Polarographic Study of Complexes of Trivalent Antimony in Sodium Fluoride Solutions

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Abstract

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Polarographic Study of Complexes of Trivalent Antimony in Sodium Fluoride Solutions

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In 1948 West, Dean, and Breda (^{1}) reported data on the polarographic behavior of 30 ions in fluoride solutions. They gave the following brief characterization of antimony: "it has a wave with half-wave potential $\pi_{1/2} = -0.683$ V at pH = 3-4.4. The limiting-current constant is 5.91. Reduction of Sb^{+++} to Sb^0 is assumed. The wave is well defined, although a prewave is also observed, which gives grounds for assuming the existence of an equilibrium form of an antimonous complex." Taking this report into account, as well as the fact that the fluoride ion has a small radius and forms stable complexes with many ions, we set ourselves the aim of studying the behavior of Sb^{+++} in NaF solutions and establishing the nature of the complexes obtained.

All polarographic investigations were carried out on a "Heyrovský V-301" polarograph at a temperature of $25.00 \pm 0.02°$. The pH was determined with an LP-5 potentiometer using a quinhydrone or glass electrode. Constancy of ionic strength was ensured by means of 0.5 M KCl. Buffer solutions based on HCl/KCl and CH_3COOH/NH_4OH were used.

The investigations were carried out in parallel by two methods: 1) at constant total concentration of F^-, the dependence of $\pi_{1/2}$ on the pH of the solution was studied; 2) at constant pH, changes in $\pi_{1/2}$ as a function of the concentration of F^- were investigated. In both cases the concentration of Sb^{+++} was kept constant. Both series of experiments showed that over the entire range of pH values from 1 to 14, Sb^{+++} is bound in different ways in complexes. At pH values from 1 to 3, Sb^{+++} is free; at pH from 3-6, an antimony fluoride complex is formed, which decomposes in the pH interval from 6 to 8; above pH 8 the complexes obtained do not contain F^-; at pH > 13, anodic and cathodic waves are observed on the polarogram. These investigations gave us grounds for dividing the entire pH range into three parts.

Complexes of Sb^{+++} in Acidic NaF Solutions

The results of several series of experiments are represented graphically in the coordinates $-\pi_{1/2}$, pH in Fig. 1. In other experiments it was established that in this pH region (from 3 to 6) the current is diffusional and strictly obeys the

Fig. 1

Figure 1: Fig. 1

Ilkovič equation.

In order to determine the composition and instability constant of the complex formed, it is necessary to calculate the activity of the fluoride ions. In acidic solutions the equilibria are established: $F^- + H^+ = HF$ ($K_1 = 6.89 \cdot 10^{-4}$) and $HF + F^- = HF_2^-$ ($K_2 = 0.32$). Bearing in mind that part of the F^- is bound with Sb^{+++} in the complex (we assume that the complex contains $6F^-$), one may write, for the total concentration of fluoride ions F_{tot}, the equation

$$F_{\mathrm{tot}} = a_{F^-} + \frac{a_{F^-} \cdot a_{H^+}}{K_1} + 2\frac{a_{H^+} \cdot a_{F^-}^2}{K_1 \cdot K_2} + 6\mathrm{Sb}^{+++}.$$

Calculations of a_{F^-} were made from this equation when the fluoride complex of antimony was obtained in solution.

Figure 2 shows the dependence of $\pi_{1/2}$ on $-\lg a_{F^-}$. The straight line obtained is well expressed by the equation $\pi_{1/2} = -0.950 - 0.120 \lg a_{F^-}$. From the slope of this equation we determined that the composition of the complex corresponds to $[SbF_6]^{---}$, and from the intercept found the instability constant $K_c = 10^{36-}$. Experiment showed that this complex is stable as long as the ratio $a_{OH^-}/a_{F^-} = 10^{-8}$, after which its hydrolysis begins. The black points in Figs. 1 and 2 correspond to samples in which this ratio is higher. Consequently, the complex of the type $[SbF_6]^{---}$ is stable up to the maximum on the $\pi_{1/2}$, pH curves (Fig. 1).

