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ADSORPTIVE STRIPPING VOLTAMMETRY: ADSORPTION OF DIOXIME LIGANDS AND COBALT AND NICKEL COMPLEXES AT MERCURY THIN-FILM ELECTRODES

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The pre-concentration step in adsorptive stripping voltammetry involves adsorption accumulation of metal ion complexes of low solubility at the electrode surface, generally mercury, at a small negative applied potential in order to ensure maximum adsorption. In the case of cobalt and nickel, dioxime ligands form sufficiently specific complexes for their identification and determination. After adsorption accumulation, the adsorbed metal ion complexes are reduced by a negative scan to the zero oxidation state resulting in a current peak, the height of which is proportional to concentration.

We have developed a procedure for quantification of cobalt and nickel in flowing solution at the wall-jet mercury thin-film electrode, using nioxime (1,2-cyclohexanedioxime) ligand in a biological buffer, HEPES (pK_a 7.5) [1]. The optimised experimental procedure involves, after formation of the mercury film in acidic nitrate medium, adsorption accumulation of the complexes at -0.7V vs. Ag/AgCl in 30mM HEPES/0.1M $NaClO_4$ at pH 7.6 followed by a differential pulse negative scan from -0.8V. The nickel peak appears at -0.93V and the cobalt peak at -1.01V, there being catalytic enhancement of the cobalt current peak. This method works well in the nanomolar concentration range - at higher concentrations the mercury surface rapidly becomes saturated with complex.

Investigations into the nature of the adsorption and reduction processes were carried out using a rotating disc mercury thin-film electrode (MTFE) formed on a glassy carbon substrate of geometric area 0.4cm^2 , and dioxime ligands in the same 30mM HEPES buffer/0.1M $NaClO_4$ medium by impedance and linear sweep voltammetry. Experiments focussed particularly on nioxime ligands. Previous work at the hanging mercury

drop electrode involved dimethylglyoxime (dmg) ligand [2]. The structure of the dioxime ligand and HEPES are shown in Fig.1. Dioxime forms square planar complexes with Co and Ni; some differences between dmg and nioxime can be predicted from ligand size and the more rigid structure of nioxime.

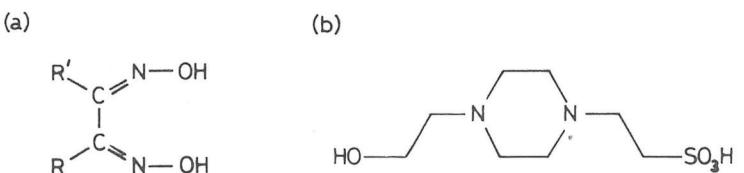


Fig.1 Formulae of (a) dioxime ligand (dmg: R=R'=CH₃; nioxime: R—R'=(CH₂)₄); (b) HEPES.

Impedance spectra in solutions containing only ligand and containing ligand plus metal ion are extremely similar and are of the same form as from substrates covered by a thin conducting film and evidencing some surface roughness, as illustrated in Fig.2. Additionally, they do not vary with potential over the range -0.3 to -0.8V vs. SCE. This suggests that the adsorbed complexes are neutral caused by loss of protons from the dioxime ligands.

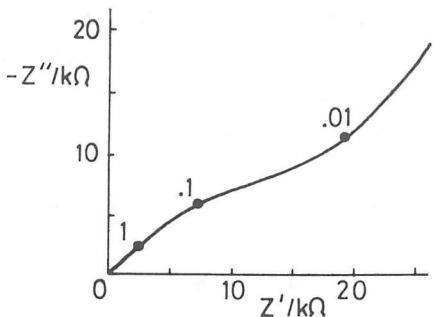


Fig.2 Typical impedance spectrum for nioxime ligand adsorbed on the rotating disc MTFE in 30mM HEPES/0.1M NaClO₄. E=-0.7V vs. Ag/AgCl. Frequencies in Hz.

It can be deduced that adsorption of the complexes probably takes place by metal ion exchange. The mercury surface is covered with adsorbed ligand molecules: a complex approaches from bulk solution, there then occurring

transfer of the metal ion to ligand molecules already adsorbed. Such a mechanism helps to explain saturation effects observed even at very low metal ion concentration, since a contribution from equilibrium effects between adsorbed and non-adsorbed complexes can be envisaged.

In linear sweep voltammetry experiments, three minutes preconcentration was carried out at -0.7V followed by a negative scan at sweep rates varying between 5 and 200mV s⁻¹. Parameters of interest were the variation of peak potential, E_p, and peak current, i_p, with ligand and metal ion concentration, with pH and with scan rate. Typical reduction peaks after background subtraction are shown in Fig.3 - it can be seen that the nickel peak is fairly symmetrical and the cobalt peak very asymmetrical.

