SELENIUM OXYCHLORIDE AS A SOLVENT[1]

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I. INTRODUCTION

The concept of solvo-systems which Franklin (7, 8) applied with such spectacular success to liquid ammonia has been extended in somewhat modified forms in more recent years to a number of other solvents. Among these researches the following studies of solvents have peculiar significance in connection with this paper: (*1*) acetic acid by Davidson and his coworkers (2, 3, 4, 5), (*2*) hydrogen sulfide by Wilkinson and Quam (27, 28, 33), (*3*) sulfuric acid by Kendall, Davidson, and others (19, 20), (*4*) hydroxylamine by Audrieth (1), (*5*) phosgene by Germann (10, 11), and (*6*) sulfur dioxide by Jander and his coworkers (13, 14, 15, 16, 17). The most recently reported studies are of especial interest to the author, since Jander's views are so closely in accord with those expressed in this paper.

It will be recognized, therefore, that there is gradually being accumulated a body of facts from which general similarities of behavior may be recognized. Kahlenberg's view that a solution is "a chemical compound which does not obey the law of definite proportions" is a qualitative one, but it provides a basis for rational chemical approach to the problem. There can be, from the broad point of view of a modern inorganic chemist, no serious question that when a solute dissolves in a solvent a chemical change occurs. (The ideal solution is analogous to the ideal gas.) The nature of this chemical change is intimately related in many instances at least to the tendency of the solute to act either as an electron pair donor or as an electron pair acceptor toward the solvent. If the solvent is polar the formation of complex ions may be expected. Many "definitions" of acid have been proposed. The Brønsted statement has been the one most generally accepted in the last few years, but it is by no means of "universal"

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[1] This paper is respectfully dedicated by the author to the late Professors Victor Lenher and Edward Curtis Franklin in appreciation of the continuing inspiration of their extensive and classical work in the fields reviewed here. It was presented at the Second Annual Symposium of the Division of Physical and Inorganic Chemistry of the American Chemical Society, held at Cleveland, Ohio, December 27–29, 1937.

application. The author proposes the following as useful and rational broad definitions for the terms "acid" and "base": *A solute is an acid when its molecule (neutral or charged) is an electron pair acceptor toward the molecule or an ion of the solvent;* on the other hand, *a solute is a base when its molecule (neutral or charged) is an electron pair donor toward the molecule or an ion of the solvent.* These statements are similar to the Brønsted statement but they are more universal, since they permit application to solvents other than "hydrogen" solvents.

The fundamental concept which is expressed in the above definitions was stated very clearly and concisely by Gilbert N. Lewis (24) in 1923 in his monograph on "Valence and the Structure of Atoms and Molecules."

> "We are inclined to think of substances as possessing acid or basic properties, without having a particular solvent in mind. It seems to me that with complete generality we may say that a basic substance is one which has a lone pair of electrons which may be used to complete the stable group of another atom, and that an acid substance is one which can employ a lone pair from another molecule in completing the stable group of one of its own atoms. In other words, the basic substance furnishes a pair of electrons for a chemical bond, the acid substances accept such a pair."

Walden (31) gives an excellent review of acid–base concepts and points out that the Lewis views have not been accepted generally because classical dissociation constants "become meaningless" and other acid–base characteristics appear to be "purely incidental observations." The author, however, believes that the Lewis view is useful in working in the field of non-aqueous solutions (particularly in non-hydrogen solutions) and he also believes that the use of such a term as "pseudo-acid" is unnecessary.

This paper will outline the selenium oxychloro solvo-system of compounds. The unusual interest in the classical investigations on selenium oxychloride by Lenher (18, 22, 26, 29) and his coworkers at the University of Wisconsin was due to the demonstrated reactivity of this compound toward very many substances. Thus most of the published papers on selenium oxychloride deal with the substance as a reagent rather than as a solvent as this term is usually understood.

Selenium oxychloride has a dielectric constant which approaches the same order of magnitude as the dielectric constant of water.[2] The high conductance, 2×10^{-5} mhos (18), indicates that the ion concentration of the pure liquid is relatively very high. In this respect it is similar to sulfuric

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[2] Wildish measured the dielectric constant and reports 46 at 20°C. (32). This higher value is the result obtained from some preliminary observations made by Dr. Eric Ackerland in the Research Laboratory of Electrical Engineering of the Polytechnic Institute of Brooklyn.

acid, and this property is probably related to the fact that these solvents are powerful solvolyzing agents.

II. IONIZATION

In table 1 the ionization of selenium oxychloride is postulated. This ionization is similar to the ionization of other typical solvents, as becomes apparent when we compare these several equations. This postulation for the ionization (autoionization) of selenium oxychloride is based upon the following evidence: (*a*) the conductance of the pure liquid, (*b*) the products formed when solutions are subjected to electrolysis, (*c*) the products formed when a metal reacts with selenium oxychloride, (*d*) the composition of solvates of selenium oxychloride, such as stannic chloride disolvate and pyridine monosolvate, and (*e*) the metathetical reactions which have been carried out in selenium oxychloride solutions. It is admitted that this evidence is all indirect. This is true likewise of all evidence in support of postulations regarding ionization.

TABLE 1

Ionization of various solvents

$$
\begin{aligned}
2SeOCl_2 &\rightleftharpoons (SeOCl\cdot SeOCl_2)^+ + Cl^- \\
2H_2O &\rightleftharpoons (H_3O)^+ + (OH)^- \\
2NH_3 &\rightleftharpoons (NH_4)^+ + (NH_2)^- \\
2HC_2H_3O_2 &\rightleftharpoons (H_2C_2H_3O_2)^+ + (C_2H_3O_2)^- \\
2H_2SO_4 &\rightleftharpoons (H_3SO_4)^+ + (HSO_4)^- \\
2COCl_2 &\rightleftharpoons (COCl\cdot COCl_2)^+ + Cl^{-*} \\
\text{or } COCl_2 &\rightleftharpoons (CO)^{++} + 2Cl^- \qquad \text{(Germann)} \\
2SO_2 &\rightleftharpoons (SO)^{++} + (SO_3)^{--} \qquad \text{(Jander)} \\
\text{or } 4SO_2 &\rightleftharpoons (SO\cdot 2SO_2)^{++} + (SO_3)^{--\dagger}
\end{aligned}
$$

* The author believes that primary rather than secondary ionization predominates, and the probable electronic configuration suggests solvation of the cation.

