ELECTROLYTIC DISSOCIATION IN ANHYDROUS SYSTEMS

I. STANNIC CHLORIDE-ETHYL ACETATE

S. P. Miskidzhyan

Numerous complex compounds found by physico-chemical methods of analysis in various bi-component systems have been defined in the general form, $nA \cdot mB$, owing to a lack of data regarding their structures. As examples, such known complex compounds as $C_3H_5CNS \cdot C_5H_{10}NH$; $C_6H_5NH_2 \cdot 2CH_3COOH$ and many other molecular compounds discovered by Academician N. S. Kurnakov and his students, can be cited.

Of special interest are those instances of complex formation wherein the components from which the complex compound is formed are non-electrolytes, while the complex compound resulting from them is a good conductor of the electric current. The above-mentioned compounds can be referred to as examples. Thus, the specific electroconductivity isotherm for the aniline-acetic acid system, studied for the first time by D. P. Konovalov [1], possesses a sharply-pronounced maximum, corresponding to the composition of the compound formed in the system. In like manner, corrected electroconductivity diagrams for such systems as allyl mustard oil-piperidine, and others, can be mentioned, from which it can be determined that the complex compound forming in the system is an electrolyte.

A clarification of the type of electroconductivity of similar complex compounds is of interest since it permits a clarification not only of the mechanism of electrolytic dissociation for these compounds, but also because it permits determination, to some degree, of the structures of these complexes, since, up to the present time, there can be found no data on the structures for a majority of the compounds in question.

A study of the electrolytic dissociation in anhydrous systems is also of considerable practical value for a clarification of the mechanisms of electrochemical processes for the industrial synthesis of a variety of products by electrolysis in organic solvents.

The author has selected stannic chloride-ethyl acetate, the viscosity of which and the electroconductivity of which have been studied by N. S. Kurnakov and E. B. Shternina [2]. According to these investigations, the system forms a complex compound of the composition $SnCl_4 \cdot 2CH_3COOC_2H_5$. Formation of such a compound is indicated by a sharply-defined maximum on the viscosity isotherms, the heats of combination, and the minimum on the electroconductivity diagram for this system [3, 4]. If one neglects the viscosity effect, then there will result on the electroconductivity diagram a maximum at approximately the composition of the compound, i.e., at 33.3 mole % stannic chloride, indicated by a high electroconductivity for the chemical compound formed in the system. As is known, none of the components of this system will conduct the electric current. Thus, for example, the specific electroconductivity for ethyl acetate and stannic chloride is $\kappa < 10^{-9} \Omega^{-1} cm^{-1}$. It seemed to the author, therefore, that a study of the electrolytic dissociation mechanism and the nature of the conductivity of the compound could lead to a determination of a structure for the complex.

EXPERIMENTAL

To study the nature of conductivity of the electric current, electrolysis of the above-indicated complex compound was carried out with various mixtures of this system, followed by investigation of the composition and some of the physical properties of the liquid areas around the anode and the cathode, before and after electrolysis.

Electrolysis was carried out in an H-shaped vessel with platinum electrodes, where the cathode space was separated from the anode. A lamp rectifier with terminal voltage of 300 V served for the current source. To measure the amount of electricity, a copper coulometer was switched into the circuit. The current strength fluctuated from 2 to 5 mA at the start of the experiment, and from 15 to 20 mA at the end. Duration of experiments lasted from 8 to 48 hours. Temperature varied from 16 to 19°.