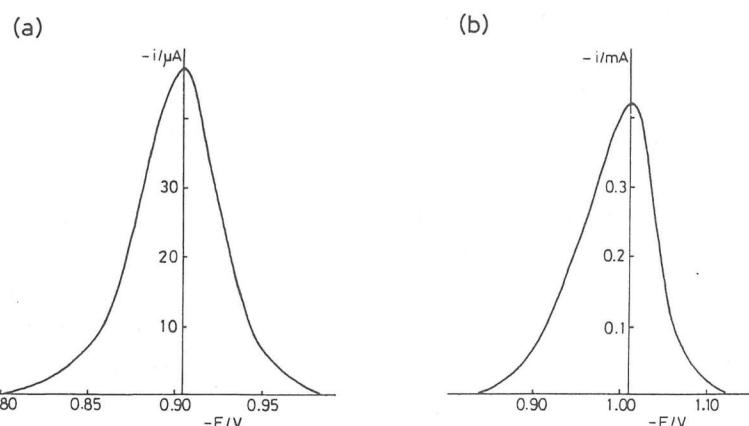


Fig.3 Typical LSV reduction peaks after background subtraction for (a) Ni and (b) Co. pH=6.8, [nioxime]=10⁻⁴M; [M²⁺]=1.0×10⁻⁶M; v=200mV s⁻¹.

Other deductions that can be made are:

- direct proportionality between peak current and scan rate, confirming the reduction of irreversibly adsorbed reactants;
- variation of E_p with pH;
- the rate determining step is 1st order in H⁺, since plots of log i vs. pH at fixed potential and scan rate have slope of ~-1;
- catalytic enhancement of the cobalt peak current, such that it is approximately ten times the height of the nickel peak.

Analysis of the wave shape shows current peaks for the reduction process of nioxime complexes different from those with dimethylglyoxime ligand [2], and differences between nickel and cobalt. Applying Laviron's expression for the reduction of irreversibly adsorbed reactants [3]:

$$i = -Z(\sigma t)nFA\sigma\Gamma_c$$

where $Z(\sigma t)$ is a current function, $\sigma = (nF/RT)v$, Γ_c is the surface concentration and other symbols have their usual meaning, gives a reasonably good fit for the main part of the peak if values of $\alpha n=1.2$ for Ni and 0.65 for Co are assumed, and which corresponds to calculated coverages of 0.19 and 1.7 nmol cm⁻² respectively. The less good fit at the tail end of the peak can be attributed to the fact that the metal reaction product is confined to the thin mercury film. Unlike the dm_g case where αn values of approximately 1.5 were found corresponding to a pre-equilibrium followed by a rate-determining step, here addition of the first electron appears to be included in the rate-determining step. The difference in the calculated Γ_c values of an order of magnitude is probably due to the catalytic enhancement of the Co signal such that the Ni value is the correct one.

It is not at present clear how the catalytic regeneration of Co(II) occurs. Apart from catalysis by ammonia buffer, this has been found in the presence of nitrite, where it was deduced that the reduction of this species caused reoxidation of Co(I) [4]. The formula and structure of HEPES (Fig.1) suggest that its involvement in this regeneration process should be considered.

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ESTUDIO VOLTAMPEROMETRICO DE LOS COMPLEJOS Cd-LIGANDOS INORGANICOS A BAJAS CONCENTRACIONES

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INTRODUCCION

Las vías fluviales son unos de los cauces más importantes de dispersión de los metales pesados en el medio ambiente. Por esto y por su carácter tóxico y no biodegradable, lo que les confiere propiedades acumulativas y en muchos casos carcinogénicas, es de suma importancia conocer su comportamiento medioambiental. Entre dichos metales y por su gran toxicidad el Cd ha originado algunos problemas graves, como la enfermedad del itai-itai, por lo que su estudio es de primordial importancia. Para su determinación pueden utilizarse técnicas polarográficas o voltamperométricas, aunque a los niveles en que se encuentra en las aguas de río ($\mu\text{g/l}$) se escogerá la última de ellas. Con relación al tipo de complejos que forma, pueden agruparse en dos categorías límites: lábiles e inertes. Limitaremos este estudio a los complejos lábiles que forma el Cd con los diferentes ligandos inorgánicos predominantes en el río Pisuerga: HCO_3^- , HPO_4^{2-} , Cl^- y SO_4^{2-} .

Puesto que el Cd se reduce reversiblemente sobre mercurio, si forma un complejo que lo hace de acuerdo con la reacción



la determinación de la constante de estabilidad y del número de ligandos puede hacerse mediante la expresión:

$$\Delta E_{1/2} = (E_{1/2})_c - (E_{1/2})_f = - RT/nF \ln (\beta_{\text{MX}_j} [X]^j)$$

Cuando se producen equilibrios sucesivos la determinación de las constantes y el número de ligandos se realiza a través del método de De Ford y Hume, mediante la ecuación generalizada

$$(E_{1/2})_c - (E_{1/2})_f = - RT/nF \ln \sum \beta_j [X]^j$$

cuya reordenación da lugar a las funciones de Leden:

$$F_o(x) = \sum \beta_j [X]^j = \exp(-RT/nF E_{1/2}) + \ln I_m/I_o = \\ \beta_0 + \beta_1 [X] + \beta_2 [X]^2 + \dots$$

Un ajuste polinómico por mínimos cuadrados de $F_o(x)$ en función de la concentración de ligando nos permitirá obtener la estquimetría y las constantes de los complejos.