Fig. 1. Change in $\pi_{1/2}$ as a function of pH at constant total concentration of NaF ($\pi_{1/2}$ was measured relative to the saturated calomel electrode). The ionic strength for all samples was $\mu = 0.3$. Open points correspond to samples for which $-\lg a_{F^-} + \mathrm{pH} < 6$, and black points to $-\lg a_{F^-} + \mathrm{pH} > 6$.

Complexes of Sb^{+++} in the moderately alkaline region

This region begins with the decomposition of $[SbF_6]^{---}$ and ends in an alkaline medium (up to pH 11-12). In this interval several complexes are obtained in an unstable form. Investigation of the range of pH values from 5 to 8 gave no unambiguous results for $\pi_{1/2}$, but in all cases a minimum of these curves was observed (Fig. 1).

In the pH region from 8 to 11 two waves are distinguished on the polarogram: the main wave II and the prewave I (Fig. 3).

The prewave disappears on standing or heating of the solution, with formation of a white precipitate. In addition, it does not depend on the concentration of

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

F^- and, when pH is changed, shifts to more negative values according to the equation

$$\pi_{1/2} = -1.100 - 0.060 \lg a_{H^-}$$

(Fig. 4, I). The slope of this equation shows that 3 OH^- groups participate in the complex. Since the antimony complex must contain more than 4 addends, we assume that the remaining coordination sites are occupied by other molecules or ions. Experiments performed showed that F^-, Cl^-, and NH_3 do not participate in the structure of the complex. Consequently, it may be assumed that a hydroxo complex $[Sb(OH_2)_{p-3}(OH)_3]$ was formed, which on standing splits off water and precipitates as $Sb(OH)_3$. The instability constant of this complex is $K_c = 2.7 \cdot 10^{-44}$.

Fig. 2. Dependence of $\pi_{1/2}$ of the Sb^{+++} wave on $-\lg a_{F^-}$. $\pi_{1/2}$ in the pH interval from 3 to 6 does not depend on the pH of the solutions. Black points correspond to samples for which $-\lg a_{F^-} + \mathrm{pH} > 6$, open points to $-\lg a_{F^-} + \mathrm{pH} < 6$.

The main wave also decreases in height, but much more slowly, and the pH of the solutions changes as well. $\pi_{1/2}$ does not depend on the concentration of F^-, Cl^-, or NH_3, and when the pH is changed it shifts toward more negative

Fig. 3. Polarogram of hydroxo complexes of Sb^{+++} in freshly prepared solutions. $\pi_{1/2}$ depends on pH; $1 \cdot 10^{-3}$ *M* $SbCl_3$; buffer solutions CH_3COOH/NH_4OH. *I*—prewave, *II*—main wave. The lowest curve was recorded in a solution of 1.5 *N* KOH and has an anodic and a cathodic wave ($\pi_{1/2}$ was measured relative to the N.C.E.).

values according to the equation $\pi_{1/2} = -1.150 - 0.020 \lg a_{OH^-}$ (Fig. 4, *II*). This equation gives grounds to assume the following composition of the complex:

$$[Sb(OH_2)_{p-1}(OH)]^{++}, \qquad K_c = 10^{-46}.$$

After the solutions stand, the character of the polarographic wave changes. It rises more steeply, and the dependence of $\pi_{1/2}$ on pH is expressed by a straight line according to the equation $\pi_{1/2} = -1.180 - 0.040 \lg a_{OH^-}$ (Fig. 4, *III*). In this case the complex obtained has the composition $[Sb(OH_2)_{p-2}(OH)_2]^+$, $K_c = 10^{-47}$. The same results can be obtained if the solutions are heated beforehand. When the solutions stand, the precipitate continuously increases and the wave

Fig. 4

Figure 4: Fig. 4

height decreases. This occurs more rapidly in more alkaline solutions (at pH above 12).

Study of the behavior of Sb^{+++} in strongly alkaline media

This region begins with the dissolution of the $Sb(OH)_3$ precipitate, which is associated with the formation of an alkaline salt of meta-antimonous acid. In strongly alkaline solutions, pH 14, a well-defined cathodic wave is obtained at $\pi_{1/2} = -1.270$ V and an anodic wave at $\pi_{1/2} = -0.355$ V, deformed by a peculiar maximum. The heights of the two waves are related to one another as $3:2$ (Fig. 3).

