# Equilibrium Studies of Polyanions

19. Polyselenite Equilibria in Various Ionic Media

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The reactions of H^+ and $SeO_3{}^{2-}$ ($= L^{2-}$) in nine different ionic media have been studied by emf titrations, using glass electrodes. The results may be explained by assuming, besides the mononuclear products HL^- and H_2L, also the binuclear $HL_2{}^{3-}$, $H_2L_2{}^{2-}$, $H_3L_2{}^-$, and H_4L_2. The equilibrium constants found in the various ionic media are given in Table 2.

The aim of the present paper is a study of reactions between the selenite ion, $SeO_3{}^{2-}$ ($= L^{2-}$), and protons in various ionic media. The general reaction is then

$$p L^{2-} + q H^+ \rightleftharpoons H_q L_p{}^{(2p-q)-}; \quad [H_q L_p] = \beta_{pq} l^p h^q \tag{1}$$
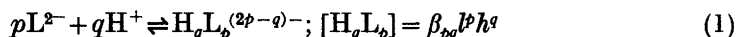
$$[H^+] = h, \quad [L^{2-}] = l \tag{1 a}$$

For brevity, we shall often denote the species $H_q(SeO_3)_p{}^{(2p-q)-}$ as the (p,q) species. We shall thus in this paper follow the nomenclature of the *Stability Constants*,[1] whereas p and q are reversed in our computer programs and in some other papers in this series.

In dilute solution, the main products are the mononuclear species $(1,1)$ and $(1,2)$, HL^- and H_2L. Their formation may be characterized by the equilibrium constants

$$K_1 = \beta_{11} = [HL^-] \, h^{-1} l^{-1}; \quad K_{12} = \beta_{12} \beta_{11}{}^{-1} = [H_2L] \, [HL^-]^{-1} h^{-1} \tag{2}$$

In literature,[1] there are several determinations of K_1 and K_{12}. In dilute solutions, around $20-25°C$, the values thereof are usually around $\log K_1 \approx 8.1$, $\log K_{12} \approx 2.5$. In the pioneer work of Blanc,[2] a lower value for $\log K_{12}$, 7.3, was found by determining colorimetrically the pH of a Na_2SeO_3 solution. This value was taken over by Schott *et al.*[3] and seems to be the basis for the thermo-

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chemical calculations leading to Latimer's value,[4] 6.60 (25°C, 0 corr), which is, however, outside the range of all other data, including the present ones.

As for the existence of polynuclear species, only qualitative evidence was available at the time when this work was begun.

Besides the normal selenites, like Na_2SeO_3, which presumably contain pyramidal SeO_3^{2-} units, a number of solid acid selenites are known, like $NaHSeO_3$, $NaH_3(SeO_3)_2$, and $Na_2Se_2O_5$.

In so far as crystal structures are known, they have indicated no separate polynuclear groups, but rather infinite chains or sheets of SeO_3 units, held together by hydrogen bonds (solid H_2L,[5] solid NaH_3L_2 [6]). According to Simon and Paetzold, the Raman and IR spectra of solid and aqueous H_2L [7] and of solid $NaHL$ [8] also indicate the formation of hydrogen bonds.

As early as in 1901, Miolati and Mascetti [9] found that they could not explain the conductance of $NaHL$ solutions or of mixtures $H_2L + NH_3$ by assuming the formation of only L^- and HL^-, and they concluded that other, presumably polynuclear, species are also formed. Ley and König [10] have found deviations from Lambert-Beer's law in the UV absorption of concentrated solutions of H_2L which they ascribed to polymers $(H_2L)_n$. Venkateswaran,[11] from the shifts of Raman spectra of solid, aqueous and alcoholic H_2L, concluded that several species are formed, although he mentions only mononuclear isomers.

Janickis and Gutmanaite [12] studied the freezing point and conductance of solutions of various acid selenites of Na^+, H^+, and NH_4^+, and found deviations which they ascribed to the formation of $H_3L_2^-$, besides HL^- and H_2L.

