Solutions in Selenic Acid. Part 9.[1] Higher Acids of Selenic Acid; the SeO_3–H_2SeO_4 System

By **Mohammed A. Hussein, George M. Iskander, Maher M. Nour, Saad Wasif,*** and **Hussein M. Zeidan,**
The University, Khartoum, Sudan

The SeO_3–H_2SeO_4 system has been studied cryoscopically. A maximum freezing point of 18.84 ± 0.01 °C indicated the existence of diselenic acid $H_2Se_2O_7$. Self-dissociation in diselenic acid is discussed and the presence of triselenic acid is predicted. The acidity function (H_0) of SeO_3–H_2SeO_4 solutions increases with progressive increase of SeO_3 content and a value of −12.77 is reported for 68% SeO_3 solution.

In continuation of current investigations of highly acidic solvents in which selenic acid solutions have been studied,[2] the properties of selenoleum (diselenic acid) are reported. It is expected to have higher acidity than selenic acid [3] and it dissolves a number of organic and inorganic solutes and also gives highly coloured solutions of Se and I_2.[4] There has been little work on SeO_3 solutions; a report by Dostal and Cernohorsky [5] predicted the presence of polymer selenic acids.

The present work includes two parts that are treated separately but give similar results about the nature of selenoleum solutions: (*A*) the cryoscopy of the SeO_3–H_2SeO_4 systems; and (*B*) acidity function of the SeO_3–H_2SeO_4 and H_2SeO_4–H_2O systems.

TABLE 1

Freezing point data of the SeO_3–$H_2Se_2O_7$–H_2SeO_4 system *

% SeO_3 (w/w)	Weight of solute (H_2SeO_4)/g	Molality of solute ($H_2Se_2O_7$)/mol kg^{-1}	Freezing point/°C	% SeO_3 (w/w)	Weight SeO_3/g	Molality of SeO_3/mol kg^{-1}	Freezing point/°C
92.56	2.540	0.1800	15.78	93.48	0.2660	0.2111	18.82
92.60	2.430	0.1720	16.23	93.57	0.5104	0.0410	18.74
92.62	2.360	0.1670	16.46	93.60	0.5920	0.0468	18.71
92.64	2.281	0.1611	16.62	93.72	0.9180	0.0720	18.54
92.68	2.180	0.1580	16.93	93.75	1.0010	0.0795	18.50
92.72	2.060	0.1450	17.13	93.83	1.2180	0.0972	18.33
92.74	1.990	0.1401	17.32	93.87	1.3260	0.1060	18.25
92.80	1.805	0.1270	17.60	93.91	1.4350	0.1148	18.17
92.86	1.619	0.1140	17.83	93.96	1.5710	0.1257	18.05
92.88	1.557	0.1090	18.03	93.98	1.6260	0.1303	18.03
92.90	1.497	0.1050	18.10	94.03	1.7620	0.1413	17.75
92.96	1.308	0.0915	18.26	94.06	1.8430	0.1480	17.64
93.00	1.187	0.0830	18.36	94.19	2.1970	0.1770	17.24
93.05	1.031	0.0720	18.47	94.27	2.4140	0.1948	17.85
93.10	0.875	0.0610	18.56	94.29	2.4690	0.2000	16.44
93.12	0.813	0.0567	18.60	94.37	2.6860	0.2180	16.34
93.22	0.503	0.0348	18.75	94.39	2.7410	0.2220	16.20
93.35	0.100	0.0069	18.82	94.43	2.8500	0.2310	15.90
93.40	Nearly 100% $H_2Se_2O_7$		18.83				

* Total weight of the system was 100 g in all runs; in all cases weight solvent : weight solute = 100 : 1.

EXPERIMENTAL

(*A*) *Cryoscopic Studies.*—In all experiments, one addition of SeO_3 was made to 100% H_2SeO_4 and the freezing point determined by the method employed by Gillespie *et al.*[6] The cryoscope was designed to allow the use of small quantities (50—80 g) of 100% H_2SeO_4 and was placed in a thermostat adjustable in the range 13—30 °C which was kept one degree below the freezing point of the system. To make a series of measurements a known weight of selenic acid was introduced into the cryoscope and its composition adjusted by adding a known weight of SeO_3 in a dry-box, and the freezing point of the system was determined. The data of such measurements are given in Table 1 and are plotted in the Figure.