† Solvation of the doubly charged cation SO^{++} follows quite logically from a consideration of the probable electronic structure.

III. ELECTROLYSIS

The conductance of selenium oxychloride is so low that it is not convenient to electrolyze the pure liquid. However, electrolytic decomposition of the substance does yield chlorine at the anode, and the liquid around the cathode becomes reddish brown, which indicates that selenium monochloride is formed.

A solution of potassium chloride (saturated at room temperature) (30) was electrolyzed for 90 min. Chlorine was liberated at the anode, and selenium dioxide was precipitated in the neighborhood of the cathode.

The solution around the cathode became red brown in color, and when a portion was treated with water elementary selenium was deposited.

A solution of stannic chloride in selenium oxychloride when subjected to electrolytic decomposition likewise yielded chlorine at the anode and selenium dioxide and selenium monochloride at the cathode. Accordingly we may formulate the equation for the electrolytic decomposition of selenium oxychloride as follows:

$$\text{anodic} \quad 2\,Cl^- - 2\ominus \rightarrow Cl_2$$

$$\text{cathodic} \quad 6(SeOCl)^+ + 6\ominus \rightarrow 6SeOCl$$

$$6SeOCl \rightarrow 2SeO_2 + Se_2Cl_2 + 2SeOCl_2$$

In table 2 these reactions are compared with those of water, ammonia, and phosgene.

TABLE 2

Comparison of electrolysis of water, ammonia, phosgene, and selenium oxychloride

SOLVENT	CATHODIC REACTION	ANODIC REACTION
Water.....	$2(H_3O)^+ + 2\ominus \rightarrow H_2 + 2H_2O$	$4(OH)^- - 4\ominus \rightarrow 2H_2O + O_2$
Ammonia..	$2(NH_4)^+ + 2\ominus \rightarrow H_2 + 2NH_3$	$6(NH_2)^- - 6\ominus \rightarrow 4NH_3 + N_2$
Phosgene..	$2(COCl \cdot COCl_2)^+ + 2\ominus \rightarrow CO + 3COCl_2$	$2Cl^- - 2\ominus \rightarrow Cl_2$
Selenium oxychloride.	$6(SeOCl \cdot SeOCl_2)^+ + 6\ominus \rightarrow 2SeO_2 + Se_2Cl_2 + 2SeOCl_2$	$2Cl^- - 2\ominus \rightarrow Cl_2$

IV. ACTION ON METALS

The action of selenium oxychloride on several metals has been studied by W. L. Ray (29). Copper, lead, cobalt, nickel, iron, tin, and silver yield the chlorides of the metals, selenium dioxide, and selenium monochloride. Ray formulated the reaction of copper and selenium oxychloride as follows:

$$3Cu + 4SeOCl_2 \rightarrow 3CuCl_2 + Se_2Cl_2 + 2SeO_2$$

Ray's analytical data may be explained by the following formulation, which is in accordance with the electrolytic decomposition:

$$3Cu + 6SeOCl^+ \rightarrow 3Cu^{++} + Se_2Cl_2 + SeO_2 + 2SeOCl_2$$

$$3Cu^{++} + 6Cl^- \rightarrow 3CuCl_2$$

This action with copper demonstrates that the selenium oxychloro ion is a powerful oxidizing agent, and this fact accounts in part at least for the reactivity of selenium oxychloride. (For comparison see table 3.)

Erickson (6) compared qualitatively the action of selenium oxychloride and the action of a 20 per cent solution of stannic chloride in selenium oxychloride on the following metals: magnesium, calcium, lead, mercury, copper, zinc, and sodium. It was observed that in general the metals are more reactive and more soluble in the solution of stannic chloride than in selenium oxychloride alone. These observations are analogous to those of Germann (10) on the action of a solution of aluminum chloride in phosgene on metals as compared with the action of phosgene alone. Stannic chloride is to be regarded as an acid of the selenium oxychloro system.

Another series of experiments showed that the solubilities of barium chloride, calcium chloride, and potassium chloride were greater in a solution of stannic chloride in selenium oxychloride than in selenium oxychloride alone (*vide infra*).

TABLE 3

Comparison of action of metals on water, ammonia, phosgene, and selenium oxychloride

SOLVENT	REACTION
Water	$2M' + 2H_3O^+ \rightarrow H_2 + 2M^+ + 2H_2O$
Ammonia	$2M' + 2NH_4^+ \rightarrow H_2 + 2M^+ + 2NH_3$
Phosgene	$2M' + 2COCl \cdot COCl_2^+ \rightarrow CO + 2M^+ + 2COCl_2$
Selenium oxychloride	$6M' + 6SeOCl \cdot SeOCl_2^+ \rightarrow 2SeO_2 + Se_2Cl_2 + 6M^+ + 8SeOCl_2$

TABLE 4

Disolvates formed from selenium oxychloride and certain chlorides

ANALYTICAL FORMULAS	RATIONAL FORMULAS
$TiCl_4 \cdot 2SeOCl_2$	$(SeOCl)_2^{++}$ $TiCl_6^{--}$
$SnCl_4 \cdot 2SeOCl_2$	$(SeOCl)_2^{++}$ $SnCl_6^{--}$
$SiCl_4 \cdot 2SeOCl_2$	$(SeOCl)_2^{++}$ $SiCl_6^{--}$
$FeCl_3 \cdot 2SeOCl_2$	$(SeOCl)_2^{++}$ $FeCl_5^{--}$

V. ELECTRON PAIR ACCEPTORS (ACIDS)

In selenium oxychloride, chlorides of non-metals or of amphoteric elements are to be regarded as acids. Several chlorides which are soluble in selenium oxychloride separate from supersaturated solutions as solvates (34). Titanium tetrachloride, tin tetrachloride, silicon tetrachloride, and ferric chloride all form disolvates. If these substances are formulated in accordance with the usual ionic forms we find that this formulation is consistent with the postulation regarding the autoionization of the parent solvent (see table 4). Many oxides are solvolyzed by selenium oxychloride, but several appear to dissolve. Lenher (22) demonstrated the powerful solvent action of a solution of sulfur trioxide in selenium oxychloride. It is evident from our studies that this solution is a chlorosulfonic acid of the selenium oxychloro system $(SeOCl)(SO_3Cl)$. Molybdic oxide likewise appears as an acid when dissolved in selenium oxychloride:

$$(SeOCl)(MoO_3Cl) \text{ or } (SeOCl)_2(MoO_3Cl_2)$$

Stannic chloride acts as an electron pair acceptor toward chloride ions as follows:

$$SnCl_4 + 2Cl^- \rightarrow SnCl_6^{--}$$

and sulfur trioxide behaves in a similar manner:

$$SO_3 + Cl^- \rightarrow SO_3Cl^-$$

Chemists have been familiar with these ions for a long time.

