[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Neutralization Reactions in Selenium Oxychloride. Potentiometric Titration.[1a]

BY W. S. PETERSON,[1b] C. J. HEIMERZHEIM[1b] AND G. B. L. SMITH

The high dielectric constant makes selenium oxychloride the most "water like" of any of the non-protonic solvents which have been studied in detail thus far. Investigations in these Laboratories[2] have been carried out on selenium oxychloride as a solvent, as a parent solvent of a system of compounds, and on the products of the reactions of selenium oxychloride with water and with certain electron pair donors. Neutralization reactions[2a] have been followed by conductometric titrations in a manner similar to conductometric titrations in water.

This paper presents the results obtained in the application of two modifications of a potentiometric technique using concentration cells in the study of neutralization reactions in selenium oxychloride. Concentration cells were essential since the nature and properties of selenium oxychloride prevent the use of "classical" aqueous reference electrodes with salt bridges, and bimetallic systems have not been found which give large enough electrical potential differences to be useful. We have obtained titration curves, similar to those obtained for neutralization reactions in water, for neutralization reactions between non-protonic acids and non-protonic bases in the non-protonic solvent, selenium oxychloride. Potentiometric titrations have been employed to follow neutralization reactions in non-aqueous solutions but these have been limited to protonic acids and bases and usually in protonic solvents.[3] These are the first potentiometric titrations to be carried out in a non-protonic solvent.

Experimental

Materials.—Selenium oxychloride was prepared by a modification of the method first proposed by Muehlberger and Lenher[4] and was finally distilled at about 20–25 mm., m. p. 10.8–10.9°. This substance was preserved in sealed glass ampules. Sulfur trioxide was distilled from "fuming" sulfuric acid. Pyridine, quinoline and isoquinoline of "technical" grade (Eastman Kodak Co.) were dried over potassium hydroxide and distilled under reduced pressure. Other compounds used were of "C. P." or "Reagent" grade. Resublimed ferric chloride prepared from pure iron wire was used in later experiments.

Standard Solutions.—In the early experiments weighed quantities of solutes were dissolved in weighed quantities of the solvent, selenium oxychloride. Later it became desirable to prepare relatively large volumes of solutions by dissolving weighed quantities of solutes in selenium oxychloride and diluting to desired volumes in ordinary volumetric flasks (25, 50, 100, and 250 ml.). Such solutions were preserved in sealed glass ampules until they were used. Because of the large "heat of solution" or heat of reaction involved, solutions of sulfur trioxide, stannic chloride, pyridine, quinoline and isoquinoline were usually prepared by adding these substances to solid selenium oxychloride. Sulfur trioxide was distilled directly from fuming sulfuric acid into a tared flask containing solid selenium oxychloride. In all these and subsequent operations care was exercised to minimize contamination with atmospheric moisture since water reacts with (is a base in) selenium oxychloride.

Apparatus.—The e. m. f. of the primary cells was measured by means of a conventional circuit employing a Leeds and Northrup *p*H type potentiometer.

The primary cell assembly consisted of a cylindrical titration cell of Pyrex glass, 3″ high × $1^{1}/_{16}''$ I. D., closed by a rubber stopper in which four openings accommodated the following: a motor-driven glass stirrer, a buret, a platinum wire indicator electrode, and the Müller "retarded" electrode or the 0.1 *M* potassium chloride "reference" electrode. The buret, of 25 ml. capacity, engraved in units of 0.05 ml., was fitted with a ground glass stopper and air vent at the top. The indicator electrode was a heavy platinum wire sealed into glass tubing, electrical contact to the potentiometer being provided by a mercury pool within the tubing.

The Müller electrode[5] consisted of a piece of capillary tubing (0.5 mm. bore) with a platinum wire extending into the capillary to within $^{3}/_{4}''$ of the bottom aperture. Strands of glass wool were packed into the bottom of the capillary to a depth of 1″ and sintered in place. This latter arrangement, original in this investigation, effectively minimizes diffusion of the solution into the electrode.