(*B*) *Acidity Function of Selenoleum Solutions.*—The measurement was based on the method suggested by Hammett and Deyrup.[7] Equation (1) was used throughout the measurements in selenoleum (B = base). Selenoleum is a

$$H_0 = pK_{BH_2^{2+}} - \log\left(\frac{[BH_2^{2+}]}{[BH^+]}\right) \qquad (1)$$

difficult solvent to handle and few indicators respond favourably to the measurement of its acidity. For the acid range 50—90% methoxybenzophenones were quite appropriate.[3] For the range 90—100% anthracene-9,10-dione was used as a monoprotonated species BH^+ and for the higher acidities over the range 1—68% SeO_3 the diprotonated species BH_2^{2+} was useful. An isosbestic point exists between the two species as acidity is gradually increased, equation (2).

$$BH^+ + H^+ \longrightarrow BH_2^{2+} \qquad (2)$$

Peaks at which Beer's law is obeyed	312 nm	344 nm

---

* *Present address*: Faculty of Science, Zagazig University, Zagazig, Egypt.

The evaluation of pK_{BH^+} and $pK_{BH_2^{2+}}$ was achieved with the help of sulphuric acid and sulphuric oleum solutions of known acidity functions and Tables 2 and 3 include such data.

Using the data in Tables 2 and 3 the acidity function was evaluated for the selenic acid range 90—100%, Table 4, and the oleum range 15—68% SeO_3, Table 5.

TABLE 2

Evaluation of pK_{BH^+} of anthracene-9,10-dione

% H_2SO_4	$-H_0$ *	log([BH⁺]/[B])	$-pK_{BH^+}$
78	7.13	−1.14	8.27
80	7.46	−0.80	8.25
84	8.13	−0.16	8.29
88	8.71	0.44	8.27

* Data from R. J. Gillespie and T. E. Peel, *Prog. Phys. Org. Chem.*, 1972, **1**, 1.

TABLE 3

Evaluation of $pK_{BH_2^{2+}}$ of anthracene-9,10-dione

% SO_3	$-H_0$ *	log([BH_2^{2+}]/[BH^+])	$-pK_{BH_2^{2+}}$
2	12.42	0.48	11.94
6	12.78	0.83	11.95
10	13.03	1.12	11.91

* Data from R. J. Gillespie and T. E. Peel, *Prog. Phys. Org. Chem.*, 1972, **1**, 1.

TABLE 4

Acidity functions for the range 90—100% H_2SeO_4

% H_2SeO_4	log([BH^+]/[B])	$-H_0(H_2SeO_4)$ *	$-H_0(H_2SO_4)$ *
92	−0.33	7.94	9.34
95	0.02	8.29	9.90
98	0.55	8.82	10.43
100	0.75	9.02	11.93

* Same concentrations of H_2SeO_4 and H_2SO_4.

TABLE 5

Acidity functions for the range 15—68% SeO_3

% SeO_3	log([BH_2^{2+}]/[BH^+])	$-H_0$ (selenoleum) *	$-H_0$ (sulphuric oleum) *
15	−0.42	11.51	13.23
27	−0.19	11.74	13.58
36	0.01	11.94	13.94
45	0.20	12.13	14.28
53	0.42	12.32	14.59
61	0.57	12.50	14.74
68	0.84	12.77	14.92

* Same concentrations of selenoleum and sulphuric oleum.