Arsenic trichloride dissolves to an unlimited extent in selenium oxychloride, and the behavior of this solution is typical of an acid of this system, $(SeOCl)AsCl_4$. No solid phases have been observed.

VI. ELECTRON PAIR DONORS (BASES)

Ammonia and selenium oxychloride

Ammonia is regarded as a typical base. The reaction of ammonia with water is formulated as

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

The primary reaction between ammonia and selenium oxychloride is regarded by us to be entirely analogous, as

$$NH_3 + SeOCl_2 \rightarrow NH_3SeOCl^+ + Cl^-$$

This material has only a limited solubility. When ammonia is passed into selenium oxychloride white platelets separate. However, this material undergoes progressive decomposition and its exact composition has not been established. The reaction was studied by allowing standard solutions of ammonia and of selenium oxychloride in carbon tetrachloride to react and, after separating the solid, the solution was analyzed for chlorine, ammonia, and selenium. These results indicated that the monoammonate was formed as a solid phase when less than 1 mole of ammonia was used. If more than 1 mole of ammonia was used a higher ammonate was also formed (23). Substituted ammonias which have been studied, with the exception of pyridine and quinoline, appear to undergo immediate solvolysis.

Pyridine and selenium oxychloride

Pyridine reacts with selenium oxychloride to form a monosolvate.[3] Selenium oxychloride (8.3 g.) was dissolved in 50 ml. of carbon tetrachloride and pyridine (3.9 g.) was dissolved in 50 ml. of carbon tetrachloride. The two solutions were added dropwise to 50 ml. of carbon tetrachloride cooled in an ice bath, while the reaction mixture was stirred. A white solid separated immediately. This solid was separated by filtration, and washed with carbon tetrachloride. Two portions were then taken. The first portion was dissolved in water and diluted to 1 liter, and this solution was analyzed for chloride ion, selenium, and pyridine. The second portion was placed in an Abderhalden oven and heated at 61°C. ($CHCl_3$) for 5 hr. The material was allowed to cool; a sample was weighed and analyzed for chloride ion, selenium, and pyridine. A second sample was prepared in the same manner, except that the solid was dried for a period of 21 hr. Analytical data are given in table 5. These facts prove that pyridine forms a simple "addition" compound with selenium oxychloride.

TABLE 5

Analytical data for the reaction product of selenium oxychloride and pyridine

SAMPLE	DATA			
Sample A: material moist with CCl_4:				
Se	0.0794	0.0774	0.0787	0.0768
AgCl	0.2811	0.2823	0.2818	0.2804
ml. of 0.1503 *N* NaOH	6.5	6.9	7.1	6.6
Average ratio Se:Cl:C_5H_5N	1:1.986:1.027			
	Se	Cl	C_5H_5N	
Sample A: material dried at 61°C. *in vacuo* (7 hr.):				
Calculated for $SeOCl_2 \cdot C_5H_5N$	32.24	28.96	32.31	
Found	31.60	28.24	31.11	
	31.70	28.24	30.70	
Sample B: material dried at 61°C. *in vacuo* (21 hr.):				
Found	31.81	28.61	32.97	
	31.81	28.56	31.57	
			32.41	
			33.46	

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[3] Studies on the reaction between selenium oxychloride and pyridine are now being carried on by Julius Jackson in this laboratory.

When taken in conjunction with the reactions of pyridine with stannic chloride, ferric chloride, etc., described in the next section of this paper they indicate conclusively that pyridine is an electron pair donor (base) toward selenium oxychloride. This reaction may be formulated as follows:

$$C_5H_5N + SeOCl_2 \rightarrow (C_5H_5N\ SeOCl)^+\ Cl^-$$

Quinoline and selenium oxychloride

Quinoline reacts with selenium oxychloride in a manner quite similar to that in which pyridine reacts. An addition compound is formed which may be explained by the following equation:

$$C_9H_7N + SeOCl_2 \rightarrow (C_9H_7N\ SeOCl)^+\ Cl^-$$

Therefore quinoline may be regarded as a base, because it is an electron pair donor toward the selenium oxychloro ion.

Water and selenium oxychloride

The Ditte compound $SeO_2 \cdot 2HCl$ is to be regarded either as a hydrate of selenium oxychloride ($H_2OSeOCl^+\ Cl^-$) or as dichloroselenious acid, ($H_2SeO_2Cl_2$). When water is dissolved in selenium oxychloride it acts as an electron pair donor toward the solvent and the increased conductance of the solution is due to the presence of $H_2OSeOCl^+$ ions and chloride ions. Labile protons account for the thermal decomposition of $SeO_2 \cdot 2HCl$, and these reactions may be formulated as follows:

$$H_2O \cdot SeOCl \cdot Cl \rightleftarrows H_2SeO_2Cl_2$$

$$H_2SeO_2Cl_2 \rightarrow 2HCl + SeO_2$$

$$H_2O \cdot SeOCl \cdot Cl \rightarrow H_2O + SeOCl_2 \qquad (12)$$

These characteristics of selenium oxychloride and water will be made the subject of a future communication.

Salts of strong metals and selenium oxychloride

Hydroxides of the alkali and alkaline earth metals are usually regarded as typical bases. On the basis of the definition which has been proposed sodium hydroxide is a salt which quite incidentally acts as a base in aquo solution. The molecule which is an electron pair donor is the charged molecule (the hydroxide ion). In an exactly analogous manner chlorides of the alkali and alkaline earth metals function as bases in selenium oxychloride, and the molecule which is an electron pair donor is the charged molecule (the chloride ion).

