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Polarographic Catalytic Currents of Complexes of Metals in Catalysis by a Ligand

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This review gives the characteristics of catalytic systems and results on the kinetics and mechanism of electrode chemical reactions, describes methods of determining the instability constants of complexes from the catalytic currents and the analytical use of catalytic boundary waves, and makes a comparison with results on corresponding non-electrode reactions of complex formation.
Among the bulk electrode chemical processes considered are theoretical and experimental results on an electrode reaction with two successive rate-determining chemical stages, and also on a double catalytic effect: that of the ligand and that of an addition of a polarographically active complex which is regenerated at the electrode.
The kinetics and mechanism of processes involving an adsorbed ligand-catalyst have been analysed on the basis of a concept of heterogeneous parallel reactions of complex formation.
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I. INTRODUCTION

The prewaves of the polarographic wave of the aquo-ions of a metal, linked with the participation of polarographically active complexes (PAC) in the electrode process during catalysis by a ligand, were termed[1,2] catalytic prewaves (points) of the metal complexes. Here we will not consider the catalytic currents of complexes in catalysis by the ions of a metal[3], the catalytic release of hydrogen, and the catalytic effect of the ligand in the presence of an inhibitor of the electron transfer stage[4], although this effect shows certain resemblances[5,6] to the catalytic influence of the ligand in the absence of an inhibitor.

The characteristics of catalytic currents of metal complexes in catalysis by a ligand are: (1) the prewaves arise at potentials that are more positive (cathodic)[7-12] or more negative (anodic)[11] than the reduction or oxidation potentials respectively of the aquo-ions of the metal; (2) a catalytically active ligand can be either charged[7] or electrically neutral[9]; (3) in the PAC the metal ions are reduced or oxidised with regeneration at the electrode of the ligand, which again participates in the formation of PAC[1,2]; however, when there is an excess of the ligand

(prewaves arise either when there is an excess of the ligand or when there is an excess of the metal ions)[13,14] or when the PAC is of low stability this phenomenon does not play a significant part; (4) the prewaves are of a kinetic nature[1,2,7-12], and increase with the concentration of the ligand, in many instances reaching the limit of the diffusion wave of the aquo-ions of the metal. However, when ligand adsorbed on the electrode participates in the formation of PAC, the prewave limiting current, having reached the region of diffusion current corresponding to potentials of maximal adsorption of the ligand, can fall again as the potential is changed, owing to partial desorption of the ligand (minimum on the polarisation curve)[8]; (5) the prewaves can exceed the initial diffusion wave of the aquo-ions of a metal when the solution contains, in addition to the ligand, certain components which regenerate PAC at the electrode. When components which do not form complexes are chosen the nature of the PAC remains unchanged[15,17].

Polarographically catalytic currents of metal complexes in catalysis by a ligand are of theoretical and practical importance: in electrocatalysis (especially chemical factors), electrodeposition (mechanism of the effect of a catalytically active ligand), the chemistry of coordination compounds (new methods of investigation of the instability constants of complexes and of the kinetics of complex formation, including the kinetics of complex formation under heterogeneous conditions), and analytical chemistry (polarographic determination of metals in the presence of catalytically active ligands and in a newer direction—determination of the ligands themselves with the aid of the prewaves). All these aspects of this problem will be covered in the present review.

II. CATALYTIC SYSTEMS

The choice of metal ions for the production of these catalytic prewaves is determined mainly by the presence of a high overpotential in the reduction or oxidation of the corresponding aquo-ions of the metal[18].

Catalytically active ligands can belong to various classes of inorganic and organic compounds, usually readily adsorbed on an electrode.

Usually prewaves have been observed in aqueous solutions, but there have been examples of catalytic currents in non-aqueous or mixed solvents[19-23].

A large number of catalytic systems are known (with the exception of the two examples of an anodic process given below, all cathodic processes): Ni^{II}–NCS^-,[7,10,12,24-29] Ni^{II}–Cl^- (Br^-, I^-),[19,20,23,30] Ni^{II}–pyridine and its alkyl, amino-, and hydroxo-derivatives,[1,2,9,14,21,29,31-42] Ni^{II}–1,2- and 1,5-diaminonaphthalenes,[2] Ni^{II}–3,4-diaminotoluene,[2] Ni^{II}–3,4-diaminobenzoic acid,[2] Ni^{II}–4,4′-diaminostilbene-2,2′-disulphonic acid,[2] Ni^{II}–aminoethylpiperazine,[2] Ni^{II}–2,2′-bipyridyl,[2] Ni^{II}–2-aminoethanol,[2] Ni^{II}–*o*-phenylenediamine,[2,43-51] Ni^{II}–*p*-phenylenediamine,[51] Ni^{II}–ethylenediamine,[52] Ni^{II}–thiourea and its derivatives[53-60], Ni^{II}–cysteine[61], Ni^{II}–selenocysteine[62], Ni^{II}–*o*,*o*′-diethyldithiophosphate[63], Ni^{II}–xanthogenate[22], Ni^{II}–thiosemicarbazide[57], Ni^{II}–rubeanic acid[57], Ni^{II}–unithiol[57], Co^{III}(ammonia complex)–Cl^-(Br^-),[64,65] Co^{II}–ethylenediamine (anodic process),[66] Co^{II}–cysteine and its derivatives[67-70], Co^{II}–selenocysteine[71], Co^{II}–acetylacetone[72], Co^{II}–pyridine[73,74], In^{III}–halide ions[5,8,75-80], In^{III}–NCS^-,[5,77-83] In^{III}–thiourea and its derivatives[6,75,77,79,84], In^{III}–thioacetic and mercaptoacetic acids[77], In^{III}–mercaptoethanol[77], In^{III}–cysteine[84], In^{III}–thiosemicarbazide[56,84], In^{III}–*o*-phenylenediamine[77], In^{III}–2,2′bipyridyl[77], In^{III}–1,10-phenanthroline[77], In^{III}–phthalic acid[75], In^{III}–oxalic acid[77,85-87], In^{III}–tartaric acid[8], In^{III}–acetylacetone[88], Ga^{III}–NCS^-,[89-92] Ga^{III}–halide ions[93], Ga^{III}–N_3^-,[94] Ga^{III}–salicylic and aminosalicylic acids[92], Ga^{III}–methylthiourea[92], Ga^{III}–2-amino-4-hydroxythiazole[92], Ga^{III}–2-amino-4-methyl-5-thiocyanothiazole[92], Sn^{IV}–cysteine[95], Ti^{IV}–NCS^-,[11,17,96-100] Ti^{III}–NCS^- (anodic process),[11] Ti^{IV}–SO_4^{2-},[101,102] Ti^{IV}–F^-,[103] Ti^{IV}–citric acid[15,104], Ti^{IV}–polyphenols[16,104-106], Ti^{IV}–salicylic and sulphosalicylic acids[16,104,105], Ti^{IV}–oxalic acid[104], Ti^{IV}–pyrocatechol[107], Ge^{IV}–polyphenols and their derivatives[108-114], Ge^{IV}–polyhydroxyanthraquinones[113,115], Ge^{IV}–hydroxyflavones[113,116].