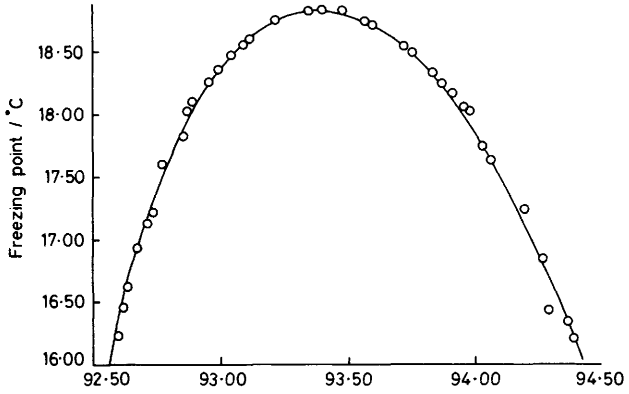
RESULTS AND DISCUSSION

(*A*) *Cryoscopic Study of the* SeO_3–H_2SeO_4 *System*.—The progressive addition of SeO_3 to 100% H_2SeO_4 causes depression in the freezing point of pure selenic acid.[1] When the mol ratio $SeO_3 : H_2SeO_4$ reaches unity the freezing point of the system has a maximum in the freezing point–composition diagram. Mixtures with such high SeO_3 content are very hygroscopic and become explosive in the presence of some organic solutes, particularly amines and some ketones.[4]

Freezing point-composition diagram. The Figure shows a maximum freezing point at composition 93.4% SeO_3 (w/w) and this represents a mol ratio $SeO_3 : H_2SeO_4$ of unity.

A reasonable way to explain the existence of this maximum at such a mol ratio would be to assume the formation of a new phase representing diselenic acid (selenoleum), equation (3). At compositions greater than 93.40% SeO_3 we may consider the system as consisting of pure selenoleum with excess of SeO_3. It is possible that SeO_3 does not exist free but combines partly or completely with $H_2Se_2O_7$ to give higher polymer acids of selenic acid. In the absence of definite information on higher polymer acids ($H_2Se_3O_{10}$ or higher) we would represent the composition as SeO_3 + $H_2Se_2O_7$. At compositions with less than 93.4% SeO_3 the system consists of $H_2Se_2O_7$ as solvent and H_2SeO_4 as solute. The two nearly linear branches round the maximum thus represent the acidic and the basic sides of a titration curve in selenoleum.

$$H_2SeO_4 + SeO_3 \rightleftharpoons H_2Se_2O_7 \qquad (3)$$



Freezing point *versus* % SeO_3 (w/w) for the SeO_3–H_2SeO_4 system

The flat maximum of the Figure shows that selenoleum is self-dissociated. The conductivity of the system at maximum freezing point was found to be $3 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$ at 25 °C. This conductivity is higher than water ($K = 10^{-8}\ \Omega^{-1}\ cm^{-1}$) but lower than pure selenic acid ($5.9 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$). The relatively low conductivity of selenoleum shows that the self-dissociation is partly ionic [equation (4)], and partly molecular [equation (5)]. Selenic acid [from equation (5)], being more basic than the higher acids $H_2Se_2O_7$ and $H_2Se_3O_{10}$, would ionise as a base [equations (6) and (7)]. The ionic species of equations (6) and (7) contribute in reducing ionic self-dissociation, leaving the major part of self-dissociation to the molecular mode, equation (5).

$$2\ H_2Se_2O_7 \longrightarrow H_3SeO_4^+ + HSe_3O_{10}^- \qquad (4)$$

$$2\ H_2Se_2O_7 \longrightarrow H_2SeO_4 + H_2Se_3O_{10} \qquad (5)$$

$$H_2SeO_4 + H_2Se_2O_7 \longrightarrow H_3SeO_4^+ + HSe_2O_7^- \qquad (6)$$

$$H_2SeO_4 + H_2Se_3O_{10} \longrightarrow H_3SeO_4^+ + HSe_3O_{10}^- \qquad (7)$$

No attempt was made to determine the cryscopic constant of selenoleum and self-dissociation will be discussed only qualitatively.

By extrapolating the two nearly linear branches of the freezing point curve, they meet at 21.6 °C. Self-dissociation products, therefore, cause a depression of 2.8 °C which is nearly three times that of selenic acid.[1]

The slopes of the lines are 21 for the SeO_3 branch and 30 for the H_2SeO_4 branch, which suggests that selenic acid behaves as a stronger base than does SeO_3 as a weak acid ($H_2Se_2O_7$). Similar behaviour has been noted for H_2O and SeO_3 in H_2SeO_4 as a solvent.[1]

TABLE 6

Cryoscopic titration of $[NH_4]_2[SeO_4]$ with SeO_3 in selenoleum *

Initial molality of $[NH_4]_2[SeO_4]$/ mol kg^{-1}	Maximum f.p. attained/°C	Molar ratio at maximum f.p. $SeO_3 : [NH_4]_2[SeO_4]$
0.052	18.62	2.7
0.153	17.00	2.5
0.170	16.43	3.0

* f.p. = Freezing point.