The 0.1 *M* potassium chloride "reference" electrode was made of 7 mm. glass tubing, closed at the lower end with a ground glass stopper and at the top a sealed-in platinum wire extended to within $^{1}/_{2}''$ of the stoppered end. This electrode was filled with an 0.1 *M* solution of potassium chloride in selenium oxychloride.

Method.—Customary titration procedures were followed. Readings constant to one millivolt were generally obtained after thirty seconds stirring of the solution.

Results

Numerous preliminary titrations with both types of indicator electrode showed that in selenium oxychloride solution titration curves of satisfactory form and with stoichiometric "breaks" extending over as much as 0.4 volt could be obtained.

Curves which are comparable and which indicate relative strengths of the acids and bases used are presented in Figs. 1 and 2. Titration curves obtained when solutions of the bases (in order of decreasing basicity) isoquinoline, quinoline, pyridine, and potassium chloride (all 0.1 *M*) were titrated with a solution of sulfur trioxide

---

(1a) Original manuscript received September 28, 1942.

(1b) Abstract of theses submitted to the Graduate Faculty of Polytechnic Institute of Brooklyn by W. S. Peterson (Research Fellow 1941–42, present address: Aluminum Research Laboratory, New Kensington, Pa.) in partial fulfillment of the requirement for the degree of Doctor of Philosophy in June, 1942, and by C. J. Heimerzheim (present address, Brooklyn College of Pharmacy, Brooklyn, N. Y.) in partial fulfillment of the requirement for the degree of Master of Science in Chemistry in June, 1939.

(2) (a) Smith, *Chem. Rev.*, **23**, 165 (1938); (b) Jackson and Smith, THIS JOURNAL, **62**, 543 (1940); *ibid.*, **62**, 544 (1940); (c) Jackson, Ph.D. Thesis, Polytechnic Institute of Brooklyn, (1941); (d) Waring, Steingiser and Hyman, THIS JOURNAL, **65**, 1068 (1943).

(3) (a) Hantzsch, *Z. Elektrochem.*, **29**, 221 (1923); *Ber.*, **60**, 1933 (1927); (b) Hall and Conant, THIS JOURNAL, **49**, 3047, 3062 (1927); Hall and Werner, *ibid.*, **50**, 2367 (1928).

(4) Muehlberger and Lenher, *ibid.*, **47**, 1842 (1925).

(5) Müller, *Z. Elektrochem.*, **31**, 323 (1925).

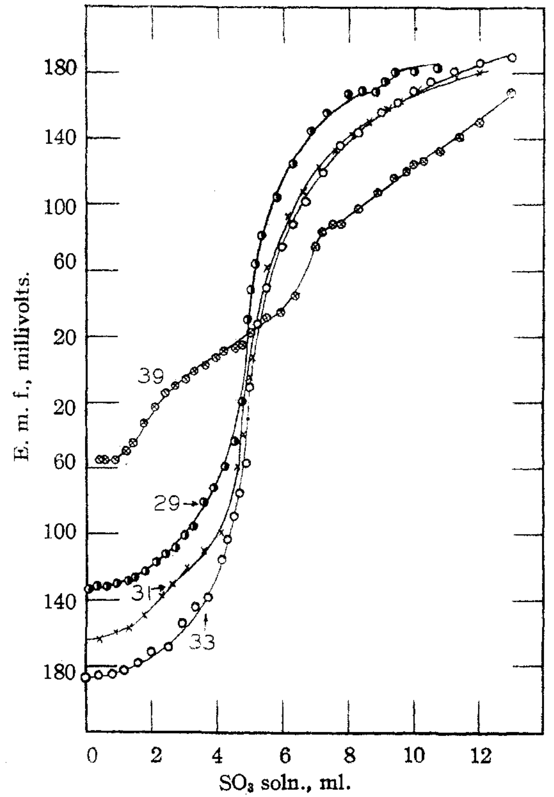

Fig. 1.—Titration curves of (39) potassium chloride, (29) pyridine, (31) quinoline and (33) isoquinoline with sulfur trioxide.