Chemical analysis of the composition of the mixture and of liquid in the anodic and cathodic areas after the electrolysis was carried out as follows. The quantity of tetravalent tin was determined by precipitating it in the form of hydroxide, and subsequent calcining to SnO_2 [5]. The quantity of ethyl acetate in the run was calculated by weight difference in tin tetrachloride for the run. A preliminary control determination indicated that the presence of ethyl

acetate does not interfere with tin determination. Tin tetrachloride was obtained by passing chlorine through chemically-pure tin foil [6]. The resulting tin tetrachloride was distilled. The fraction boiling at 112-114° was taken for the work. Density of the preparation obtained at 0° was 2.276. To prepare the second component, the author used ready-prepared, chemically-pure ethyl acetate, which had been kept over anhydrous sodium acetate and sodium carbonate for several days, and distilled with precautionary measure against access of moisture. The fraction boiling at 76-77.5° was collected. Density of the distilled ethyl acetate was 0.9002 at 20°, and the refractive index at the same temperature was 1.3722.

Two initial mixtures were prepared for the investigation: first, from 20 mole % tin tetrachloride and 80 mole % ethyl acetate, and the second mixture of 60 mole % tin tetrachloride and 40 mole % ethyl acetate. A mixture of such composition was taken because such ratios of components corresponded to the maximum electroconductivity for this system.

Preparation of these mixtures was carried out in an H-shaped vessel, as was done by N. S. Kurnakov [3]. In such a vessel gradual mixing of the components, and of cooling, is assured, since otherwise the mixture evolves heat spontaneously due to the heat of chemical reaction, and leads to a partial resinification.

Electrolytic data are given in Table 1 for various mixtures of the system studied by the author, along with the analytical results of liquids at the anodic and cathodic areas, after electrolysis.

TABLE 1

Expt. No.	$SnCl_4$ content in the mixture before electrolysis (in weight %)	$SnCl_4$ content after electrolysis (in %)				Amount of electrolyte passed through the solution (in coulombs)
		in liquid of the anode space	change	in liquid of the cathode space	change	
1	46.91	50.11	+3.60	–	–	318
2	39.10	50.56	+11.46	27.13	−11.97	753
3	39.10	44.76	+5.66	28.41	−10.79	676
4	44.23	48.41	+4.18	38.26	− 5.97	520
5	80.77	84.50	+3.73	80.31	− 0.46	250

There is given in the second column of the Table the composition of the initial mixtures found on the basis of chemical analysis.

The following phenomena were observed during electrolysis:

1) directly following switch-on of the current, accumulation of a gray precipitate of metallic tin occurred at the cathode;

2) at the completion of electrolysis, current increased markedly, due to heating of the liquid at the expense of Joules of heat at the cathode, at which a white precipitate separated, which, by chemical analysis, proved to be $SnCl_2$;

3) evolution of gas bubbles was not observed at the anode; some evolution of gas bubbles was observed at the cathode at the end of an experiment in some cases (when electrolysis had been continued for a long time).

On the basis of Table 1 data, and observations during electrolysis, the following assumptions can be made with regard to the mechanism of electrolytic dissociation of the complex compound in the system, and with regard to the electrochemical processes occurring at the anode and cathode during electrolysis.

1. Apparently, molecules of the complex compound in the system are associated, and are in the form of $(SnCl_4 \cdot 2CH_3COOC_2H_5)_n$. This is indicated by the presence of a sharp maximum on the viscosity isotherm for this system, which occurs at a composition of 1:2, i.e., at the composition of the complex compound forming in the system. On the other hand, the viscosity of the complex compound exceeds by about 250-fold the viscosity of the most viscous of the components, which, in all probability, is related to an association phenomenon for the complex compound molecules. A. N. Sakhanov [7] pointed out formation of associated complex compounds in current-conducting systems.

2. If the presence of association of complex compound molecules is assumed to be possible for the system, then the main process of electrolytic dissociation can be represented in the following manner:

$$(SnCl_4 \cdot 2CH_3COOC_2H_5)_2 \rightleftharpoons [Sn(CH_3COOC_2H_5)_4Cl_2]^{++} + [SnCl_6]^{--}$$

In this case we take the position that aggregated molecules with a high number, n, break down into smaller aggregates, where n = 2.

