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Abstract

Full Text

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M. Usanovich, V. Klimov, and T. Sumarokova

ON THE ELECTROLYTIC DISSOCIATION OF COMPLEX COMPOUNDS OF TIN AND ANTIMONY

(Presented by Academician I. I. Chernyaev, 25 X 1956)

The appearance of electrical conductivity in systems consisting of nonconducting components is associated with acid-base interaction, as a result of which complex compounds of a salt-like character are formed (1-3). When halides of tetravalent tin and trivalent antimony (arsenic) are mixed with monocarboxylic acids of the fatty series and their esters, electrolytes of the general formula are formed:

$$\mathrm{SnX_4 \cdot 3RCOOR'}, \quad \mathrm{SnX_4 \cdot 4RCOOR'}, \quad \mathrm{SbX_3 \cdot RCOOR'}, \quad \mathrm{2SbX_3 \cdot RCOOR'},$$

where R′ is hydrogen or an aliphatic radical; X is Cl or Br.

The electrolytic dissociation of these compounds, in our opinion (4, 5), proceeds as follows:

$$1. \quad \mathrm{SnX_4 \cdot 2RCOOR' + RCOOR' \rightleftharpoons [SnX_4(RCOO)_2]R'^{-} + RCOO'^{+}_{2}}.$$

$$2. \quad \mathrm{SnX_4 \cdot 2RCOOR' + 2RCOOR' \rightleftharpoons [SnX_4(RCOO)_2]^{--} + 2RCOOR'^{+}_{2}}.$$

$$3. \quad \mathrm{SbX_3 + RCOOR' \rightleftharpoons [SbX_2 \cdot RCOOR']^{+} + X^{-}}.$$

$$4. \quad \mathrm{2SbX_3 + RCOOR' \rightleftharpoons [SbX_2RCOOR']^{+} + [SbX_4]^{-}}.$$

It follows from equations 1 and 2 that, in the complex compounds $\mathrm{SnX_4 \cdot 3RCOOR'}$ and $\mathrm{SnX_4 \cdot 4RCOOR'}$, the organic molecule is included in both the cation and the anion, while the halide of tetravalent tin is included only in the anion. In the complex compounds of trivalent antimony the organic molecule is included in the cation (equations 3 and 4).

To verify the schemes of electrolytic dissociation of these complex compounds, ion transfer was studied in the systems

$$SnCl_4—CH_3OH, \quad SnCl_4—CH_3COOC_5H_{11}, \quad SnCl_4—CH_3COOC_2H_5, \quad SbCl_3—CH_3COOH,$$

in which the organic component contained the isotope C^{14}.

The results of experiments on the electrolysis of solutions of stannic chloride in methyl alcohol, acetic acid, and ethyl acetate showed that, under the action of an electric current, in all cases stannic chloride is transported to the anode, while the organic molecules move both to the anode and to the cathode. Thus, we have established that stannic chloride is part of the anion, while CH_3OH, CH_3COOH, and $CH_3COOC_2H_5$ are included in both the cation and the anion. These results are in agreement with equations 1 and 2.

During the performance of the present work, two articles appeared ([6], [7]) devoted to the same question. The authors of these works proposed their own schemes of electrolytic dissociation. Common to these schemes is the assumption that the formation of complex compounds is an addition reaction, i.e., that the molecule of the organic substance enters into the complex cation. However, our experiments on ion transfer in systems in which the organic component contained the isotope C^{14} refute these schemes.

Experiments on the transport of ions in the system $SbCl_3—CH_3COOH$, in which CH_3COOH contained the isotope C^{14}, showed that CH_3COOH is transported only toward the cathode. The results of the experiments, in agreement with equations 3 and 4, show that the complex compounds of antimony (and arsenic) trihalides with organic oxygen-containing substances, unlike the compounds of the same organic substances with tin tetrahalides, are addition products ([1]).

In electrolysis experiments on the $SbCl_3—CH_3COOH$ system, wishing to trace the fate of the molecule of the organic substance under the influence of an electric current, we, in addition to using CH_3COOH labeled with C^{14}, also added a dye—methyl red—to the solution. It was thereby established, as we had expected, that methyl red moves in the same direction as the labeled CH_3COOH, i.e., toward the cathode. Thus, from the experiments with the dye it is clearly evident that the molecule of the organic substance is transported to the cathode, i.e., enters into the composition of the cation, as is expressed by equations 3 and 4.

Institute of General and Inorganic Chemistry
named after N. S. Kurnakov
Academy of Sciences of the USSR

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