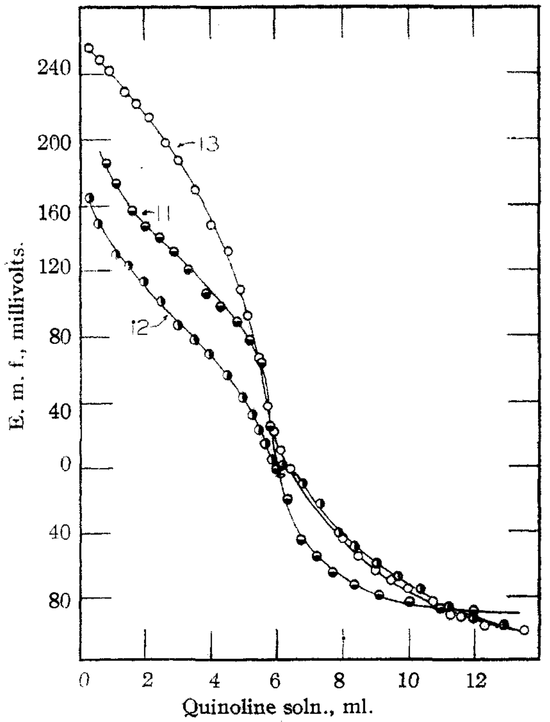

Fig. 2.—Titration curves of (13) sulfur trioxide, (11) ferric chloride, and (12) stannic chloride with quinoline.

TABLE I

System (the titrant is written first in each case)	Molar ratios obsd. (the first figure refers to the titrant)	Expt. error, of observed molar ratio per cent.
("Müller Retarded "Electrode" Employed")		
$FeCl_3$–Pyridine	1:1	14
Pyridine–$FeCl_3$ (5 expts.)	1:1	18, 14, 22, 14, 13
$SnCl_4$–Pyridine	1:2	14
Pyridine–$SnCl_4$	2:1	11
Pyridine–SO_3	1:1	1.5
$CaCl_2$–$FeCl_3$	1:2	14
$CaCl_2$–$SnCl_4$	1:1	0.7
KCl–$FeCl_3$	2:1	0.8
H_2O–$FeCl_3$	2:1	7.2
H_2O–$SnCl_4$	4:1	0.7
H_2O–$AsCl_3$	no inflection	...
Pyridine–SO_3 (3 expts.)	1:1	1, 1, 3.8
(0.1 *M* Potassium Chloride Electrode Employed)		
Pyridine–$FeCl_3$ (2 expts.)	1:1	8.5, 5.6
Pyridine–$FeCl_3$	1:1	0
	also 2:1	6.2
Pyridine–$FeCl_3$	1:1	2.2
	also 1:2	6.7
Pyridine–$SnCl_4$	1:1	0.0
Pyridine–SO_3 (2 expts.)	1:1	1.7, 0.0
Quinoline–$FeCl_3$ (4 expts.) (includes expt. 11)[a]	1:1	0.2, 0.3, 0.3, 0.4
Quinoline–$SnCl_4$ (12)[a]	1:1	0.0
Quinoline–SO_3 (13)[a]	1:1	2.6
Isoquinoline–$FeCl_3$	1:1	3.7
Isoquinoline–$SnCl_4$	1:1	2.0
Isoquinoline–SO_3	1:1	0.9
H_2O–$FeCl_3$	2:1	3.9
H_2O–$SnCl_4$	1:1	1.4
	also 1:2	3.8
H_2O–SO_3	1:1	0.6
$FeCl_3$–Pyridine	1:1	3.1
$FeCl_3$–Quinoline	1:1	0.0
$FeCl_3$–Isoquinoline	1:1	2.3
	also 1:2	3.5
$SnCl_4$–Pyridine	1:1	1.9
$SnCl_4$–Quinoline	1:1	1.8
$SnCl_4$–Isoquinoline	1:1	0.5
$SnCl_4$–H_2O	1:1	1.0
	also 1:2	1.0
SO_3–(Pyridine 3 expts.) (includes expt. 29)[a]	1:1	0.6, 22.9, 1.2
SO_3–Quinoline (2 expts.) (30, 31)[a]	1:1	0.4, 0.6
SO_3–Isoquinoline (2 expts.) (32, 33)[a]	1:1	2.9, 0.2
SO_3–H_2O	1:1	2.7
KCl–$FeCl_3$	1:1	0.5
	also 1:2	5.9
KCl–$SnCl_4$ (2 expts.)	1:1	0.9, 0.4
	also 1:2	3.5, 2.3
SO_3–KCl (39)	1:1	20