III. KINETICS AND MECHANISM OF THE PROCESSES

As in the catalytic liberation of hydrogen[117], the formation of PAC may take place either in the body of the solution (bulk currents; we will thus refer to processes with a reaction layer much thicker than the diffusion part of the electrical double layer[11,15,16,28,66,100]), or with participation of the adsorbed ligand-catalyst (heterogeneous or surface processes)[1,2,35,43-51,62,77-87].

It must be borne in mind that the effect of certain anions and surface-active agents can be linked not only with the surface nature of prewaves, but also with the formation in the solution of new complexes[36-38,51]. Therefore in the present instance it is more important to study the effect of the nature and concentration of the background cation[35,47-50], especially in using alkali metal cations which differ in surface activity[118] but at the same time hardly produce a block-effect and are sufficiently inert to complex formation.

Unlike the catalytic wave of hydrogen with participation of an adsorbed catalyst[119], the temperature coefficient of the limiting current in the heterogeneous reaction for the formation of a PAC is usually sufficiently high (predominance of chemical kinetics)[2,28,35,55,77] but a lower temperature coefficient has also been observed[114] (predominance of the adsorption effect).

The regeneration of a ligand at an electrode is often due to rapid decomposition of the product from the reduction of PAC in the form of the corresponding zerovalent complex[120]. Although extremely unstable zerovalent complexes are usually formed, the difference in the magnitudes of the calculated halfwave potentials of the aquo-ions from a single metal in the presence of different catalytically active ligands[121] allowed the difference in the rate of deactivation of an amalgam[121], or more precisely, in the rate of decomposition of the corresponding zerovalent complexes, to be found. Thus the rates of decomposition of the zerovalent complexes of nickel were found to increase in the following sequence of ligands: pyridine < imidazole < NCS^-.[121]

In many instances the shift in the reduction or oxidation potentials of the PAC is due to the very stable primary hydration of the corresponding aquo-ions of the metals and the weakening (labilisation) under the influence of the ligand of the bonding of the metal ion with the water molecules which remain in the first hydration shell[43,52,122,123]. This conclusion is confirmed by studies[124,125] in which the labilisation of water molecules in a complex was observed with the aid of non-electrochemical methods. For some aquo-ions of metals (for example, Ni^{2+}) which form prewaves, hydration is so strong that in solutions with a high concentration of supporting electrolyte, owing to the marked reduction in the concentration of the aquo-ions of

the metal in the near-electrode layer (the ψ_1-effect[126,127]) a kinetic current was observed: kinetic limitation of the dehydration step[128].

When a PAC is formed in the adsorbed layer, then an electric field evidently exerts a considerable effect on the acceleration of the dehydration[129,130]. It cannot be ruled out that in certain instances the acceleration of the electron transfer stage is linked with the fact that the adsorbed ligand entering into the PAC plays the part of an "electron bridge"[4,131,132]. Attention must be paid to the special state of the adsorbed ligand entering the PAC; it is not impossible that coordination with mercury and with the reacting ion of the metal is effected simultaneously[41,73,133,134]. Some investigators[131,132] pay more attention to the "electron bridge" than to complex formation, although we do not think it very expedient to regard these phenomena as mutually exclusive.

Observations which indirectly characterise the chemical nature of the slow step of the electrode process are of great interest: (1) the steric effect of the ligand (In^{III}–thiourea and its derivatives[84]; Ni^{II}–pyridine and its derivatives[39,39a]). A similar effect was noted in certain complex formation reactions by use of non-electrochemical methods[135]; (2) the relation of the catalytic effect to the structure of isomeric ligands (Ni^{II}–isomers of phenylenediamine[44,45,51]); (3) the inhibition of the catalytic process in the Ni^{II}–pyridine (or its derivatives) systems when the solution is acidified[2,35,39,39a], which is also characteristic for the corresponding non-electrode reactions in complex formation (protonation of the ligand); (4) the inhibition of the catalytic process in the Ni^{II}–thiourea[59] and Ge^{IV}–polyphenol[111] systems on the addition of oxalic, citric, or tartaric acids, in the Ni^{II}–thiourea[36-38], Ni^{II}–pyridine[36-38], Co^{II}–ethylenediamine[66] systems on addition of SO_4^{2-} ions, in the Ni^{II}–thiourea[59] system on addition of NH_3 and Trilon B and the acceleration of the catalytic process under the influence of AcO^- ions (Ni^{II}–pyridine[2,37,38], Ni^{II}–thiourea[37,38], and Ni^{II}–*o*- and *p*-phenylenediamine[51] and N_3^- ions (Ni^{II}–*o*- and *p*-phenylenediamine[51]). Similar effects were also observed in a study of the kinetics of ordinary (non-electrode) complex formation reactions[136-138]; (5) the faster catalytic process in the Co^{II}–pyridine system[74] in comparison with the Ni^{II}–pyridine system[35], which correlates with the kinetics of non-electrode complex formation reactions of particular metal aquo-ions[135].

The bulk catalytic current simplest in mechanism was evidently observed in the Ti^{IV}–NCS^- system[11,96,100]. By use of Koutecky's equation[139,140]:

$$\frac{\bar{i}_k}{\bar{i}_d - \bar{i}_k} = 0.886 \cdot \left(\frac{k_1 \cdot t_1}{K_1'}\right)^{1/2} \cdot c_{NCS^-} \qquad (1)$$

(where $\bar{i}_k$ and $\bar{i}_d$ are the limiting currents, catalytic and diffusion respectively; k_1 and K_1' are the formation rate constant and instability constant of the PAC respectively); it was shown[11,96,100] that the electrode process can be described by the following scheme:

$$Ti^{IV} \xrightarrow[\text{diff.}]{} Ti^{IV} \xrightarrow[k_1]{NCS^-} [Ti^{IV}(NCS^-)] \xrightarrow[\text{red.}]{} \cdot \qquad (2)$$

For simplicity, in scheme (2) and below we do not show the stage of regeneration of the ligand at the electrode and the diffusion noted relates to the transfer of the substance from the depth of the solution to the surface of the electrode (the PAC concentration in the body of the solution is insignificant[141]).