Fig. 4. Change in $\pi_{1/2}$ of hydroxo complexes of Sb^{+++} as a function of the pH of the solution. *a*—solutions containing 0.02 *N* NaF, *b*—solutions containing 0.2 *N* NaF, *c*—the same solutions after 48 h. For *I*, $\pi_{1/2} = -1.100 - 0.060 \lg a_{\mathrm{OH}^-}$; for *II*, $\pi_{1/2} = -1.150 - 0.020 \lg a_{\mathrm{OH}^-}$; for *III*, $\pi_{1/2} = -1.180 - 0.040 \lg a_{\mathrm{OH}^-}$.

The cathodic wave is analogous to the wave described by Kachirkova (^{2}) and by Kolthoff and Lingane (^{3}) in $1N$ NaOH. Since the concentration of F^- has no effect on it, it is clear that the electrode mechanism is the same:

$$\mathrm{SbO_2^- + 2H_2O + 3e = Sb^0 + 4OH^-}.$$

The anodic wave, in appearance and in the value of $\pi_{1/2}$, is analogous to that noted by Koch (^{4}) in alkaline tartrate solutions ($\pi_{1/2} = -0.360$ V). Since

in the absence of F^- the same results were obtained, we assume the anodic reaction:

$$\mathrm{SbO_2^- + 2OH^- = SbO_3^- + H_2O + 2e}.$$

Mechanism of transformation of individual complex forms of Sb^{+++} upon changing the pH of the solution

In a strongly acidic medium (up to pH 2-3), the F^- ions are bound in the form of HF and HF_2^-, while Sb^{+++} is free. With an increase in pH, the activity of F^- increases and conditions are created for the formation of $[SbF_6]^{---}$. It is stable until the ratio $a_{\mathrm{OH}^-}/a_{\mathrm{F}^-}$ becomes equal to 10^{-8}, after which its hydrolysis begins. First of all, the F^- ions are replaced by water molecules, which leads to the formation of $Sb(OH)_p$. The latter participates in the equilibrium

$$\mathrm{[Sb(OH_2)_p]^{+++} \rightleftarrows [Sb(OH_2)_{p-1}(OH)]^{++} + H^+},$$

which in an alkaline medium (pH from 8 to 11) is shifted to the right. The resulting complex is unstable and, on standing, decomposes according to the scheme

$$[\mathrm{Sb(OH_2)_{p-1}(OH)}]^{++} \rightarrow [\mathrm{Sb(OH_2)_{p-2}(OH_2)}]^{+} \rightarrow [\mathrm{Sb(OH_2)_{p-3}(OH)_3}] \rightarrow \mathrm{Sb(OH)_3} \downarrow .$$

Therefore, in freshly prepared solutions, large amounts of $[\mathrm{Sb(OH_2)_{p-1}(OH)}]^{++}$ and negligible amounts of $[\mathrm{Sb(OH_2)_{p-3}(OH)_3}]$ are observed. The presence of small amounts of $[\mathrm{Sb(OH_2)_{p-2}(OH)_2}]^{+}$ is also possible, but the latter does not give an independent wave, since its $\pi_{1/2}$ value is very close to that of $[\mathrm{Sb(OH_2)_{p-1}(OH)}]^{++}$. On standing, dissociation proceeds with the elimination of water; moreover, the transition from the second to the third stage occurs most slowly, and measurable amounts of $[\mathrm{Sb(OH_2)_{p-2}(OH)_2}]^{+}$, which gives an independent wave, already predominate in the solution.

The observed hydro- and hydroxy complexes are unstable and may be considered only as intermediate forms in the hydrolysis of $[\mathrm{SbF_6}]^{---}$. They are obtained only if one starts from the prepared complex. Thus, the presence of F^- ions is obligatory, although they do not take direct part in the formation of the hydroxy complex.

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CITED LITERATURE

1. P. W. West, I. F. Dean, E. I. Breda, *Collection*, **13**, 1 (1948).
2. K. Kacirkowa, *Collection*, **1**, 477 (1929).
3. . . , . . , , M., 1948, p. 256.
4. D. Cozzi, *Anal. Chim. Acta*, No. 4, 204, 300 (1950).

Note: Figure translations are in progress. See original paper for figures.