[a] These figures identify experiments whose data were used in Figs. 1, 2, 3.

(0.2026 *M*) are shown in Fig. 1. The curves in Fig. 2 represent titrations of the acids sulfur trioxide, ferric chloride and stannic chloride (all 0.1 *M*) with a solution of quinoline (0.1560 *M*). These substances are, in order of decreasing acidity, sulfur trioxide, ferric chloride and stannic chloride. Experimental results of these titrations are included in Table I. When more than one reflection was noted in the titration of a given system, the molar ratios corresponding to these inflections are included in the Table.

Discussion

The foregoing results demonstrate that both the Müller electrode and the 0.1 *M* potassium chloride electrode serve in following neutralization reactions in selenium oxychloride. The production of an e. m. f. in a cell employing either of these electrodes is due to a concentration differential existing between the ions of the cell solution and the ions surrounding the platinum wire within the reference electrode. In the simple concentration cell

$$\underset{(1)}{\mathrm{Pt}\ |}\ 0.1\ M\ \mathrm{KCl}\ \|\ 0.01\ M\ \mathrm{KCl}\ \underset{(2)}{|\ \mathrm{Pt}}$$

if molecular concentrations were the same as the activities, then the potential existing would be 59 millivolts, as calculated from the equation

$$E = 0.059 \log \frac{(\mathrm{Cl}^-)^{(1)}}{(\mathrm{Cl}^-)^{(2)}}$$

Experimentally, in selenium oxychloride as solvent, the e. m. f. of this cell was found to be 47 millivolts (room temperature), electrons flowing through the outside circuit from the electrode surrounded by the solution of high (Cl^-) to the solution of low (Cl^-).

The 0.1 *M* potassium chloride electrode has been found preferable in that it yielded reproducible values and also that it established a fixed point on the scale in order to measure relative acidities and basicities with reasonable precision. No account has been taken of the liquid junction potential in these measurements since it cannot be estimated at the present time. Since, however, the titrations performed have been roughly comparable as to concentration, the corrections for this potential probably will be of the same order of magnitude in each case. The present investigation has been primarily of exploratory nature, directed toward the development of a satisfactory technique and it is hoped that future studies will be more rigorously quantitative.

Form of the Titration Curves.—The titration curves appear to be of the weak acid–weak base type. To test this assumption, the following logarithmic plot of several typical titrations was made (see Ref. 3 b). If we take n as equal to the number of ml. of reagent at the equivalence point and x as the number of ml. of reagent at any point on the curve before the equivalence point then the ratio $X/(n - x)$ will be the ratio of salt to acid in terms of molecular concentration. If the curves are indeed of the weak acid–weak base type, then a plot of e. m. f. against $\log x/(n - x)$ will yield a straight line with a theoretical slope of 59 millivolts per unit change in the logarithmic ratio. Figure 3 presents several curves of this type with slopes almost identical with the theoretical for the last two-thirds of the curve to the inflection point. This shows quite conclusively the weak acid–weak base characters of these neutralizations for that part of the reaction.