The rate constants for the formation of PAC (scheme 2) calculated by Eqn. (1), are given in Table 1. In addition, Tribalat and Delafosse[11] found the rate constant for the formation of another PAC, $[Ti^{III}(NCS^-)]$, from the anodic catalytic prewave, $k \cong 10^6$ litre mole^{-1} s^{-1} (0.55 M HCl; 21°C).

Table 1. Rate constants for the formation of the complex $[Ti^{IV}(NCS^-)]$ in $HClO_4$ solution at 25°C.

c_{HClO_4}, M	$10^{-3}k_1$, litre mole^{-1} s^{-1}	c_{HClO_4}, M	$10^{-3}k_1$, litre mole^{-1} s^{-1}
0.024	13.0	0.51	6.5
0.044	7.9	0.55*	6±2*
0.10	7.3	1.05	4.8
0.51	6.5	2.0	5.2

*HCl(21°)[11]

The catalytic prewaves of Ti^{IV} in the presence of pyrocatechol (H_2Ph), pyrogallol (H_3Pg), citric acid (H_4Cit), and sulphosalicylic acid (H_2Ssal^-) in acid solutions ($HClO_4$) also had a bulk nature[15,16]. The PAC in these systems, with the exception of H_2Ssal^- are formed with the participation in the reactions of electrically neutral ligands, with the release (including H_2Ssal^-) of hydrogen ions[15,16]. Like the catalytic systems with Ge^{IV},[113] Ti^{IV} ions form both PAC and polarographically inactive complexes with these ligands[15,16]. As the concentration was increased, the accumulation of the inactive complexes inhibited the electrode process[15,16]. If it is assumed that the stability of the PAC of Ti^{IV} correlates with the stability of the corresponding polarographically inactive chelates, the rate of formation of the PAC correlates with their stability: $H_2Ph < H_3Pg < H_2Ssal^- < H_4Cit$.[16]

Since the first investigation[142] the effect of ClO_3^- (BrO_3^-) ions on the polarographic wave of Ti^{IV} complexes has been investigated repeatedly, but as found earlier[142], under conditions when there is a large excess of the ligand, whereas in the absence of ClO_3^- ions the prewave was reached along the height of the diffusion wave of the Ti^{IV}. The effect of ClO_3^- ions was first studied at a low concentration of the ligand (NCS^-, H_2Ph, H_3Pg, H_4Cit, H_2Ssal^-), that is, under conditions where there is a double catalytic effect on the process: by the ligand and ClO_3^- ions. An increase in the catalytic prewave of Ti^{IV} complexes with increase in $C_{ClO_3^-}$ (maximally by 5–7 times in comparison with the initial prewave) has been observed[15-17]. A similar comparatively small increase in the limiting current was explained (in greatest detail for the NCS^- ions[17]) on the basis of the following scheme for the electrode process:

$$Ti^{IV} \xrightarrow[(IV)]{NCS^-} [Ti^{IV}(NCS^-)] \xrightarrow[(I)]{\bar{e}} [Ti^{III}(NCS^-)] \xrightarrow[(II)]{} Ti^{III} + NCS^- \qquad (3)$$

$$\uparrow(IV) \qquad \uparrow(III) \quad ClO_3^- \qquad \text{(III)}$$

$$ClO_3^-: (V)$$

by assuming that there are parallel reactions for the oxidation of $[Ti^{III}(NCS^-)]$: to PAC (stage III) and to the initial Ti^{IV} (stage IV). The latter, like stage V, makes little contribution to the increase in current, since it is followed by the slow stage (I).

Another example of bulk catalytic prewaves was observed in the Ni^{2+}–NCS^- system (first prewave)[12,28].

This prewave corresponds to an electrode process with two successive rate-determining chemical stages[12,28]

$$\begin{array}{ccccccc} Ni^{2+} & \xrightarrow[(I,\,k_1)]{NCS^-} & [Ni(NCS)]^+ & \xrightarrow[(II,\,k_2)]{NCS^-} & [Ni(NCS)_2] & \xrightarrow{red.} & \\ \uparrow\downarrow diff. & & \uparrow\downarrow diff. & & & & \\ Ni^{2+} & \xrightleftharpoons{NCS^-} & [Ni(NCS)]^+ & & & & \end{array} \quad (4)$$

The kinetic equation for a similar electrode process was first obtained in studies[12,143] by the present author and by Tanaka and coworkers but verified experimentally only in other investigations[12,28]; this became especially convenient after appropriate transformations and the development of a graphical solution of the equations obtained[144]: ($c_{NCS^-} \gg c_{Ni^{2+}}$):

$$y = \frac{\bar{i}_d - \bar{i}_k}{\bar{i}_k} \cdot c_{NCS^-}^2 + 1.13 \left(\frac{K_1'}{k_1 t_1}\right)^{1/3} \cdot \frac{\bar{i}_d}{\bar{i}_k} \cdot \frac{c_{NCS^-}^2}{K_1' + c_{NCS^-}} = A + B \cdot c_{NCS^-} \quad (5)$$

where K_1' is the instability constant of the complex $[Ni(NCS^-)]^+$ and A and B are constants:

$$A = 1.13 \cdot K_1' \cdot \left(\frac{K_2'}{k_2 \cdot t_1}\right)^{1/3}, \quad (6)$$

$$B = 1.13 \left[\left(\frac{K_1'}{k_1 \cdot t_1}\right)^{1/3} + \left(\frac{K_2'}{k_2 \cdot t_1}\right)^{1/3}\right]. \quad (7)$$

K_2' is the consecutive instability constant of the complex $[Ni(NCS)_2]$.

When in scheme (4) the diffusion of the second species (the complex) from the depth of the solution can be neglected Eqn. (5) is greatly simplified even when there are still two successive rate-determining stages[145-147].