Simon and Paetzold [13] found identical Raman spectra with concentrated solutions of $MHSeO_3$ and $M_2Se_2O_5$, and concluded that there is a rapid equilibrium between $Se_2O_5^{2-}$ and $HSeO_3^-$, both species being present.

In 1966, when the present work was being completed, Sabbah and Carpéni [18] published a series of emf titrations with a glass electrode of selenite solutions in 3 M Na(Cl) and 3 M K(Cl) medium. They could explain their data assuming only mononuclear and binuclear species, the same explanation as we have reached independently. Their equilibrium constants will later be compared with ours.

METHOD

Our experiments were carried out as a series of emf titrations, using a glass electrode, and an Ag, AgCl electrode as reference electrode. For each of the nine different ionic media (solvents) used, titrations were made at a series of constant values for the total selenite concentration, L. For each point of a titration curve (each equilibrium solution), one then knew the values for L and H (the hydrogen ion excess above the level of H_2O and L^{2-}) from the analytical data; and from the emf, one could calculate the free hydrogen ion concentration, h, using the equation

$$E = E_0 + 59.16 \log h + E_j \tag{3}$$

As usual, E_0 was determined for each titration from solutions with excess of H^+. The liquid junction potential E_j was usually negligible in our measurements.

Knowing L, H, and h, one could calculate Z, the average number of protons bound to L,

$$Z = (H - h + K_w h^{-1}) L^{-1} \qquad (4)$$

In our measurements, the term for hydroxide ions could be neglected. The data could then be represented as curves $Z(\log h)_L$.

EXPERIMENTAL DETAILS

Reagents and analysis

Sodium perchlorate was prepared from perchloric acid (*p.a.*) and recrystallized *p.a.* Na_2CO_3. On careful neutralization, the heavy metals precipitated together with the silica present,[14] and could be separated. The solution was analyzed by evaporating and drying at $120-140°C$ to constant weight.

Sodium chloride (Merck *p.a.*) was ignited and weighed without further purification. *Sodium nitrate* and *sodium sulfate* (*p.a.*) were recrystallized twice. No nitrite was found in the $NaNO_3$ solution. The $NaNO_3$ solution was analyzed by evaporation to constant weight, and the Na_2SO_4 solution by weighing as $BaSO_4$.

Lithium perchlorate was prepared from lithium carbonate (*p.a.*) and perchloric acid, and recrystallized twice. The solutions were analyzed by evaporating and drying at $140°C$ to constant weight.

Potassium chloride (Merck *p.a.*) was ignited and weighed without further purification.

Calcium perchlorate was made as follows. Calcium carbonate *p.a.* was repeatedly washed with water to remove soluble impurities, and then dispersed in water. A slightly less than equivalent amount of perchloric acid (*p.a.*) was added, and the excess carbonate filtered off together with most impurities. The solution was analyzed complexometrically for Ca, and potentiometrically for excess H^+.

Potassium hydrogen carbonate (*p.a.*) was recrystallized from a solution saturated by CO_2, and dried in a CO_2 atmosphere.

Perchloric acid (*p.a.*) was standardized against *p.a.* $KHCO_3$ and against *p.a.* HgO. The results agreed within $\pm 0.1 \%$.

Hydrochloric, sulfuric, and *nitric acid, p.a.*, were used and standardized against $KHCO_3$. The small amount of nitrogen oxides in nitric acid was removed by boiling after dilution.

Sodium hydroxide solution was prepared as usual by way of a concentrated solution, then stored under a CO_2-free atmosphere in a polyethylene bottle, and standardized against $HClO_4$.

Potassium hydroxide was prepared from solid KOH, *p.a.*, which had been stored in a well-closed bottle; the upper layer was thrown away after opening the bottle. The underlying KOH was dissolved in deaerated redistilled water under CO_2-free nitrogen. KOH solutions made this way contained as little, or less, carbonate as NaOH solutions prepared in the traditional way.

Selenium dioxide was sublimed twice, and the Se content of its solutions was measured gravimetrically by reduction with hydrazine sulfate, and also by direct potentiometric titration with a glass electrode. The difference was never more than $\pm 0.2 \%$.