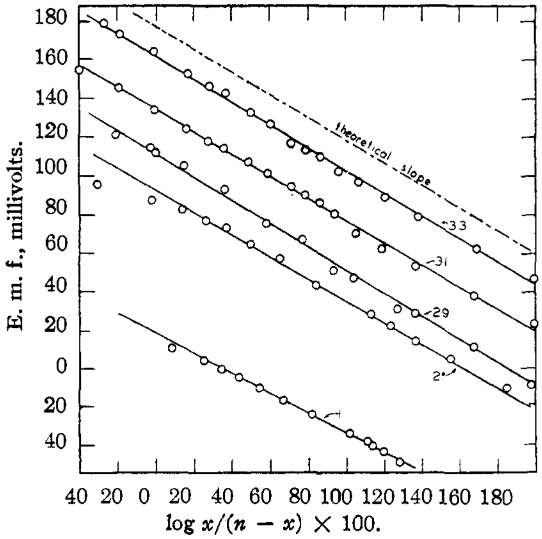

Fig. 3.—Log $x(n - x)$ plotted as a function of e. m. f.

Neutralization Reactions in Selenium Oxychloride.—It has been stated previously[2a] that chlorides of electropositive elements are bases in selenium oxychloride, but they may be regarded as incidental bases since they merely furnish ions identical to the anions of the solvent, namely, the chloride ion. In this respect they are analogous to sodium hydroxide in water, sodium amide in liquid ammonia, and sodium acetate in acetic acid. In these investigations the alkali and alkaline earth chlorides have been studied, they have all been found to act as very weak bases in selenium oxychloride, and this is attributable to the fact that the selenium oxychloride is a strongly acidic solvent. Potassium chloride has been studied in considerable detail. When sulfur trioxide solutions are added to a solution of potassium chloride, a precipitate is formed rapidly which, upon analysis, contains potassium and sulfur in a 1:1 ratio. Selenium and chlorine are present in varying amounts. It is believed that the precipitate is solvated potassium chlorosulfate. The formation is given by the over-all equation

$$\mathrm{K}^+ + \mathrm{Cl}^- + \mathrm{SeOCl}^+ + \mathrm{SO_3Cl}^- \longrightarrow \mathrm{SeOCl_2} + \mathrm{KSO_3Cl}$$

We are neglecting the selenium oxychloride of solvation. This reaction is confirmed by the stoichiometry of the titration curves obtained. The more general neutralization reaction is represented simply by the formation of the solvent molecules from its ions

$$\mathrm{SeOCl}^+ + \mathrm{Cl}^- \longrightarrow \mathrm{SeOCl_2}$$

The second type of bases which have been studied are neutral molecule electron pair donors, isoquinoline, quinoline, and pyridine. These are all *very much stronger* bases in selenium oxychloride than the alkali and alkaline earth chlorides. On the basis of previous studies[2b] it is believed that these substances react with selenium oxychloride to give the corresponding selenium oxychloro onium chlorides, which are strong electrolytes. In the case of pyridine the reaction may be formulated as follows

$$C_5H_5N + SeOCl_2 \longrightarrow C_5H_5NSeOCl_2^+ + Cl^-$$

It has been found that pyridine reacts with sulfur trioxide in selenium oxychloride in stoichiometric ratio of 1:1. This neutralization reaction may be formulated in two ways

$$C_5H_5NSeOCl^+ + Cl^- + SeOCl^+ + SO_3Cl^- \longrightarrow SeOCl_2 + C_5H_5NSeOCl^+ + SO_3Cl^-$$

and

$$C_5H_5NSeOCl^+ + Cl^- + SeOCl^+ + SO_3Cl^- \longrightarrow 2SeOCl_2 + C_5H_5NSO_3$$

Luder[6] believes that the second formulation is correct but the authors of this paper believe that both reactions take place and that the predominance of one reaction over the other depends on the concentrations of the reactants. A more complete study of the system $SeOCl_2$–SO_3–C_5H_5N is projected and it is hoped that the solid phases may be isolated and their composition investigated. In titrations of the base, water, with the acid, sulfur trioxide, it appears likely that sulfuric acid, is formed. A further observation is that in some neutralization reactions salts are formed (electrolytes) while in other instances molecular "salts" (non-electrolytes) are formed at the equivalence point.