The rate constants k_1 and k_2 (Table 2) were found[28] by graphical solution on the basis of Eqn. (5) (in the first paper[12] an inaccuracy was introduced in finding k_1 and k_2, since no allowance was made for the distortion of the limiting diffusion current of Ni^{2+} at high concentrations of the supporting electrolyte[128]). The most important conclusion from the results in Table 2 is the similarity between the rate constants obtained from catalytic currents and those found[148] by a non-electrolytic (flow) method ($k_1 = 5.6 \times 10^3$ litre mole^{-1} s^{-1}; 25°C; ionic strength 0.5). In addition, it is noteworthy that on the basis of the variations in $E_{\frac{1}{2}}$ and c_{NCS^-},[7,31] and also by a potentiostatic method[149], the reduction of the complex $[Ni(NCS)_2]$ in the Ni^{2+}–NCS^- system has been demonstrated, which agrees with the results discussed above.

Table 2. Rate constants for the formation of the complexes $[Ni(NCS)]^+$ (k_1) and $[Ni(NCS)_2]$ (k_2) at 25°C.

Ionic strength KNO_3 + KNCS	$10^3 k_1$, litre mole^{-1} s^{-1}	$10^{-4} k_2$, litre mole^{-1} s^{-1}	Ionic strength KNO_3 + KNCS	$10^3 k_1$, litre mole^{-1} s^{-1}	$10^{-4} k_2$, litre mole^{-1} s^{-1}
0.05	6.5±1.5	4.2±0.4	0.15	3.0±1.0	2.1±0.3
0.075	4.5±0.5	3.1±0.1	0.20	3.0±1.0	1.9±0.3
0.1	5.0±1.0	2.1±0.1			

Since $c_{Ni^{2+}} > c_{Ni(NCS)^+}$, as c_{NCS^-} is reduced, stage (I) in scheme (4) approaches equilibrium[27,29]:

$$\begin{array}{ccccccc} Ni^{2+} & \xrightleftharpoons{NCS^-} & [Ni(NCS)]^+ & \xrightarrow[k_2]{NCS^-} & [Ni(NCS)_2] & \xrightarrow{redn.} & \\ \uparrow\downarrow diff. & & \uparrow\downarrow diff. & & & & \\ Ni^{2+} & \xrightleftharpoons{NCS^-} & [Ni(NCS)]^+ & & & & \end{array} \quad (8)$$

The kinetic equation for such a process was first considered in studies[150,151] of dicarboxylic acids, and then in an investigation of metal complexes[143]:

$$\frac{\bar{i}_k \cdot (K_1' + c_{NCS^-})}{(\bar{i}_d - \bar{i}_k) \cdot c_{NCS^+}} = 0.886 \cdot \left(\frac{k_2 \cdot t_1}{K_2'}\right)^{1/3} \cdot c_{NCS^-}. \quad (9)$$

It has been shown theoretically[29] that conversion of scheme (4) into scheme (8) is possible at $c_{NCS^-} \ll 0.1$ M ($c_{NCS^-} \gg c_{Ni^{2+}}$); this conclusion has been confirmed experimentally[29] at $c_{NCS^-} \leqslant 1.5 \times 10^{-2}$ M. Although there is no single opinion about the bulk nature of the catalytic prewaves in the Co^{II}–cysteine (or its derivatives) systems[67-70] it is worth noting the relation[68]:

$$\bar{i}_k = k \cdot c_{Co^{II}}^{1/3} \quad (10)$$

characteristic for a bulk process[70,152] under the conditions c_L = const, $c_{CoII} \gg c_L$ (L is the ethyl ester of cysteine) and the high stability of the PAC:[68]

$$Co^{II} \xrightarrow{diff.} CoII \xrightleftharpoons[k_1]{L} [Co^{II}(L)] \xrightarrow{redn.} \quad (11)$$

Since $c_{CoII} \gg c_{CoII(L)}$, the effect of the diffusion of the PAC from the depth of the solution can be neglected. $k_1 = (3.7-4.3) \times 10^3$ litre mole^{-1} s^{-1}.[68]

The following bulk reactions correspond to the anodic catalytic process in the Co^{2+}–ethylenediamine(En) ($NaClO_4$) system[66]:

$$\begin{array}{ccccccc} Co^{2+} & \xrightleftharpoons{En} & [Co(En)]^{2+} & \xrightleftharpoons{En} & [Co(En)_2]^{2+} & \xrightarrow[k_3]{En} & [Co(En)_3]^{2+} \xrightarrow{oxn.} \\ \uparrow\downarrow diff. & & \uparrow\downarrow diff. & & \uparrow\downarrow diff. & & \\ Co^{2+} & \xrightleftharpoons{En} & [Co(En)]^{2+} & \xrightleftharpoons{En} & [Co(En)_2]^{2+} & & \end{array} \quad (12)$$

and are describable by the kinetic equation[66,153,154]:

$$\frac{\bar{i}_k}{\bar{i}_d - \bar{i}_k} = 0.886 \cdot \left(\frac{k_3 \cdot t_1}{K_3'}\right)^{1/3} \cdot \frac{c_{En}^3}{K_1' \cdot K_2' + K_2' \cdot c_{En} + c_{En}^2}, \quad (13)$$

where K_1, K_2', and K_3' are the consecutive instability constants of $[Co(En)]^{2+}$, $[Co(En)_2]^{2+}$, and $[Co(En)_3]^{2+}$ respectively. $k_3 = 1.85 \times 10^7$ litre mole^{-1} s^{-1}.[66]

A more complex electrode process is associated with the chemical reactions for the formation of PAC in an adsorbed layer (heterogeneous reactions).

The idea of parallel heterogeneous reactions has been formulated[35,58,74,80]:

$$\begin{array}{ccccccc} M & \xrightarrow{diff.} & M & \xrightarrow[(I,\,\bar{k}_1)]{L_{ads.}} & [M(L_{ads.})] & \xrightarrow{redn.} & \\ L\downarrow\uparrow & & L\downarrow\uparrow & & & & \\ [M(L)] & \xrightarrow{diff.} & [M(L)] & \xrightarrow[(II,\,\bar{k}_2)]{L_{ads.}} & [M(L)(L_{ads.})] & \xrightarrow{redn.} & \\ & & L\downarrow\uparrow & & & & \\ & & [M(L)_2] & \xrightarrow[(III,\,\bar{k}_3)]{L_{ads.}} & [M(L)_2(L_{ads.})] & \xrightarrow{redn.} & \\ & & etc. & & etc. & & \end{array} \quad (14)$$

These obviously most completely characterise such catalytic processes. In scheme (14) (the charges of the species are omitted) M denotes the aquo-ions of the metal, L the ligand, [M(L)], $[M(L)_2]$, etc. are complexes in the bulk of the solution, and $[M(L_{ads})]$, $[M(L)(L_{ads})]$, $[M(L)_2(L_{ads})]$, etc. are PAC.