TABLE 7

Cryoscopic titration of CH_3CO_2H with SeO_3 in selenoleum *

Initial molality of CH_3CO_2H/mol kg^{-1}	Maximum f.p. attained/°C	Molar ratio at maximum f.p. $SeO_3 : CH_3CO_2H$
0.061	18.52	2.1
0.102	18.06	2.6
0.151	16.95	2.7

* f.p. = Freezing point.

Behaviour of Solutes in Selenoleum.—The solution of ammonium selenate in selenoleum depresses the freezing point. The mode of ionisation of $[NH_4]_2[SeO_4]$ can be deduced from the following observations. It is noted that if SeO_3 is added to a solution of $[NH_4]_2[SeO_4]$ in selenoleum, the freezing point of the system increases. This continues with progressive addition of SeO_3 until a maximum freezing point is reached and then it starts to fall. This increase in the freezing point when SeO_3 is added to a solution of $[NH_4]_2[SeO_4]$ suggests that the solution of ammonium selenate in selenoleum is accompanied by the formation of H_2SeO_4, equation (3). The formation of H_2SeO_4 can take place by one of the following equations (8)—(10). From equations (8)—(10)

$$[NH_4]_2[SeO_4] + 2\ H_2Se_2O_7 \longrightarrow H_2SeO_4 + 2\ NH_4^+ + 2\ HSe_2O_7^- \quad (8)$$

$$[NH_4]_2[SeO_4] + 4\ H_2Se_2O_7 \longrightarrow 3\ H_2SeO_4 + 2\ NH_4^+ + 2\ HSe_3O_{10}^- \quad (9)$$

$$[NH_4]_2[SeO_4] + 6\ H_2Se_2O_7 \longrightarrow 5\ H_2SeO_4 + 2\ NH_4^+ + 2\ HSe_4O_{13}^- \quad (10)$$

it is obvious that the ratio $SeO_3 : [NH_4]_2[SeO_4]$, at the maximum freezing point, would be expected to offer information about the correct stoicheiometry for the reaction of alkali-metal selenates with selenoleum. Table 6 shows that this maximum, for $[NH_4]_2[SeO_4]$ in selenoleum, occurs at a mol ratio $SeO_3 : [NH_4]_2[SeO_4]$ of 3 : 1 and the correct stoicheiometry would then be that of equation (9).

Organic Solutes.—The solution of acetic acid in selenoleum bears resemblances to the behaviour of ammonium selenate. Table 7 includes the data for the cryoscopic titration of acetic acid solution in selenoleum against SeO_3. The data of Table 7 show that the ratio $SeO_3 : CH_3CO_2H$ falls between 2 : 1 and 3 : 1, with a possible reaction stoicheiometry similar to equation (9).

$$CH_3CO_2H + 3\ H_2Se_2O_7 \longrightarrow CH_3CO^+ + 3\ H_2SeO_4 + HSe_3O_{10}^- \quad (11)$$

Equations (9) and (11) favour the existence of the polymer species triselenic acid, $H_2Se_3O_{10}$. The radical CH_3CO^+ was shown to exist by i.r. spectroscopy (peak at 2 300 cm^{-1}).

Solution of Elements in Selenoleum.—Selenoleum shows similarities to higher sulphuric acids in dissolving iodine and selenium. Iodine gives yellow and brown solutions with absorbances at 410 and 490 nm, and weakly at 310 nm. This accounts for the presence of I_3^+, I_5^+, and $IOHSeO_4$, which were reported in the superacid media of H_2SO_4 and HSO_3F.[8]

Selenium dissolves to give a green solution which rapidly turns yellow and finally colourless. The coloured solutions absorb at 350, 410, and 680 nm. The green and yellow colours are due to the presence of Se_8^{2+} and Se_4^{2+} respectively, which were reported by Gillespie [9] in the superacid media of HSO_3F. Selenoleum, being a powerful oxidising agent, stabilises the higher valency cation Se^{2+} which is colourless.