Lithium selenite was obtained from LiOH, *p.a.*, and resublimed SeO_2. The solutions were analyzed like SeO_2 by gravimetry and potentiometry.

A solution of *calcium hydrogen selenite* was made by boiling a H_2SeO_3 solution with a very small excess of $CaCO_3$ suspension. The Se content of this solution was determined gravimetrically, Ca was measured complexometrically (by two methods), and the excess of H^+, H, by an emf titration after dilution.

Nitrogen gas was taken from a commercial cylinder, purified by passing through activated copper and through wash bottles containing 10 % NaOH, 10 % H_2SO_4, and then two bottles with 3 M $NaClO_4$.

Cell

The cells were of the type

RE | equilibrium solution | glass electrode

where the reference electrode in the example of 3 M $NaClO_4$ solvent, was

RE = Ag,AgCl | 2.990 M $NaClO_4$, 0.010 M NaCl | 3.00 M $NaClO_4$

With the other electrolytes, the composition of RE was similar, except that for 3 M NaCl and 3 M KCl, the Ag,AgCl electrode was immersed in a saturated solution of AgCl in 3 M NaCl(KCl).

The "Wilhelm cell" was of the usual type.[15]

The titration vessel and the rest of the cell were immersed in an oil thermostat at $25.0 \pm 0.1°C$, and the whole equipment was kept in a thermostat room at $25.0 \pm 0.5°C$. The glass electrode was a Beckman type.

The emf was measured with a Radiometer PHM4 potentiometer, with reading accuracy of $\pm$ 0.1 mV. Equilibrium was reached very quickly after each addition, and the emf kept stable over several hours.

Table 1. Survey of titrations.