VII. REACTIONS IN SELENIUM OXYCHLORIDE SOLUTIONS

Calcium chloride and stannic chloride (precipitation)

Anhydrous calcium chloride was dissolved in a hot solution of stannic chloride in selenium oxychloride. When the solution was cooled crystals separated from it (6). These crystals were removed by filtration and washed with chloroform; the moist material was analyzed for tin, calcium, chloride ion, and selenium. Four samples were prepared; the details of their preparation are given in table 6. The atomic ratios were computed from the analytical data and are given in table 7. While these results do not show that a pure substance is formed, they do indicate that calcium chloride reacts with stannic chloride. The solid phase is probably a mixture of two or more of the possible calcium chlorostannates. Potassium chloride forms a precipitate with stannic chloride. This precipitate contains chlorine, potassium, and tin, but it has not been examined quantitatively. Other solid phases have been observed, also, and studies of these phases are projected.

TABLE 6

Preparation of samples

SAMPLE NO.	$SnCl_4$	$CaCl_2$ TAKEN	$SeOCl_2$ TAKEN
	grams	*grams*	*grams*
1	3.4	0.3	12.2
2	3.4	0.4	12.2
3	2.28	0.4	12.2
4	5.7	0.4	12.2

TABLE 7

Atomic ratios computed from the analytical data

SAMPLE NO.	TIN	CHLORINE	CALCIUM	SELENIUM
1	1.00	10.76	0.72	2.97
2	1.00	9.39	0.56	3.13
3	1.00	14.59	0.75	2.79
4	1.00	14.06	0.81	3.07
Calculated for $CaSnCl_6\cdot 3SeOCl_2$....	1.00	12.00	1.00	3.00

Conductance titrations

The conductance method has been employed to follow the course of reactions between substances dissolved in selenium oxychloride. Definite breaks in titration curves indicate that chemical changes occur. Seven typical titrations will be described.

Apparatus. The conductivity measurements were made employing a circuit similar to that used by Garman and Kinney (9). A glass conductivity cell with sealed-in platinum electrodes was used. The cover of the cell was of ground glass, and a stirrer and the tip of a buret were admitted through openings in the cover. A special 15-ml. buret graduated in 1/20 ml. was used. The buret was fitted with a ground-glass stopper, and a groove in the stopper could be made to correspond with a groove in the buret so that a small air passage was formed. Volumetric flasks of 10- and 15-ml. capacity were used for preparing standard solutions.

TABLE 8

*Experimental details of conductance titrations**

SYSTEM	BASE		ACID		TITRATION REAGENT	STOICHIOMETRICAL RATIOS INDICATED
	Weight	Volume of solution	Weight	Volume of solution		
	grams	*ml.*	*grams*	*ml.*		
C_5H_5N-$SnCl_4$	0.2043	12	1.3267	10	Acid	$2C_5H_5N$, $1SnCl_4$
C_5H_5N-$SnCl_4$	0.5000	13.5	0.3090	9	Base	$1C_5H_5N$, $2SnCl_4$ $1C_5H_5N$, $1SnCl_4$ $2C_5H_5N$, $1SnCl_4$ $3C_5H_5N$, $1SnCl_4$
KCl-$SnCl_4$	0.0912	12	0.9209	10	Acid	$1KCl$, $2SnCl_4$ $1KCl$, $1SnCl_4$
$CaCl_2$-$SnCl_4$	0.2881	15	0.2131	12	Base	$1CaCl_2$, $2SnCl_4$ $1CaCl_2$, $1SnCl_4$ $3CaCl_2$, $2SnCl_4$
C_5H_5N-$FeCl_3$	0.8173	14	0.3013	11	Base	$1C_5H_5N$, $1FeCl_3$ $2C_5H_5N$, $1FeCl_3$ $3C_5H_5N$, $1FeCl_3$
C_5H_5N-SO_3	0.4652	10	0.0971	12	Base	$1C_5H_5N$, $1SO_3$ $2C_5H_5N$, $1SO_3$
C_5H_5N-$AsCl_3$	0.3237	15	0.1963	12	Base	$1C_5H_5N$, $2AsCl_3$ $1C_5H_5N$, $1AsCl_3$ $2C_5H_5N$, $1AsCl_3$

* These data are from experimental studies made by Mr. Alvin Gordon. The author is pleased to acknowledge the assistance of Dr. Eric Ackerland, who helped in assembling the equipment. Mr. Lankau (21) and Mr. McGhie (25) had previously made numerous titrations using the familiar Kohlrausch equipment.

Procedure. Approximately 4 ml. of selenium oxychloride was placed in a tared 10- or 15-ml. volumetric flask, and the anhydrous chloride was added. The flask and contents were again weighed. When the anhydrous chloride had dissolved the solution was diluted to 10 or 15 ml. This solution, which was the titrating reagent, was transferred to the 15-ml. buret.

The solution to be titrated was prepared as follows: Approximately 4 ml. of selenium oxychloride was weighed in a tared weighing bottle, the anhydrous chloride was added, and the weighing bottle and contents were reweighed. The solution was transferred quantitatively to the conductivity cell. Additional selenium oxychloride was added in sufficient amounts to cover the platinum electrodes. The cell was placed in an oil bath, and the stirrer and buret were placed in position. The conductance of the solution was measured. Successive portions of the solution were then added from the buret, and the conductivities were measured after each addition. Typical data are presented graphically in figures 1 to 7. We will now take up a brief discussion of each system. Table 8 gives certain experimental details.

Pyridine and stannic chloride

A solution of pyridine in selenium oxychloride is an excellent conductor. The ions present to which we may attribute this conductance are probably the selenium oxychloropyridinium ions and the chloride ions. Curve 1 in figure 1 presents the data obtained when a solution of pyridine in selenium oxychloride was titrated with a solution of stannic chloride in selenium oxychloride. A single inflection in this curve occurs at the point where there were present in the solution approximately 2 moles of pyridine to 1 mole of stannic chloride. This may be attributed to the formation of secondary selenium oxychloropyridinium hexachlorostannate, and the equation for the molecular reaction may be formulated as follows:

$$2(C_5H_5NSeOCl)Cl + (SeOCl)_2(SnCl_6) \rightarrow (C_5H_5NSeOCl)_2(SnCl_6) + 2SeOCl_2$$

It is evident that the solution of pyridine is ionized to a marked degree and so the ionic reaction may be formulated as follows:

$$2(C_5H_5NSeOCl)^+ + 2Cl^- + (SeOCl)_2(SnCl_6) \rightarrow 2(C_5H_5NSeOCl)^+ + (SnCl_6)^{--} + 2SeOCl_2$$

or perhaps merely as follows:

$$2Cl^- + (SeOCl)_2(SnCl_6) \rightarrow (SnCl_6)^{--} + 2SeOCl_2$$

The decrease in conductance is attributed in part to dilution of the solution (since stannic chloride is a poorer conductor than pyridine), but more particularly to the replacement of chloride ion by hexachlorostannate ions.