Along with this main process, there apparently proceeds, although on a small scale, a further electrolytic dissociation of the cation according to the following scheme:

$$[Sn(CH_3COOC_2H_5)_4Cl_2]^{++} + SnCl_4 \rightleftharpoons [Sn(CH_3COOC_2H_5)_4]^{++++} + [SnCl_6]^{--}$$

3. With electrolysis at the electrodes, the following electrochemical processes apparently take place.

At the cathode. At the start of electrolysis, when the ions obtained at the expense of the second dissociation stage are sufficient in number, metallic tin separates at the cathode according to the following reaction:

$$[Sn(CH_3COOC_2H_5)_4]^{++++} + 4e \rightarrow Sn + 4CH_3COOC_2H_5.$$

At high current densities, when there is a shortage of tin ions due to the small rate of electrolytic dissociation of the second stage, $SnCl_2$ separates at the cathode according to the following reaction:

$$[Sn(CH_3COOC_2H_5)_4Cl_2]^{++} + 2e \rightarrow 4CH_3COOC_2H_5 + SnCl_2.$$

The following facts serve to confirm the indicated processes:

a) Separation of metallic tin at the cathode.

b) Separation of $SnCl_2$ as a white precipitate at the cathode; the phenomenon of simultaneous separation of the metal and the salt of the metal at the cathode is known in the literature. Thus, for example, Watkins and Denham [8] indicated the fact that upon electrolysis of aqueous or alcoholic solutions of cupric chloride or bromide, the precipitates were composed of a heterogeneous mixture of copper with copper halide, where the quantity of halide was greater in proportion as the current density was greater. Gore [9], electrolyzing a hydrochloride solution of antimony trichloride, found up to 5% $SbCl_3$ in the metallic precipitate of antimony.

c) The increase in percentage composition of ethyl acetate in the liquid of the cathode space after electrolysis, occurs because of a break-down of the complex ions

$$[Sn(CH_3COOC_2H_5)_4]^{++++} \text{ and } [Sn(CH_3COOC_2H_5)_4Cl_2]^{++}$$

during their discharge at the cathode.

At the anode. The anion discharge apparently proceeds as follows:

$$[SnCl_6]^{--} \rightarrow SnCl_4 + 2Cl + 2e.$$

Atomic chlorine at the moment of evolution enters into reaction with a molecule of ethyl acetate and chlorinates the methyl group:

$$CH_3COOC_2H_5 + 2Cl \rightarrow CH_2ClCOOC_2H_5 + HCl.$$

This assumption appears more probable if there be taken into consideration the literature data [10] with the fact that $SnCl_4$ is found to be a catalyst for chlorination of certain organic compounds. The hydrogen chloride evolved during chlorination interacts with $SnCl_4$ forming

$$2HCl + SnCl_4 \rightleftharpoons H_2SnCl_6.$$

This compound, and perhaps HCl also, has apparently accumulated by the end of the experiment in adequate amount for self-electrolysis to take place according to the reaction:

$$H_2SnCl_6 \rightleftharpoons 2H^+ + SnCl_6^{--}$$

or

$$HCl \rightleftharpoons H^+ + Cl^-,$$

by which time the evolution of gas bubbles at the cathode is limited.

As proof of the fact that the above-indicated reaction occurs at the anode, can be cited the following data: a) a noticeable increase in the stannic chloride content for the liquid of the anode space after electrolysis (Table 1); no evolution of gaseous chlorine at the anode, due to reaction with ethyl acetate molecules, as confirmed by the presence in the ether extract of an organic compound having in its composition chloride ion extracted from the aqueous solution of the anodic space liquid (after electrolysis). Chlorine was found by both the Beilstein method, and by reacting the organic substance with metallic sodium, and subsequent identification of chloride ion by use of silver nitrate.

In order to remove doubt that the chlorine could have gotten into the extracted substance from the aqueous medium where $SnCl_4$ and HCl are present in sufficient amounts, an analogous extraction from initial liquid was carried out, i.e., from the mixture before electrolysis; in this case both tests for chloride were negative.