Since surface catalytic prewaves arise most frequently in solutions which contain complexes with a low stability (K_1' not below 10^{-3}–10^{-4}), in scheme (14) the diffusion of only two species from the depth of the solution to the electrode is taken into account: M and M(L). Despite the low stability of the complex [M(L)] and higher complexes, their participation in the electrode reactions for the formation of PAC cannot be neglected in general, since the bulk rate of formation–dissociation of [M(L)], $[M(L)_2]$, etc. can be rather high. In systems which form

complexes which are more stable in the bulk solution a larger number of heterogeneous parallel reactions must be considered[80] and in systems with bulk complexes of lower stability a smaller number of reactions[35,58,74] or even only a single first (I) reaction[43-51].

Owing to the presence in the PAC (scheme 14) of a ligand adsorbed on the mercury or coordinated with the mercury, similar PAC should (as shown above) differ considerably in electrochemical properties from complexes of formally analogous composition adsorbed from bulk solution[41]. The latter are not reduced at prewave potentials[41].

Irrespective of the reduction of the various PAC in scheme (14) at similar potentials (single prewave)[74,79] or at distinguishable potentials (several prewaves)[35,58], we will examine below only the equation for the overall limiting catalytic current.

Assuming in scheme (14) that the bulk reactions of formation and dissociation of complexes are near a state of equilibrium[29,35,58,59]; that the diffusion coefficients of all the species are similar; and allowing for the effect of the electrical double layer structure on the rate of heterogeneous[117,126,155,156] electron transfer steps which are sufficiently rapid in the region of the limiting catalytic current, the following kinetic equation was found[35,80] for scheme (14) (the coefficient 0.81 has been replaced[140] by 0.886):

$$\frac{\bar{i}_k(K_1'+c_L)}{(\bar{i}_d-\bar{i}_k)\cdot\Gamma_L}=0.886\cdot 10^3\cdot\left(\frac{t_1}{D}\right)^{1/6}\left\{\bar{k}_1\cdot K_1'\cdot\exp.\left(-\frac{z\cdot F}{RT}\psi_1\right)+\right.$$
$$\left.+\bar{k}_2c_L\cdot\exp.\left(-\frac{z_1\cdot F}{RT}\psi_1\right)+\frac{\bar{k}_3}{K_2'}c_L^2\cdot\exp\left(-\frac{z_2F}{RT}\psi_1\right)+\ \ldots\right\} \quad (15)$$

where K_1' and K_2' are the successive instability constants of the bulk complexes, M(L) and M(L)$_2$ respectively; $\bar{k}_1$, $\bar{k}_2$, $\bar{k}_3$, etc. are the rate constants of the parallel heterogeneous reactions (litre mole^{-1} s^{-1}); Γ_L the surface concentration (mole cm^{-2}) of the adsorbed ligand (the existence of an adsorption equilibrium to a first approximation is assumed); for a dropping electrode this assumption is valid only up to a definite lower level c_L, for example, for *o*-phenylenediamine up to $c_L = 1\times10^{-4}$;[46,50] z, z_1, z_2, etc. are the charges of M, [M(L)], [M(L)$_2$], etc., ψ_1 a potential close to that of the Helmholtz outer layer, the value of which has been given[157] for a supporting electrolyte that is not adsorbed; the effect on ψ_1 the potential of the reacting species of their low concentration can often be neglected (the effect of adsorbed thiourea on the ψ_1 potential has been taken into account[55]); c_L the equilibrium ligand concentration (M) at the boundary between the diffusion layer and the diffusion part of the electrical double layer (c_L is close to the total concentration of the ligand; this is also true for a small excess of ligand L, owing to the regeneration of the ligand at the electrode[144]).

Since catalytic currents are usually investigated in the range of very low c_L, Γ_L can be expressed with the aid of the Henry adsorption isotherm[158]:

$$\Gamma_L=10^{-3}K_L\cdot c_L f_z\cdot\exp\left(-\frac{p\cdot F}{RT}\psi_1\right) \quad (16)$$

where K_L is the adsorption coefficient (cm) and ρ the charge of the ligand.

From (15) and (16):

$$y=\frac{\bar{i}_k(K_1'+c_L)}{(\bar{i}_d-\bar{i}_k)\cdot c_L}=0.886\cdot\left(\frac{t_1}{D}\right)^{1/6}\cdot K_L f_z\left\{\bar{k}_1\cdot K_1'\cdot\exp.\left[-\frac{(z+p)F}{RT}\psi_1\right]+\right.$$
$$\left.+\bar{k}_2\cdot c_L\cdot\exp\left[-\frac{(z_1+p)F}{RT}\cdot\psi_1\right]+\frac{\bar{k}_3}{K_2'}\cdot c_L^2\cdot\exp\left[-\frac{(z_2+p)F}{RT}\psi_1\right]+\ \ldots\right\} \quad (17)$$

At ψ_1 = const, Eqn. (17) becomes

$$y=a+b\cdot c_L+dc_L^2+\ \ldots \quad (18)$$

where a, b, and d are constants, which are conveniently determined by a graphical method[80].

By use of Eqn. (18) we showed[80] the presence of three parallel heterogeneous reactions in the In^{III}–NCS^- system—scheme (14), I, II, and III. An analysis of the variation of the surface activity of $NCS^-_{ads.}$ ions (see below) with the potential in concentrated NaNCS solution showed[83] that in this system the heterogeneous catalytic reaction

$$In^{III}\xrightarrow{{}^2NCS^-_{ads.}}[In^{III}(NCS^-_{ads})_2]\xrightarrow[redn.]{} \quad (19)$$

takes place; it should correspond to a kinetic equation of type (18) at $a = 0$ and $d = 0$, that is, schemes (19) and (14) (without stages I and III) are kinetically indistinguishable. However, as we have shown[80], coefficients a, b, and d in Eqn. (18) are significantly different from zero, which suggests that in this system under our conditions[80] (a very low concentration of NCS^-) all three parallel heterogeneous reactions take place.