Solutions of the same substances were employed in obtaining the data presented in figure 2. However, in this instance the reagent was the solution of pyridine and the conductance of the solution of stannic chloride was increased by the addition of the reagent. Concentrations of reactants were higher, and four inflections in the curve may be recognized. The following equations are presented to explain the experimental observations:

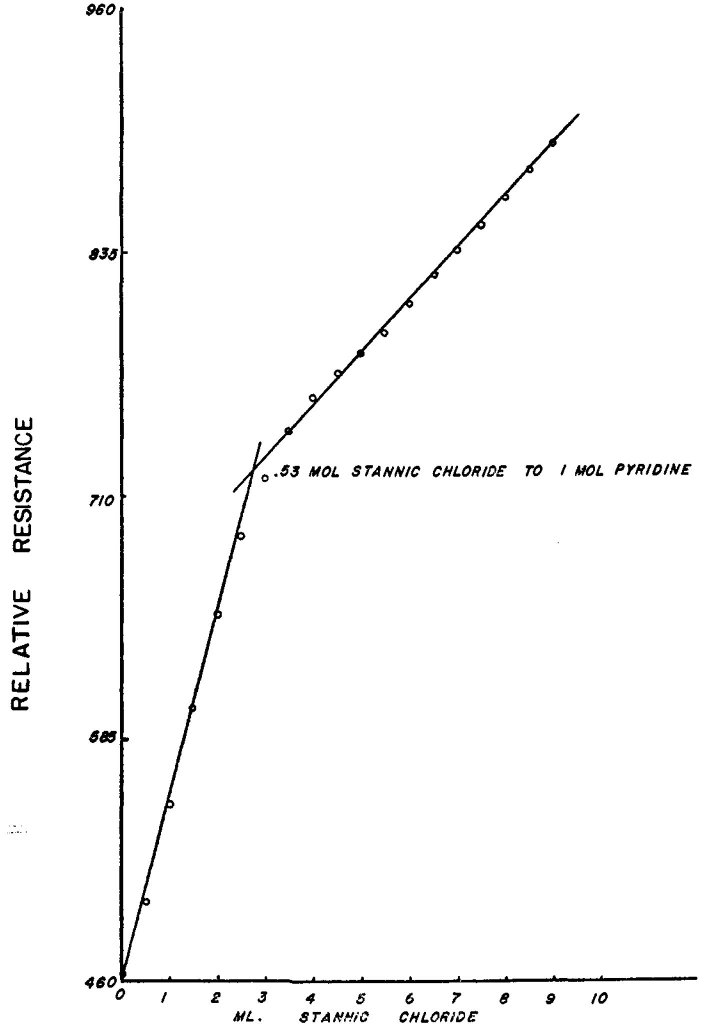

FIG. 1. Conductance titration of a solution of pyridine in selenium oxychloride with a solution of stannic chloride in selenium oxychloride.

$$2(\mathrm{SeOCl})_2\mathrm{SnCl}_6 + \mathrm{C_5H_5NSeOCl}^+ + \mathrm{Cl}^- \rightarrow (\mathrm{C_5H_5NSeOCl})^+ + (\mathrm{SeOCl})_3(\mathrm{SnCl_6})_2^- + \mathrm{SeOCl_2}$$

$$(\mathrm{SeOCl})_2\mathrm{SnCl}_6 + \mathrm{C_5H_5NSeOCl}^+ + \mathrm{Cl}^- \rightarrow (\mathrm{C_5H_5NSeOCl})^+ + (\mathrm{SeOCl})\mathrm{SnCl_6}^- + \mathrm{SeOCl_2}$$

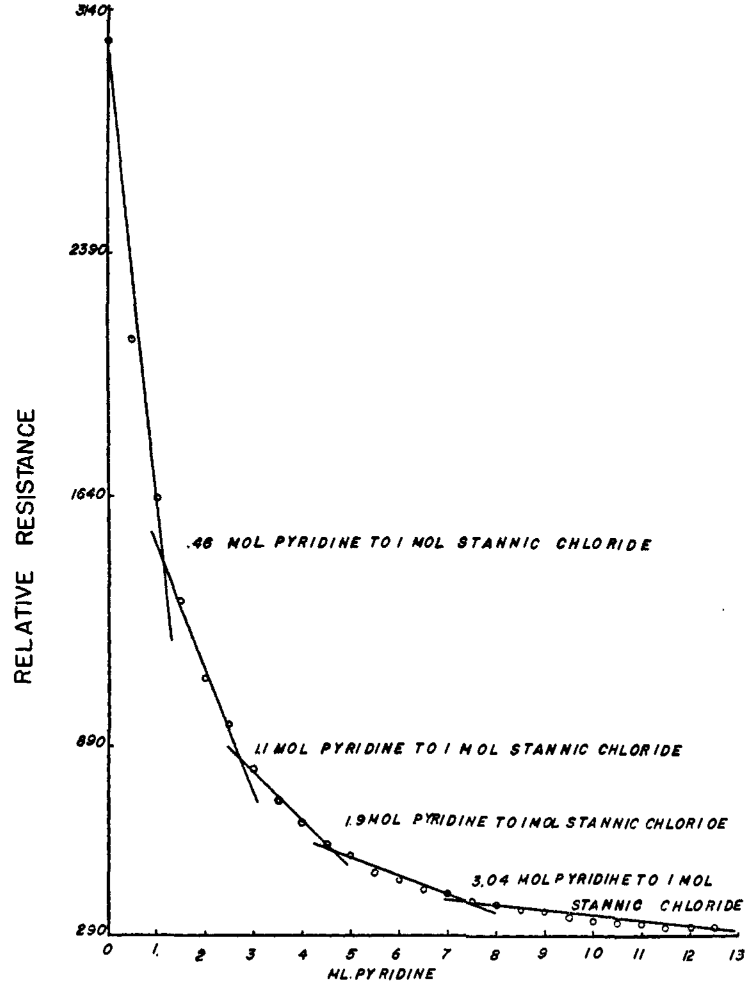

FIG. 2. Conductance titration of a solution of stannic chloride in selenium oxychloride with a solution of pyridine in selenium oxychloride.