Another proof of HCl formation in the anode space is given by the fact that the chloride ion precipitated with silver nitrate from the anode area liquid (after electrolysis) using the theoretical quantity of silver nitrate dissolved in water, the required amount of silver nitrate is noticeably greater than that required by calculating on the basis of tin tetrachloride content in the mixture. If the quantity of electricity passed through the solution is accounted for, and the amount of HCl taken into account, which could have been formed in this manner, the correspondence is then approximately in accord with the excess silver nitrate used to precipitate the chloride ions.

Electrolysis of the second of the initial mixtures proceeds, on the whole, as with electrolysis of the first mixture. The difference consists in the fact that in this case a gray precipitate separates (metallic tin) to a considerably greater extent than in the first case. This is explained by the fact that with an excess of tin tetrachloride molecules, the second stage of electrolytic dissociation:

$$[Sn(CH_3COOC_2H_5)_4Cl_2]^{++} + SnCl_4 \rightleftharpoons [Sn(CH_3COOC_2H_5)_4]^{++++} + [SnCl_6]^{--}$$

proceeds with considerably greater slowness.

Some additional proofs of the above-given electrochemical processes proceeding at the anode and cathode during electrolysis of mixtures of the system studied by the author were obtained when a number of physico-chemical constants for the initial mixture and for the anode and cathode area liquids after electrolysis were determined.

In Table 2 there are given the density and apparent molecular weights for the liquids of the anode and cathode area before and after electrolysis.

It can be seen from data given in this table that the density for the mixture in the anode area after electrolysis increases, and decreases in the cathode area. This is in agreement with a clarification of the electrode processes given above. An increase in density of the anode area liquid is caused by the increase in percent content of tin chloride after electrolysis, the density of which is approximately 2-fold greater than the density of the initial mixture.

TABLE 2

Content of $SnCl_4$ in the mixture (weight %)	Density d^{25}			Apparent molecular weight, M			Amount of electricity passed (in coulombs)
	before electrolysis	after electrolysis		before electrolysis	after electrolysis		
		anode area	cathode area		anode area	cathode area	
44.23	1.3470	1.4654	1.2526	281.5	511.4	224.5	520
80.77	1.8570	1.8789	1.8121	334.8	479.4	332.5	250

Decrease in density of the cathode area liquid is related to the increase in percent content of ethyl acetate after electrolysis as a result of the discharge of complex cations. With regard to the apparent molecular weight (measured cryoscopically in benzene solvent), here again, the sharp increase in apparent molecular weight of anode area liquid after electrolysis is explainable by the fact that the $SnCl_6^{--}$ ions, being discharged at the anode, form an additional amount of tin tetrachloride. The latter, by entering into combination with ethyl acetate which is present in excess (in the case of the 20 mole % stannic chloride mixture) forms new molecules of the complex compound: $(SnCl_4 \cdot 2CH_3COOC_2H_5)_n$, the molecular weight of which is much greater than that of the initial mixture.

A noticeable decrease in apparent molecular weight for the cathode area liquid after electrolysis is explainable on the basis that upon destruction of the complex cations $[Sn(CH_3COOC_2H_5)_4]^{++++}$ and $[Sn(CH_3COOC_2H_5)_4Cl_2]^{++}$, the amount of ethyl acetate increases, the molecular weight of which is relatively small.

SUMMARY

1. Electrolysis of a mixture of stannic chloride and ethyl acetate has been carried out.

2. On the basis of data obtained by chemical analysis of liquids at the anode and cathode area, before and after electrolysis, and on the basis of measurements of a series of physico-chemical properties for these liquids, a conclusion has been made concerning the mechanism of dissociation of the complex compound.

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Received May 20, 1953.

Lvov Medical Institute, Biochemistry Department