For the Ni^{2+}–Py,[35] Co^{2+}–Py,[74] Ni^{2+}–thiourea[58], and In^{III}–I^- [80] systems, in which less stable complexes are formed, Eqn. (18) has been found to be applicable—for the Ni^{2+}–thiourea system, Eqn. (15) at $d = 0$ ($\bar{k}_3 = 0$), that is, in these systems only the two parallel heterogeneous reactions (I) and (II) have a significant effect. It is interesting to note that an analysis of the change in the surface activity of the ions I^-_{ads} with the potential has also shown[132] a smaller stoichiometric number for the I^-_{ads} ions reacting with In^{III} than for NCS^-_{ads}.[83]

The even less stable complex [M(L)] in the Ni^{2+}–*o*-phenylenediamine system[46,47] takes almost no part in the heterogeneous process and the applicability of an equation of type (18) at $b = 0$ and $d = 0$ has been demonstrated[46,47].

In a study[83] of the In^{III}–NCS^- system at a high concentration of NCS^- ions (0.1–6.0 M) the surface activity of the NCS^-_{ads} ions (a_{ads}) was introduced into the kinetic equation instead of Γ_{NCS^-}. It was found from the thermodynamic relation[83,132]:

$$\beta=\frac{a_{ads.}}{a_{soln.}}=\lim_{\Gamma_{NCS^-}\to 0}\frac{\Gamma_{NCS^-}}{a_{soln.}} \quad (20)$$

where a_{soln} is the activity of NCS^- ions in the body of the solution. Hence the quantity βa_{soln} replaces a_{ads} in the kinetic equation:

$$v=k\cdot(\beta\cdot a_{soln.})^x \quad (21)$$

where v is the rate of the process in the region of the limiting current at constant activity coefficient of the transition state, a_M = const and $\psi_1 \simeq$ const (concentrated solution); and x the order of the reaction from the adsorbate. Hence, by use of the variation of β with the potential the applicability of scheme (19) ($x = 2$) was demonstrated[83]. Unfortunately, the accuracy of the dependence of β on the potential, found for concentrated solutions of adsorbate on the basis of model representations is evidently inadequate for the development of this interesting concept. In addition, the postulate of the constancy of the activity coefficient of the transition state—Eqn. (21)—as the potential is varied can hardly be justified[159]. We think that investigations in the range of very low catalyst concentrations, where the Henry adsorption equation applies, is preferable in this respect. It should also be noted that for an electrically neutral ligand (Ni^{2+}–thiourea)[55,58] even

in the range of medium packing it was not necessary to replace Γ_L by a_{ads} in the kinetic equation.

We[35,55] were evidently the first to find—Eqns. (15) and (17)—the rate constants of the heterogeneous electrode reactions for the formation of the PAC (Table 3). The similarity of $\bar{k}_1$ for the various ligands (Table 3), is most probably linked, as for bulk reactions[135], with a common rate-determining stage: the removal of H_2O molecules from the Ni^{2+} aquo-ion. This agrees with the kinetics of bulk reactions[125] and the ratio $\bar{k}_2 > \bar{k}_1$ (Table 3).

The total charge of the reacting species, found on the basis of an analysis of the effect of the ψ_1 potential on the kinetics of the process in the Ni^{2+}–*o*-phenylenediamine system[46,47,50], and consequently the charge of the PAC, was equal to $z + p = +1$, which is explained[46,47,50] by the coadsorption of the anion of the supporting electrolyte (ClO_4^- or NO_3^-) together with the electrically neutral ligand. For the Ni^{2+}–Py system[35,40] at a moderate supporting electrolyte concentration ($\leq$ 0.05 M $NaNO_3$), use of Eqn. (17) showed that $z + p = +2$ and $z_1 + p = +2$. Although coadsorption of the anion of the supporting electrolyte was also observed[160] for Py, the results[35,40] refer to more positive potentials and a lower concentration of supporting electrolyte. For the Co^{2+}–Py system[74], owing to its more negative potential, PAC charges ($z + p$ and $z_1 + p$) also equal to +2 were found on the basis of Eqn. (17) over a wide range of concentrations of the supporting electrolyte. Charges $z + p = +2$ and $z_1 + p = +2$ were similarly found for the PAC in the Ni^{2+}–thiourea system[55,58]. It is interesting to note that in the same system with KI supporting electrolyte[59,60] with considerable adsorption of I^- ions charges $z + p = +2$ and $z_1 + p = +2$ were obtained on using Grahame's values[161] of the ψ_1 potential on the outer layer, which again shows the position of the chemical reaction layer close to the outer surface of the compact part of the electrical double layer.

Table 3. Rate constants for heterogeneous reactions for the formation of polarographically active complexes at 25°C. $NaNO_3$ ($\psi_1 = 0$).

Reaction	$10^{-2}\bar{k}_1$, litre mole^{-1} s^{-1}	$10^{-3}\bar{k}_2$, litre mole^{-1} s^{-1}	Reference
$Ni^{2+} + Py_{ads}$	4.0		35
$[Ni(Py)]^{2+} + Py_{ads}$		1.8	35
$Ni^{2+} + Tm^*_{ads}$	3.8		55

* Thiourea.

Hence the finding by use of Eqns. (15) and (17) for an electrically neutral ligand and doubly charged cation of the expected charges of +2 for the PAC indicates the correctness of the calculation for these reactions of the effect of the electrical double layer under conditions where there are stages with rapid transport of electrons in the range of limiting current.

The complete equation for the catalytic prewave (heterogeneous chemical reaction) with allowance for limitation at the electrochemical stage also is interesting, since this equation, together with an equation of type (17), also allows the charge of the PAC to be found. Such an equation for the simplest process of scheme (14):

$$M^z \xrightarrow[\text{diff.}]{} M^z \xrightarrow[\bar{k}_1]{L^p_{ads.}} [M(L_{ads.})]^{z+p} \xrightarrow{\text{redn.}} \quad (22)$$

has been obtained[50]. This equation can after simple rearrangements be presented as follows (region of the Henry adsorption isotherm):

$$\frac{\bar{i} \cdot D^{1/2}}{(\bar{i}_d - \bar{i}) \cdot K_L \cdot t_1^{1/2}} \cdot \exp\left[\frac{(z+p) \cdot F}{RT}\psi_1\right] = 0.886 \frac{\bar{k}_1 c_L \cdot k^0_{el} \cdot \exp\left[-\frac{(E-\psi_1)\alpha n_a F}{RT}\right]}{k^0_{el} \cdot \exp\left[-\frac{(E-\psi_1)\alpha n_a F}{RT}\right] + \bar{k}_1} \quad (23)$$

where $\bar{i}$ is the catalytic current at potential E and $\bar{k}_1$ is a rate constant for the reverse reaction (dissociation of PAC).