These observations show that selenoleum is a superacid of the selenic acid solvent system.

(*B*) *Acidity Function of Selenoleum Solutions.*—Tables 4 and 5 show that sulphuric acid and its oleums are indeed stronger acids than selenic acid and its oleums, in agreement with earlier work.[3] The data in Tables 4 and 5 show that an increase in SeO_3 concentration is accompanied by an increase of acidity. This results from the acid ionisation of diselenic acid ($H_2Se_2O_7$) in selenic acid to produce the highly acidic species $H_3SeO_4^+$ (the selenic acidium cation), equation (6), and the rapid rise in H_0 function of weak selenoleum is probably due to the moderately large ionisation of diselenic acid.

As the concentration of SeO_3 increases steadily polyselenic acids are probably formed according to the general equation (12). The acidity of solutions of polyselenic

$$n\ SeO_3 + H_2SeO_4 \longrightarrow H_2Se_{n+1}O_{3n+4} \quad (12)$$

acids increases steadily with increasing chain length until the composition of 68% SeO_3 is reached. This roughly corresponds to $H_2Se_4O_{13}$. This solution is in fact a mixture of polymer acids as well as free SeO_3.[10]

Acidity function measurements of selenoleum solutions thus confirm that it is a superacid of the selenic acid solvent system. Its ability to stabilise highly electrophilic species Se^{4+}, Se_4^{2+}, I_3^+, and I_5^+ is a further confirmation.

Acidic Power of Mixed Oleum.—The addition of SO_3 to H_2SeO_4 results in the formation of the selenic acid cation $H_3SeO_4^+$ which can be titrated conductometrically against $KHSeO_4$.[11] The formation of the mixed oleum and the cations is shown by equations (13) and (14);

$$SO_3 + H_2SeO_4 \longrightarrow H_2SSeO_7 \quad (13)$$

$$H_2SSeO_7 + H_2SeO_4 \longrightarrow H_3SeO_4^+ + HSSeO_7^- \quad (14)$$

Addition of the mixed oleum to anthracene-9,10-dione gave rise to the peak at 312 nm characteristic of the monoprotonated species BH^+. No peak was noticeable at 344 nm and this may be taken as evidence that the mixed oleum is weaker than selenoleum which gave a peak at 344 nm for the diprotonated species BH_2^{2+}.[12]

Since the mixed oleum gave rise to the species $H_3SeO_4^+$, it is then stronger than H_2SeO_4 and the acidic power of H_2SSeO_7 is thus intermediate between the acid and its oleum: $H_2Se_2O_7 > H_2SSeO_7 > H_2SeO_4$. No quantitative proof can be offered at present about the H_0 function of mixed oleums.

[1/1673 *Received, 27th October,* 1981]

REFERENCES

[1] Part 8, M. M. Nour, M. A. Hussein, and S. Wasif, *J. Chem. Soc., Faraday Trans. 1*, 1975, 1041.

[2] M. M. Nour and S. Wasif, *J. Chem. Soc. A*, 1969, 474; S. Wasif, *ibid.*, 1970, 118; S. Wasif, M. M. Nour, and M. A. Hussein, *J. Chem. Soc. Faraday Trans. 1*, 1974, 929.

[3] S. Wasif, *J. Chem. Soc. A*, 1967, 142.

[4] S. Wasif, M. M. Nour, and M. Hussein, unpublished work.

[5] K. Dostal and N. Cernohorsky, *Chem. Listy*, 1956, **50**, 702.

[6] R. J. Gillespie, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 1950, 2473.

[7] L. P. Hammett and J. Deyrup, *J. Am. Chem. Soc.*, 1932, **54**, 2721.

[8] R. J. Gillespie and M. Morton, *Q. Rev.*, 1971, **25**, 553.

[9] R. J. Gillespie, *Acc. Chem. Res.*, 1971, 413.

[10] R. J. Gillespie and K. C. Malhotra, *J. Chem. Soc. A*, 1967, 1994.

[11] M. M. Nour, Ph.D. Thesis, University of Khartoum, 1975.

[12] H. M. Zeidan, M.Sc. Thesis, University of Khartoum, 1981.