} + Cl^- \qquad [5]$$

$$R_3SnX + e^- \xrightarrow{\text{slow}} R_3Sn^{\cdot} + X^- \qquad [6]$$

The second step appears to occur very fast, giving:

$$R_2SnCl^{\cdot}\ (\text{or } R_3Sn^{\cdot}) + e^- \xrightarrow{\text{fast}} R_2Sn\!: + Cl^-\ (\text{or } R^-) \qquad [7]$$

The R_2Sn: moieties thus formed may polymerize to give $(R_2Sn)_n$. However, the appearance of one reduction wave (the first one) and not two is due to the fact that the second step is too fast. We have already shown[1] that such mechanisms could exist with organotin compounds using the differential pulse polarographic technique.

Table 2 Kinetic parameters for 10^{-3} mol dm^{-3} solutions of the compounds studied in DMF and ACN

Compound[a]	DMF				ACN			
	Au		GC		Au		GC	
	$K^{\circ}/10^{-4}$ (cm s^{-1})	α	$K^{\circ}/10^{-4}$ (cm s^{-1})	α	$K^{\circ}/10^{-4}$ (cm s^{-1})	α	$K^{\circ}/10^{-4}$ (cm s^{-1})	α
nBu_2SnCl_2	7.0	0.31	3.0	0.31	4.0	0.31	2.0	0.30
Me_2SnCl_2	8.0	0.30	3.0	0.32	4.0	0.30	2.0	0.30
Ph_2SnCl_2	5.0	0.31	0.3	0.31	2.0	0.32	0.5	0.31
nBu_3SnCl	9.0	0.29	2.0	0.31	5.0	0.32	3.0	0.31
Me_3SnCl	9.0	0.32	3.0	0.31	5.0	0.30	1.8	0.31
Ph_3SnCl	4.0	0.32	0.1	0.31	3.0	0.31	0.4	0.32
Me_3SnNCS	7.0	0.31	2.0	0.32	4.0	0.29	2.5	0.32
Me_3SnN_3	8.0	0.32	2.0	0.31	4.0	0.32	2.0	0.31
Me_3SnNO_3	6.0	0.30	3.0	0.30	5.0	0.31	3.0	0.31
Ph_3SnNCO	5.0	0.31	0.2	0.30	2.0	0.32	0.4	0.31
Ph_3SnNCS	5.0	0.32	0.1	0.29	1.8	0.31	0.4	0.32
Ph_3SnOAc	5.0	0.32	0.1	0.32	1.6	0.30	0.5	0.31
Ph_3SnN_3	6.0	0.30	0.2	0.31	2.5	0.29	0.5	0.30
Ph_3SnOH	4.0	0.31	0.3	0.32	2.5	0.30	0.3	0.32
Ph_3SnNO_3	5.0	0.32	0.2	0.31	3.0	0.31	0.4	0.29

[a] Kinetic parameters for these compounds were studied in tetraethylammonium perchlorate. Kinetic parameters were determined by the mass extrapolation method (Refs 9,18). A high concentration of supporting electrolyte was used in order to make the *iR* drop as low as possible. The *iR* drop was reversible as proved by cyclic voltammetry. The cell arrangement of the three electrodes minimizes the *iR* drop.

Analytical validity

The good concentration plots in DMF and ACN encouraged us to examine the analytical application of r.d.e. voltammetry. To appraise the reliability of rapid determination, a series of four solutions of organotin standards was prepared and a single measurement of the limiting currents was made at each of five rotation speeds. The concentration was calculated from the slope and the intercept. The results are satisfactory considering the propagation of errors from five calibrations; the mean relative standard deviation is 1.15%.

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