By choosing the value of $z + p$ in this way, so that the left part of Eqn. (23) reaches a constant value when the negative quantity E is increased, the charge of the PAC is found[50].

For the approximate estimation of the effect of ligand concentration, Eqn. (23) can be simplified by assuming that in the range of potentials of the rise of the prewave from the half-wave potential ($E_{\frac{1}{2}}$) to the potential for the start of the limiting current the quantities ψ_1 and K_L vary slightly. It has been found[162] that under these conditions [Eqn. (31) in Ref. 162]

$$E_{1/2} \simeq 2.3\frac{RT}{\alpha n_a F} \lg 0.886 \cdot \left(\frac{t_1}{D}\right)^{1/2} k^0_{el} + 2.3\frac{RT}{\alpha n_a F} \lg \frac{c_L \cdot K_L}{\bar{K}_1'} + 2.3\frac{RT}{\alpha n_a F} \lg \frac{\bar{i}_d}{\bar{i}_k'} + \psi_1\left[\frac{\alpha n_a - (z+p)}{\alpha n_a}\right], \quad (24)$$

where $\bar{K}_1'$ is the equilibrium constant for the dissociation of the PAC and $\bar{i}_k'$ the limiting current at a potential close to the beginning of the limiting current region.

A complete equation for the surface catalytic prewave, but at the rapid chemical stage of formation of PAC (with allowance for the parallel reaction for the discharge of M^z ions) has also been given[6,78,84]:

$$\bar{i} = k \cdot \left(\frac{\bar{i}_d - \bar{i}}{\bar{i}_d}\right)\left[(1 - \theta_{cat.}) + \theta_{cat.} \cdot \exp\left(-\frac{\Delta U_{cat.}}{RT}\right)\right] \times \left\{\exp\left[-\frac{(E-\psi_1)\alpha n_a F}{RT}\right]\right\} \cdot \exp\left(-\frac{zF}{RT}\psi_1\right), \quad (26)$$

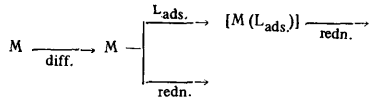
where θ_{cat} is the degree of occupation of the surface of the electrode by the adsorbed catalyst. It may be that in some systems a chemical stage, which greatly reduces the activation energy for the electron transfer (the factor ΔU_{cat}), even in the limiting current region, can take place much more rapidly than the electron transfer stage.

An equation has been obtained[71,163] for the bulk catalytic prewave on the basis of the concept of hypothetical diffusion current. Under the conditions of reduction of only the metal ions in the PAC this equation has the form:

$$\bar{i} = N \cdot \bar{i}_k^d \Big/ \left\{1 + \exp\left[(E - E_{1/2})\frac{\alpha n_a F}{RT}\right]\right\}, \quad (27)$$

where $\bar{i}_k^d$ is the diffusion current of PAC in the absence of a catalytic effect, N the number of metal ions which react in the catalytic cycle with one or more (when there are several ligands in the PAC) species of catalyst ligand. Although Eqn. (27) corresponds to the experimental results[71,163] we think it desirable[164] to use a similar equation [Eqn. (70) in Ref. 117] but with the physically real quantity $\bar{i}_{lim}(i_k)$ instead of the hypothetical diffusion current ($N.\bar{i}_k^d$).

This chapter will be concluded by noting that for the commonly encountered catalytic systems in which electrochemical limitation is almost absent in the region of the limiting current, use of equations of the limiting current type (15) and (17) is preferable. When this is done and an increase in potential results in the superimposition of a parallel process of the discharge of the aquo-ions of the metal, there is the possibility of calculating a corrected value of the limiting catalytic current. For example, for the process



(28)

it was found[40,42] that:

$$(\bar{i}_k)_{corr} = \frac{\bar{i}_d \cdot (\bar{i}_{lim.} - \bar{i}_0)}{\bar{i}_d - \bar{i}_0} \qquad (29)$$

where $\bar{i}_{lim}$ is the observable limiting current and $\bar{i}_0$ the current at the same potential but in the absence of a catalyst.

IV. DETERMINATION OF THE INSTABILITY CONSTANTS OF COMPLEXES

Solution of this problem is facilitated by complexes of low stability usually being formed in the catalytic system itself.

These methods can be divided into two groups: effect of catalytically inactive ions of the metal (method A) and effect of a catalytically inactive ligand (method B).

1. Effect of Metal Ions (Method A)

This method, first proposed by Tribalat[96], is based on the fall in the catalytic current when the catalytically inactive ions of another metal (M′) which bonds the catalyst ligand in a complex [M′(L)] are introduced into the solution. The proportion of the catalyst ligand entering into the complex is easily found from the drop in current and hence the instability constant (K_1') of this complex can be calculated:

$$K_1' = \frac{c_L[c^0_{M'} - (c^0_L - c_L)]}{c^0_L - c_L} \qquad (30)$$

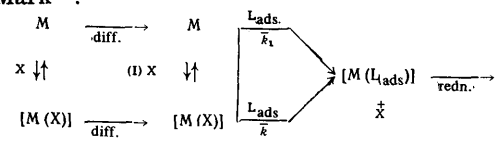
where c^0_L is the total concentration of the ligand (determined from the curve of the catalytic current in the presence of M′ against the total concentration $c^0_{M'}$), and c_L the equilibrium concentration of the ligand (determined from the curve of the catalytic current in the absence of the ions M′). This method was used to determine the instability constants, mainly, of single ligand complexes (K_1'); an excess of M′ ions was used. The results are given in Table 4. The values found for K_1' are close to those obtained by other methods.

2. Effect of the Ligand (Method B)

This direction was first taken by Yatsimirskii and Budarin[165], but they used catalytic systems, which are not discussed in the present review.

Subsequently[36-38] the effect of catalytically inactive ligands on the prewaves of metal ions was investigated and the effects of ligand addition which increase (AcO^-) or decrease (SO_4^{2-}) the currents were used to find the instability constants of the complexes with these ligands[36-38].

Theoretically the solution of this problem was based on the calculation of the parallel process of "religandisation"[36,51,166]. In the simplest example, the entire process can be represented by a scheme proposed simultaneously and independently by Tur'yan and Ruvinskii[36] and by Caja and Mark[51]:



(31)

where X is the polarographically inactive ligand. When $\bar{k} > \bar{k}_1$ the process is accelerated (AcO'); when $\bar{k} < \bar{k}_1$ it is inhibited (SO_4^{2-}).