$$(\mathrm{SeOCl})_2\mathrm{SnCl}_6 + 2\mathrm{C_5H_5NSeOCl}^+ + 2\mathrm{Cl}^- \rightarrow 2(\mathrm{C_5H_5NSeOCl})^+ + \mathrm{SnCl_6}^{--} + 2\mathrm{SeOCl_2}$$

$$(\mathrm{SeOCl})_3\mathrm{SnCl}_7 + 3\mathrm{C_5H_5NSeOCl}^+ + 3\mathrm{Cl}^- \rightarrow 3(\mathrm{C_5H_5NSeOCl})^+ + \mathrm{SnCl_7}^{---} + 3\mathrm{SeOCl_2}$$

The first equation postulates a hypothetical salt of the formula

$$(C_5H_5NSeOCl)(SeOCl)_3(SnCl_6)_2$$

which might be analogous to potassium tetraoxalate, $KH_3(C_2O_4)_2$. The second equation postulates a hypothetical primary salt of the formula

$$(C_5H_5NSeOCl)(SeOCl)(SnCl_6)$$

and the third equation gives the secondary salt postulated to explain

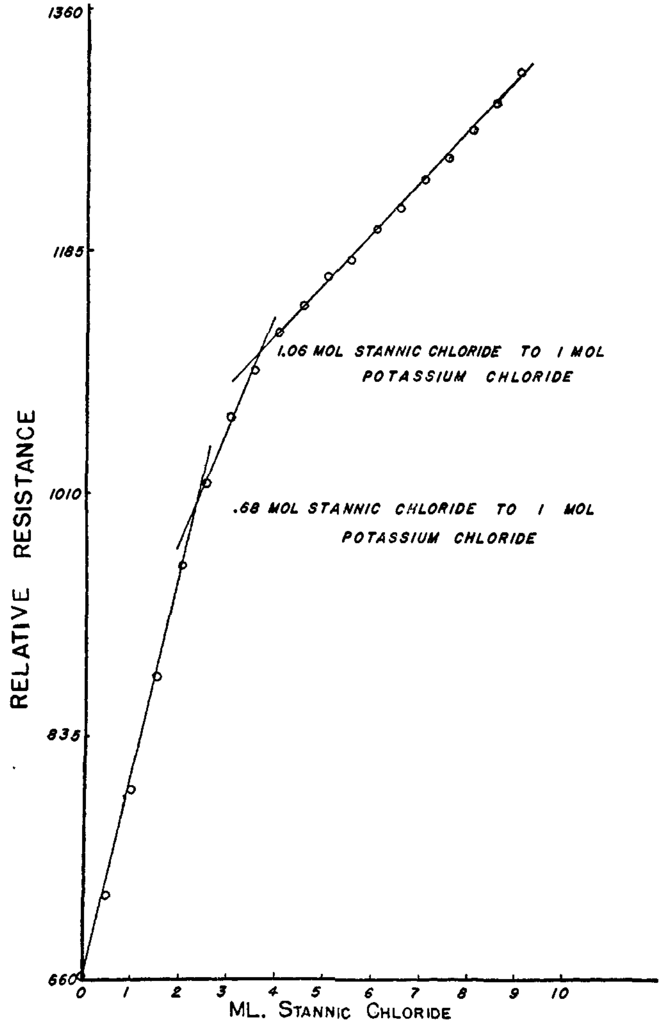

Fig. 3. Conductance titration of a solution of potassium chloride in selenium oxychloride with a solution of stannic chloride in selenium oxychloride.

curve 1. The fourth equation assumes the existence of a chlorostannate ion with a coördination number of seven, which may be possible but certainly is not usual. The author freely admits that these postulations are speculative, but their validity may be proved by future experimental work. On the other hand, future experiments will probably lead to modifications of these postulations. It should be remembered that association

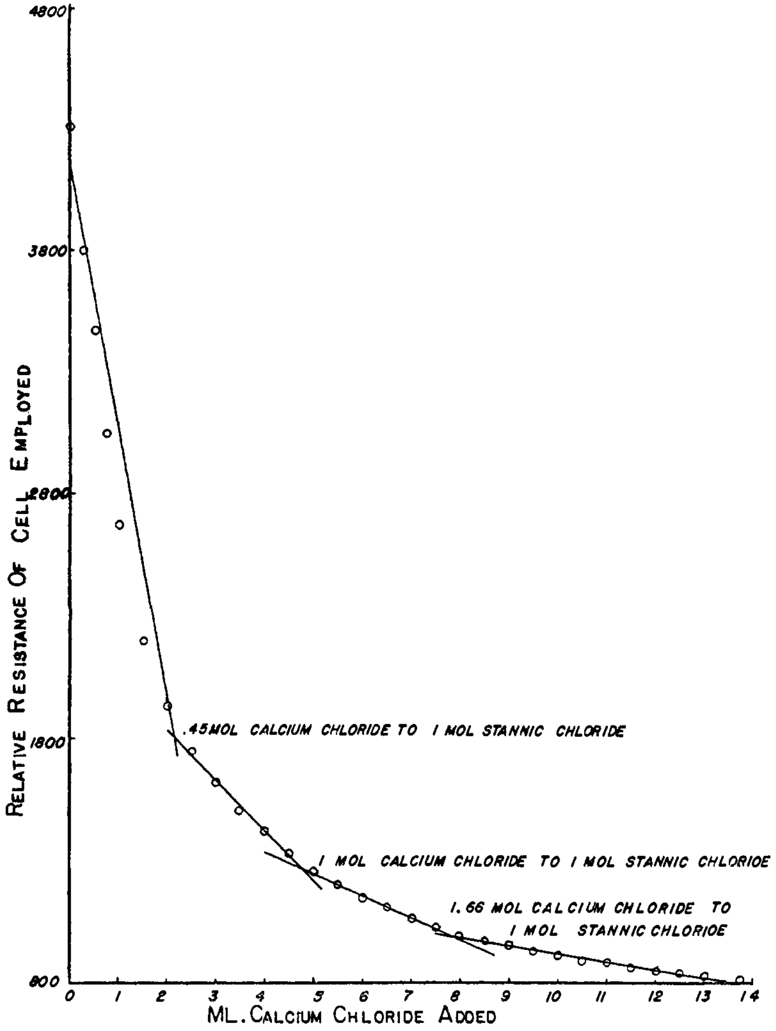

Fig. 4. Conductance titration of a solution of stannic chloride in selenium oxychloride with a solution of calcium chloride in selenium oxychloride.

