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**REMARKS CONCERNING
THE POLAROGRAPHIC BEHAVIOUR OF GALLIUM**

TRAN CHUONG HUYEN and M.KOPANICA

*J. Heyrovský Institute of Polarography, Analytical Laboratory,
Czechoslovak Academy of Sciences, Prague 1*

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Gallium does not yield many well developed polarographic waves¹⁻⁴ and for the analytical application the indirect polarographic techniques⁵⁻⁷ are mostly employed. In this laboratory it has been found that gallium produced a well developed wave in the medium of acetate buffer.

EXPERIMENTAL**Reagents and Apparatus**

All used solutions were prepared from r. g. chemicals. Polarographic measurements were carried out with the polarograph Polarecord E 261 (Metrohm, Herrisau, Swiss) using the Kalousek type cell with separate saturated calomel electrode. pH of the solutions examined was measured with a glass electrode using the pH meter pH-25 (Radiometer, Copenhagen, Denmark).

RESULTS AND DISCUSSION

The half-wave potential of the polarographic wave corresponding to the reduction of gallium ions in acetate buffers (Fig. 1) depends on the concentration of acetate buffer solution and on the concentration of hydrogen ions. In 0.1M acetate buffer solution, pH 3.8 the half-wave potential of gallium wave is -1.19 V (s.c.e.). In the pH interval from 3.5 to 4.2 the limiting current of the studied wave is diffusion controlled, the corresponding electrode reaction is, however, irreversible.

The value of the limiting current depends on the concentration of hydrogen ions. At pH 3.5 the height of the studied wave corresponds to a three electron reduction process and with increasing pH value the limiting current decreases due to the hydrolysis of gallium ions. When, on the other hand, pH is decreased below 3.5, the limiting current sharply increases, whereas the wave is developed poorly.

The dependence of the half-wave potential of the studied wave on log value of the concentration of acetate ion gives a line with a slope equal to 0.062 V. In the case of reversible reduction process this finding could be interpreted by the reversible reduction of gallium acetate complex containing three acetate groups. It has been, however, observed that the reduction of gallium acetate complex proceeded irreversibly and therefore the dependence of $\log i/(i_d - i)$ (where i is the limiting current at a given potential E and i_d is the diffusion current) on log value of the concentration of acetate ion was tested. According to Koryta⁸ this dependence was expressed by the equation

$$d \log [i/(i_d - i)] / d \log [\text{Ac}^-] = N - n, \quad (1)$$

where n is the number of ligands in the complex $\text{GaAc}_n^{(3-n)-}$ which was reduced at the dropping mercury electrode and N is the maximum possible number of ligands in the gallium acetate complex. The plot of $\log i/(i_d - i)$ vs $[\text{Ac}^-]$ measured at the potential -1.27 V gave a line with the slope equal to -1.09 as shown in Fig. 2. Under the assumption that the gallium acetate complex with the maximum number of bound ligands is GaAc_6^{3-} , the result of the dependence given in Fig. 2 leads to the conclusion that the complex reduced at the electrode has the composition GaAc_5^{2-} .

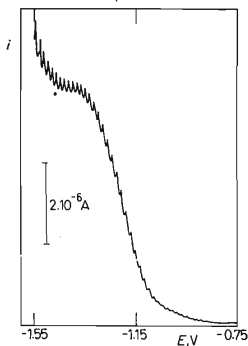


FIG. 1

Polarographic Wave of Gallium in Acetate Buffer Solution

Buffer solution 0.1 mol/l, pH 3.95, $[\text{Ga}] = 1 \cdot 10^{-3}$ mol/l.

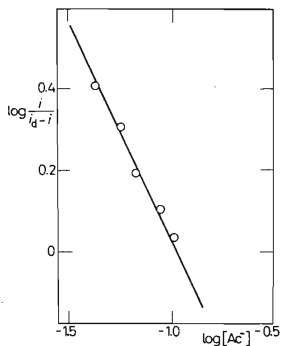


FIG. 2

Dependence of $\log [i/(i_d - i)]$ on $\log [\text{Ac}^-]$, Measured at the Potential -1.270 V

pH 4.2, total gallium concentration $1 \cdot 10^{-3}$ mol/l.

In the pH range, where gallium yields well defined wave (pH 3.5–5.0) the dependence of the half-wave potential $E_{1/2}$ of this wave on pH was examined. For an irreversible process this dependence is expressed by the equation

$$E_{1/2} = k + (a/2.303RT/\alpha\nu F) \text{pH}, \quad (2)$$

where k is a constant, R the gas constant, T absolute temperature, α transfer coefficient, ν number of the electrons involved in the electrode reaction, F is one faraday and a the number of hydrogen ions consumed during the reduction process. The value of the transfer coefficient was determined from the slope of the polarographic wave of gallium acetate complex. The value $\alpha \cdot \nu$ was found to be 0.45 with no pH dependence. Using this value the theoretical slope of the plot $E_{1/2}$ vs. pH for $n = 1$ was calculated as 0.130; the experimental data therefore show that one hydrogen ion is consumed during the electrode reaction. The plot of the dependence $E_{1/2}$ vs pH was a line with a slope of 0.140 V per pH unit.

Recent studies have shown great distorting effects of various ionic surfactants^{9,10} on irreversible waves of metal complexes and chelates. Distorting effect was usually more pronounced in the presence of a surfactant with the same charge as that of the depolarizer. In the case of the irreversible reduction of gallium acetate complex it has been, however, found that the effect of both cationic and anionic surfactants (tetrabutylammonium perchlorate, pyridine, sodium dodecyl sulphate, lauryl sulphate) is practically identical.

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