In the present investigations it has been demonstrated that the relative strengths of non-protonic acids and bases in selenium oxychloride may be estimated approximately.

Summary

1. The Müller "retarded" electrode has been adapted to potentiometric titration of non-protonic acid-base systems in selenium oxychloride.

2. An 0.1 *M* potassium chloride reference electrode for potentiometric titrations in selenium oxychloride has been developed.

3. Neutralization reactions studied are of the weak acid–weak base type.

4. The relative strength of non-protonic acids and non-protonic bases in the non-protonic solvent selenium oxychloride have been determined. The relative strengths of the acids in decreasing order are sulfur trioxide, ferric chloride, stannic chloride, and of the bases are isoquinoline, quinoline, pyridine and potassium chloride.

BROOKLYN, N. Y. RECEIVED OCTOBER 13, 1943

---

(6) Luder, *Chem. Rev.*, **27**, 547 (1940).

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Consecutive Competitive Reactions

BY RAYMOND M. FUOSS

We consider the following sequence of irreversible reactions

$$\begin{aligned} AX_4 + RY &\longrightarrow RAX_3 + XY \\ RAX_3 + RY &\longrightarrow R_2AX_2 + XY \\ R_2AX_2 + RY &\longrightarrow R_3AX + XY \\ R_3AX + RY &\longrightarrow R_4A + XY \end{aligned}$$

in which the reagent RY can replace the X's of AX_4 one at a time by R's. Obviously, after the reaction has started, four species are competing for reagent. It is of interest to calculate the relative amounts of the five species AX_4, . . ., R_4A as a function of the amount of reagent added.

Let n molecules of RY be added to N molecules of AX_4, and let N_i be the number of molecules of R_iAX_{4-i} present. The net change dN_i in any species N_i when dn molecules of reagent are added is given by

$$dN_i = dN_i' - dN_i'' \qquad (1)$$

where dN_i' is the number of molecules of species i produced from dN_{i-1}'' molecules of species $(i - 1)$ and dN_i'' is the number of molecules of species i which react to form dN_{i+1}' molecules of species $(i + 1)$ ($dN_0' \equiv 0$ because no AX_4 is produced and $dN_4'' \equiv 0$ because no R_4A reacts). Then

$$dn = dN_0'' + dN_1'' + dN_2'' + dN_3'' \qquad (2)$$

To conserve A-atoms, we have

$$N = N_0 + N_1 + N_2 + N_3 + N_4 \qquad (3)$$

Let the reaction probabilities be in the ratio $1:\alpha:\beta:\gamma$, so that

$$\begin{aligned} dN_0'' &= \zeta N_0 dn \\ dN_1'' &= \alpha\zeta N_1 dn \\ dN_2'' &= \beta\zeta N_2 dn \\ dN_3'' &= \gamma\zeta N_3 dn \end{aligned} \qquad (4)$$

Introducing variables $x = n/N$ and $y_i = N_i/N$, we thus have the following differential equations which describe the system

$$\begin{aligned} dy_0 &= -\zeta N y_0 dx \\ dy_1 &= \zeta N(y_0 - \alpha y_1)dx \\ dy_2 &= \zeta N(\alpha y_1 - \beta y_2)dx \\ dy_3 &= \zeta N(\beta y_2 - \gamma y_3)dx \\ dy_4 &= \zeta N \gamma y_3 dx \end{aligned} \qquad (5)$$

where by (2)

$$\zeta^{-1} = y_0 + \alpha y_1 + \beta y_2 + \gamma y_3 \qquad (6)$$