of ions is considered as probable in concentrated solutions, and here it is suggested that such association follows rather simple stoichiometrical ratios.

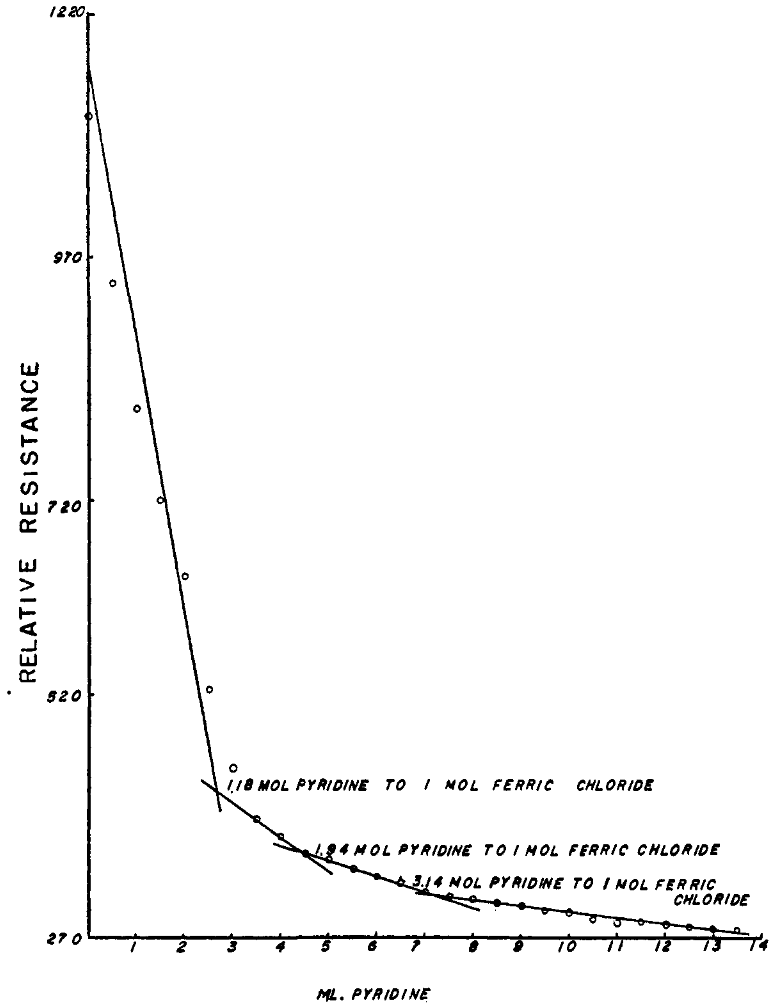

Fig. 5. Conductance titration of a solution of ferric chloride in selenium oxychloride with a solution of pyridine in selenium oxychloride.

Potassium chloride and stannic chloride

The conductance of a solution of potassium chloride in selenium oxychloride is decreased by the addition of a solution of stannic chloride. In the curve of figure 3 two inflections may be observed; these are explained on the assumption that solutions of salts of the following formulas are present at these inflection points:

$$K(SeOCl)_3(SnCl_6)_2 \text{ and } K(SeOCl)(SnCl_6)$$

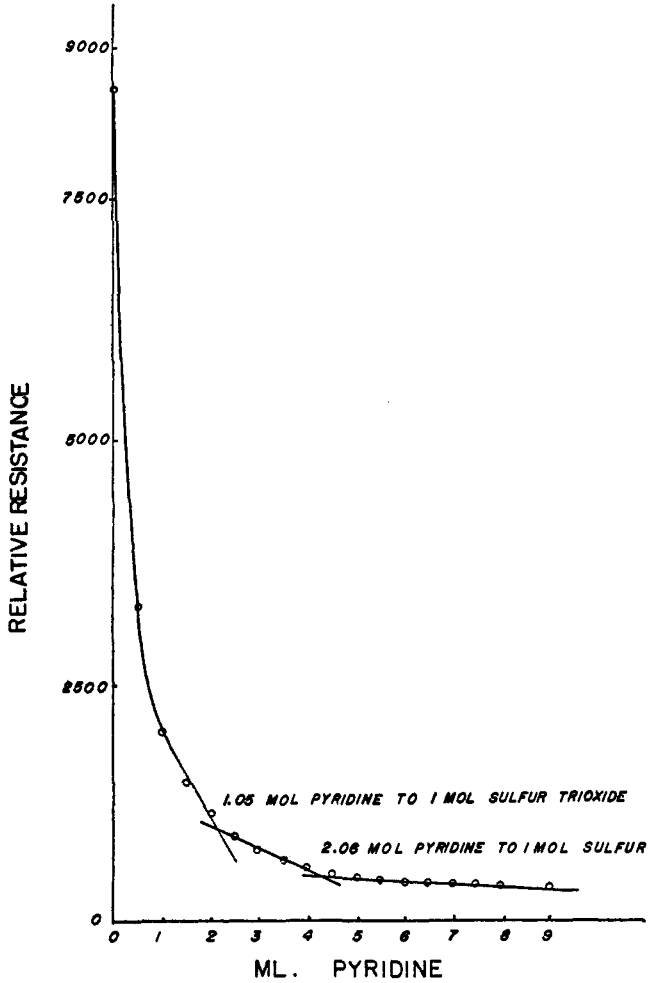

FIG. 6. Conductance titration of a solution of sulfur trioxide in selenium oxychloride with a solution of pyridine in selenium oxychloride.