The equilibrium in stage I (scheme 31) has been characterised[36-38] by use of the same type of kinetic equation as for scheme (14) but with allowance for the parallel reaction of religandisation under conditions different from those of Ref. 166:

$$Z = Z_1 + K_1' \frac{Z_0 - Z}{c^0_X}, \qquad (32)$$

where K_1' is the instability constant of the complex [M(X)], $Z = \bar{i}_k/\bar{i}_d - \bar{i}_k$, Z_L = const at c_Z = const and a constant ionic strength of the solution, $Z_0 = Z$ at $c_X{}^0 = 0$, and $c_X{}^0$ is the total concentration of ligand X introduced in an excess in relation to the ions M.

A graphical method was used[36-38] for finding K_1' with the aid of Eqn. (32). The results (Table 4) are close to those obtained by other methods.

V. ANALYTICAL APPLICATION

Catalytically active ligands introduced into a solution in very great excess greatly improve the form of the polarographic wave of a metal and significantly alter the half-wave potential. These advantages are widely used in the polarographic analysis of metals (Ni^{2+}, Co^{2+}, In^{III}, etc.) and have been described in detail in various monographs[168].

A more recent approach considered below is the analytical determination of ligands with the aid of the catalytic prewaves of the metals.

At a low ligand concentration the prewaves were first used[2] for the highly sensitive determination of the ligand (determination of pyridine from the catalytic prewave of Ni^{2+}). The analysis was made with a preliminary calibration graph[44]. Then this method was used for the determination of *o*-phenylenediamine in the presence of a tenfold excess of the *m*- and *p*-isomers (catalytic prewave of Ni^{2+}). With the aim of improving the sensitivity (to 10^{-7} M) it was proposed[45] to use 0.1 M LiI as supporting electrolyte (ψ_1 effect[45,47]). In a further investigation[49] the catalytic prewave of Ni^{2+} in the presence of *o*-phenylenediamine was used for the amperometric titration of *o*-phenylenediamine with the aid of Au^{III} ions. The sensitivity of the determination was 1×10^{-6} M.

The catalytic prewaves of Ti^{IV} in the presence of various ligands have been used[15,16] for the determination of these ligands: citric acid[15], sulphosalicylic acid[16], pyrocatechol[16] and pyrogallol[16]. The additional catalytic effect in the presence of ClO_3^- ions has been used[15,16] to

Table 4. Instability constants (K_1') of complexes, found on the basis of catalytic currents in catalysis by a ligand, 25°C.

Catalytic systems	Supporting electrolyte	Ionic strength	Complex investigated	Method	K_1'	Reference
Ti^{IV}—NCS^-	$HClO_4$	0.70—0.85	$[Co(NCS)]^+$	*A*	$(8.8\pm0.3)\cdot10^{-2}$	96
ditto	ditto	0.50	$[Fe(NCS)]^+$	ditto	$1.5\cdot10^{-2}$	96
»	»	0.6	$[Cr(NCS)]^{2+}$	»	$(5—10)\cdot10^{-4}$	96
»	»	0.7	$[Ni(NCS)]^+$	»	$6.1\cdot10^{-2}$	97
»	»	1.0	ditto	»	$6.7\cdot10^{-2}$	97
»	»	1.5	»	»	$7.6\cdot10^{-2}$	97
»	»	2.5	»	»	$7.7\cdot10^{-2}$	97
»	»	5.0	»	»	$5.4\cdot10^{-2}$	97
»	»	0.62—0.68	»	»	$(4.6\pm0.2)\cdot10^{-2}$*	99
»	»	0.62—0.68	»	»	$(5.7\pm0.2)\cdot10^{-2}$	99
»	»	0.62—0.68	»	»	$(6.7\pm0.4)\cdot10^{-2}$**	99
»	$HClO_4+NaClO_4$	3.0	HNCS	»	5 ± 0.3***	98
Ni^{2+}—NCS^-	KNO_3	1.0	$[Co(NCS)]^+$	»	$(9.0\pm0.4)\cdot10^{-2}$	26
Ni^{2+}—Py	$NaClO_4$	1.0	$[Co(Py)]^{2+}$	»	$(4.4\pm0.4)\cdot10^{-2}$	33
Ni^{2+}—thiourea	$NaNO_3$	2.0	$[Zn(Tm)]^{2+}$	»	0.29 ± 0.01	56
In^{III}—thiourea	$NaClO_4+HClO_4$	2.0	$[Zn(Tm)]^{2+}$	»	0.28 ± 0.01	56
Ni^{2+}—thiosemicarbazide (Tc)	$NaNO_3$	2.0	$[Zn(Tc)^{2+}$	»	$(5.1\pm0.1)\cdot10^{-2}$	56
ditto	ditto	1.0	$[Co(Tc)]^{2+}$	»	$(3.9\pm0.1)\cdot10^{-2}$	56
Ni^{2+}—thiourea (Tm)	$NaClO_4+Na_2SO_4$	2.0	$[NiSO_4]$	*B*	$(7.2\pm0.1)\cdot10^{-2}$	36—38
Ni^{2+}—Py	ditto	2.0	ditto	ditto	$(9.6\pm0.1)\cdot10^{-2}$	36—38
ditto	$NaClO_4+NaAcO$	2.0	$[Ni\,AcO)]^+$	»	0.44 ± 0.01	38
Ni^{2+}—thiourea (Tm)	ditto	2.0	ditto	»	0.36 ± 0.03	38
In^{III}—I^-; In^{III}—NCS^-	$NaClO_4+HClO_4$	1.1	$InSO_4^+$	»	$(1.0—1.1)\cdot10^{-2}$	167

* 15°C.
** 35°C.
*** Dissociation constants.

increase sensitivity. The sensitivity of the determination of citric and sulphosalicylic acids is ~ 1×10^{-5} M, that for pyrocatechol and pyrogallol is ~ 1×10^{-4} M. The method for the determination of citric acid is considerably faster and simpler than the analytical techniques proposed earlier.

The catalytic prewave of In^{III} has been used[77] for the determination of I^- ions (sensitivity 1×10^{-5} M) and also for the determination[86] of oxalic acid (sensitivity ~ 1×10^{-4} M).

Hence the use of the catalytic prewaves of metal complexes has allowed ligands which are polarographically inactive under ordinary conditions to be determined in several instances.

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