Nature of Polarographic Catalytic Current in the Indium–Acetylsalicylic Acid System


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Abstract—The dependence of the limiting catalytic current in the system of In(III)–acetylsalicylic acid on the concentration of indium ions and the ligand anions was described theoretically. Dissociation and protonation constants of acetylsalicylic acid molecular form and kinetic parameter connected with the rate constant of formation of polarographically active complex \( K_a = 3.59 \times 10^{-3} \) mol dm\(^{-3} \); \( K_{H} = 0.12 \) mol dm\(^{-3} \); \( k = 4.0 \times 10^2 \) A (mol/dm\(^{-3}\))^2 were calculated.

This research is based on the ability of small additives of acetylsalicylic acid (HL) to cause catalytic electroreduction of In(III) (polarographic catalytic wave). In the acidic aqueous solution of a mineral acid (HClO\(_4\)) under the influence of HL, In(III) forms a hump-shaped electroreduction wave. The catalytic nature of the wave is manifested by its hump-shaped type and, furthermore, by the independence of its limiting current of the height of mercury column [1].

The limiting catalytic current \( i_{cat} \) linearly grows with the increase in In(III) concentration, and at an increase in the HL concentration at the constant concentration of In(III) the \( i_{cat} \) increases in the value nonlinearly and approaches the limiting value (Fig. 1).

A similar dependence was observed in the systems In(III)–benzenepolycarboxylic acids [2], In(III)–monocarboxylic acids [3] and In(III)–mandelic acid [4]. We did not observe passing through a maximum by the catalytic current at the increase in the ligand concentration, as occurred in the system In(III)–isobutyric acid [5]. The rate of the increase in the limiting catalytic current falls with the increase in the concentration of the mineral acid. In this work this effect is used for estimating the protonation constant of the molecular form of the \( \sigma \)-acetylsalicylic acid. As a first approximation we accept the scheme of electrode process (1) that is well consistent with the experimental data.

\[
\text{In}^{3+} \xrightarrow{\text{diff.}} \text{In}^{3+} + L_{ads} \xrightarrow{k \text{ slowly}} \text{In}L_{ads}^{2+} \xrightarrow{+3e^{-} \text{ reduction}} \text{In}^0 + L_{ads}
\]

In this work the structure of complexes was not studied in detail. For deriving a kinetic equation corresponding to this scheme, let us write the initial Eqs. (2)–(4):

\[
i_{cat} = k [\text{In}^3+][L]_s, \tag{2}
\]

\[
c_l = [L] + [\text{HL}] + [\text{H}_2\text{L}^+] = [L]\{1 + [H^+]/K_a + [H^+]^2/(K_aK_{H})\}, \tag{3}
\]

In these equations \( i_{cat} \) is the limiting catalytic current measured at constant potential (~0.75 V), \( k \) is a kinetic parameter connected with the rate of formation of polarographically active complex \( \text{In}L_{ads}^{2+} \) on the electrode surface. This complex is formed with participation of the ligand adsorbed on the electrode. \( K_a = [L][H^+]/[\text{HL}] \) is the dissociation constant of the molecular form of acetylsalicylic acids (HL), and \( K_{H} = [\text{HL}][H^+]/[\text{H}_2\text{L}^+] \) is the dissociation constant of the protonated form (H\(_2\)L\(^+\)). Substituting the given expressions for constants into Eq. (3) we obtain Eq. (4):

\[
[L]_s = c_{L} - [H^+]/K_a + [H^+]^2/(K_aK_{H}) \tag{4}
\]

Since the \( i_{cat} \) grows linearly with the indium concentration, it possible to conclude that the complexation in the solution is insignificant, therefore we accept that:

\[
[\text{In}^3+]_s = c_{\text{In}} - c_{\text{In}}(i_{\text{lim}}^0 - i_{\text{cat}}^0)/i_{\text{lim}}^0 = (i_{\text{lim}}^0 - i_{\text{cat}}^0)/\chi, \tag{5}
\]

where \( i_{\text{lim}} \) is the limiting diffuse current (8.12 \( \mu \)A at \( c_{\text{In}} \) 0.001 mol L\(^{-1}\)); \( \chi \) is Il’kovich constant, 8.12 \( \mu \)A mmol\(^{-1}\). The index “s” concerns the concentration at the electrode surface in \( \psi_1 = 0 \) plane.
Combining Eqs. (2), (4) and (5), we obtain Eq. (6).

\[
\frac{i_{\text{cat}}^{\lim} \chi}{i_{\text{lim}}^{\text{cat}} - i_{\text{lim}}^{\text{cat}}} \left( 1 + \frac{[\text{H}^+]}{K_a} + \frac{[\text{H}^+]^2}{K_aK_H} \right) = k_{\text{CL}} .
\]

As a first approximation, we set \( c_L = c_{L_{\text{ss}}} \) for the ligand is regenerated. At \([\text{H}^+] = \text{const}\), Eq. (6) is transformed into Eq. (7).

\[
Z = k_{\text{H}^+}c_L .
\]

Here \( Z = \frac{i_{\text{cat}}^{\lim} \chi}{i_{\text{lim}}^{\text{cat}} - i_{\text{lim}}^{\text{cat}}} \), \( k_{\text{H}^+} = F(k/\chi, [\text{H}^+]) \).

Figure 2 obtained by processing the experimental data given in Fig. 1 confirms validity of Eq. (6).

As seen from Fig. 2, Eq. (7) fits well to experimental data except for 1st curve that deviates insignificantly from the linear plot. This indicates possible formation in the solution in small amount of the polarographically inactive complex \( \text{InL}_2^{+} \). The inclination of the tangent to this and other, practically linear, plots is equal to \( k_{\text{H}^+} \). Let us introduce a function \( Y \) [Eq. (8)] describing the dependence of \( k_{\text{H}^+} \) on \([\text{H}^+]\):

\[
Y = \frac{1}{k_{\text{H}^+}} = \frac{\chi/k + [\text{H}^+]^2}{kK_H} .
\]

The plot \( Y \) vs. \([\text{H}^+]\) is shown in Fig. 3 (curve 1). By extrapolation of curve 1 to \([\text{H}^+] \to 0\) the value is found of \( \chi/k \) parameter. Subtracting the found value from both parts of Eq. (8) and dividing them by the hydrogen ions concentration we obtain Eq. (9):

\[
y = \frac{Y - \chi/k}{[\text{H}^+]} = \frac{\chi/kK_H[\text{H}^+]^2}{kK_aK_H} .
\]