It will be noted that these salts are analogous to the first two pyridinium salts postulated from the data presented in figure 2.

Calcium chloride and stannic chloride

The conductance of a solution of stannic chloride in selenium oxychloride is increased by the addition of a solution of calcium chloride, and the form of the curve in figure 4 is very similar to the curve of figure 2. The formulas of the salts which may exist at the three inflection points of curve 4 may be written as follows:

$$Ca[(SeOCl)SnCl_6]_2,\ CaSnCl_6,\ \text{and}\ Ca_3(SnCl_7)_2$$

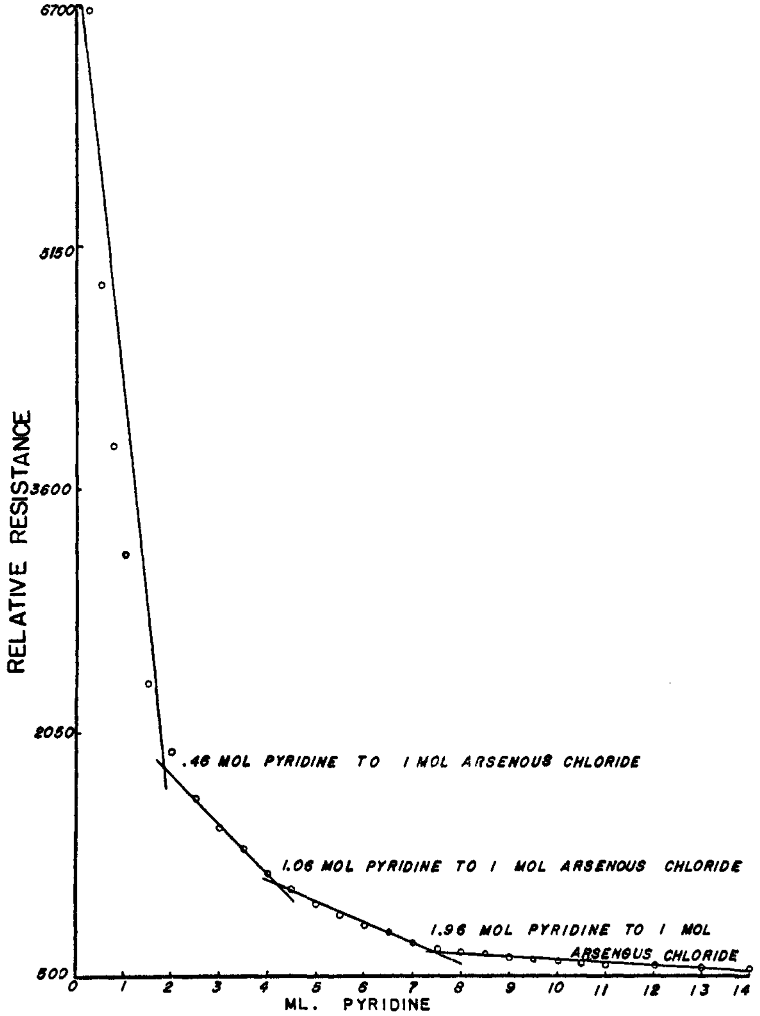

FIG. 7. Conductance titration of a solution of arsenic trichloride in selenium oxychloride with a solution of pyridine in selenium oxychloride.

and it is to be noted that these are analogous to the last three pyridinium salts postulated for figure 2.

Pyridine and ferric chloride

Ferric chloride dissolved in selenium oxychloride is a moderately good conductor, but the conductance is increased by the addition of pyridine. The curve in figure 5 indicates three inflections corresponding to the formation of primary, secondary, and tertiary salts. These may be formulated as:

$(C_5H_5NSeOCl)(SeOClFeCl_5)$, $(C_5H_5NSeOCl)_2(FeCl_5)$, and $(C_5H_5NSeOCl)_3(FeCl_6)$

A usual coördination number for iron is five and of course six occurs frequently. A solution of ferric chloride in selenium oxychloride is ruby-red in color. This color is practically identical with a solution of potassium pentachloroferrite in an aqueous solution. It will be recalled that the crystals of potassium pentachloroferrite are likewise of a ruby-red color.

Pyridine and sulfur trioxide

The curve in figure 6 presents the data obtained when a solution of sulfur trioxide is titrated with a solution of pyridine. Two inflections are indicated, and there may possibly be a third which we will neglect here. The salts formed may be written as

$(C_5H_5NSeOCl)SO_3Cl$ and $(C_5H_5NSeOCl)_2SO_3Cl_2$

Titrations at higher dilutions indicate a single inflection at the point corresponding to the formation of the primary salt.

Pyridine and arsenic trichloride

Wise (34) has shown that arsenic trichloride mixes with selenium oxychloride in all proportions. Since arsenic is a typical non-metal, we would expect arsenic trichloride to act as an acid in selenium oxychloride. The validity of this prediction is demonstrated by the results which are presented graphically in the curve of figure 7. The three inflection points indicate salts which may be formulated as:

$(C_5H_5NSeOCl)(SeOCl)(AsCl_4)_2$, $(C_5H_5NSeOCl)(AsCl_4)$, and $(C_5H_5NSeOCl)_2(AsCl_5)$

VIII. SUMMARY

1. This paper presents experimental evidence to support the thesis that selenium oxychloride is a parent solvent of a system of compounds in the Franklin–Germann sense (acids, bases, and salts). The known facts regarding selenium oxychloride as a solvent are correlated on this basis.
2. It is proposed to use the following broad definitions for the terms

"acid" and "base": *A solute is an acid when its molecule (neutral or charged) is an electron pair acceptor toward the molecule or an ion of the solvent; a solute is a base when its molecule (neutral or charged) is an electron pair donor toward the molecule or an ion of the solvent.* These statements are sufficiently broad to permit application to parent solvents such as phosgene, sulfur dioxide, and selenium oxychloride, as well as the ordinary solvents which ionize to give the solvated proton. These statements are proposed as merely extensions of the Brønsted definition and the latter should be retained ordinarily.

3. Metathetical reactions (essentially neutralization reactions) may take place in solutions of selenium oxychloride. The conductance titration method has proved to be useful in the study of these reactions.

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