Medium	No. of ti-trations	Range of [L]	No. of points	Data in Fig. No.
3 M $Na(ClO_4)$	17	0.03 – 3.00	493	1, 2
1 M $Na(ClO_4)$	10	0.02 – 1.00	256	3, 4
0.3 M $Na(ClO_4)$	6	0.05 – 0.30	127	5, 6
3 M $Na(Cl)$	7	0.03 – 3.00	170	7, 8
3 M $Na(NO_3)$	7	0.05 – 3.00	194	9, 10
0.5 M Na_2SO_4	7	0.1 – 1.0	198	11, 12
3 M $LiClO_4$	12	0.02 – 3.00	328	13, 14
3 M KCl	7	0.1 – 3.0	191	15, 16
0.5 M $Ca(ClO_4)_2$	6	0.05 – 0.80	113	17
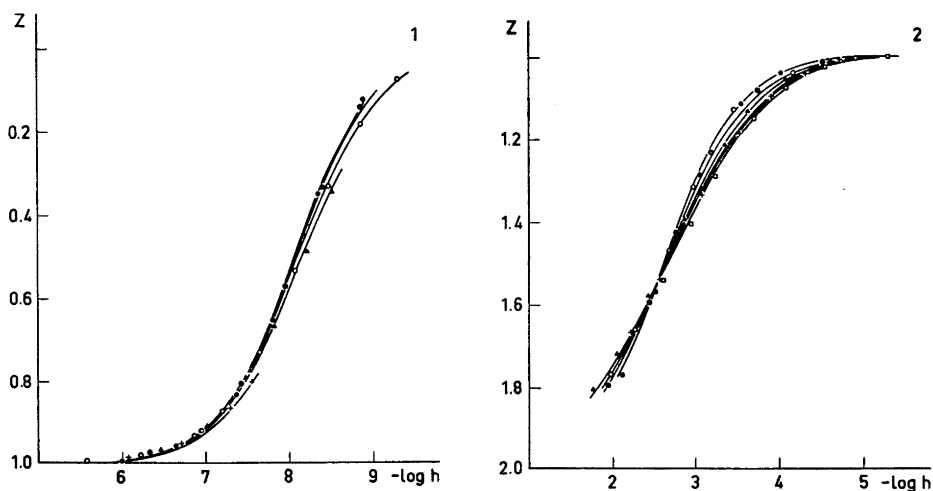
Figs. 1 and 2. Calculated (full drawn curves) and experimental data for selenite in 3 M $Na(ClO_4)$. ●, 0.07 M. ◑, 0.50 M. ○, 1.00 M. △, 1.80 M + 2.50 M. □, 3.00 M.
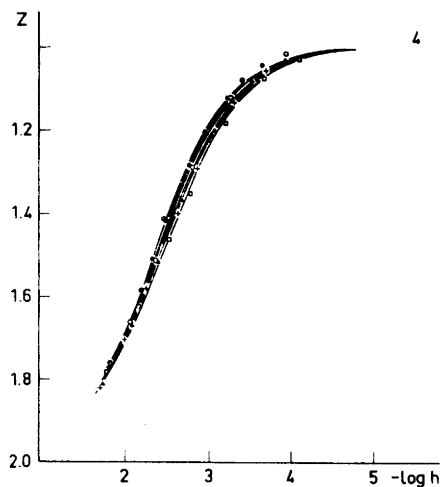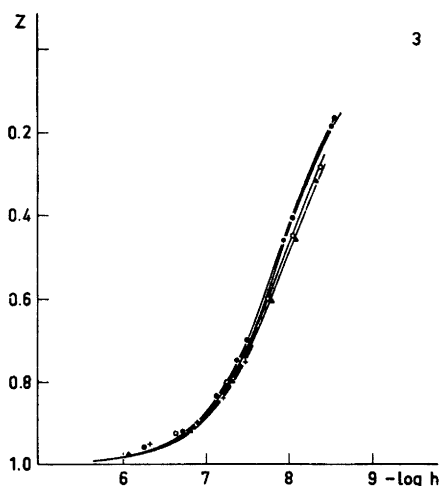
Figs. 3 and 4. Calculated (full drawn curves) and experimental data for selenites in 1 M Na(ClO₄). ●, 0.1 M. ◑, 0.2 M. ○, 0.4 M. △, 0.6 M +0.8 M. □, 1.0 M.
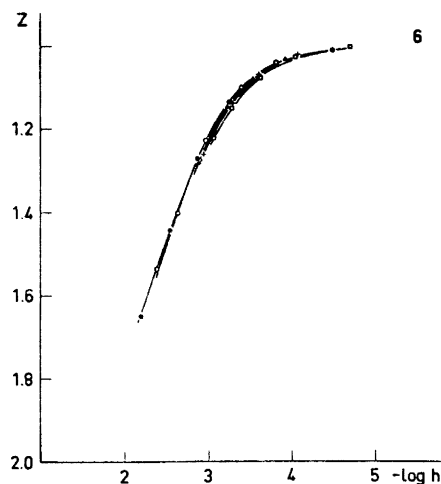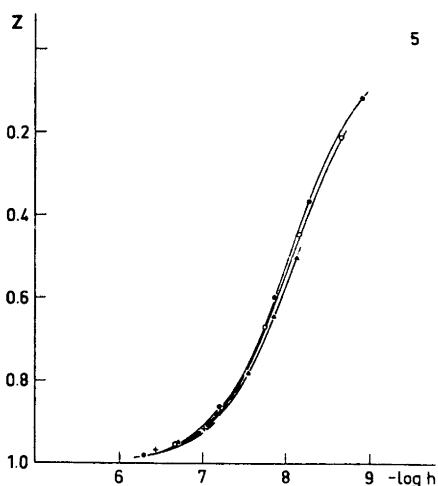

Figs. 5 and 6. Calculated (full drawn curves) and experimental data for selenites in 0.3 M Na(ClO₄). ●, 0.05 M. ○, 0.10 M. △, 0.20 M+0.25 M. □, 0.30 M.

In parallel titrations with the same values for L, and the same H, the emf was the same within better than ± 1 mV, and was independent of whether the titration was started from the acidic side ($H^+ + H_2SeO_3$) or from the alkaline side (SeO_3^{2-}).

Media used. Nine different media were used. Table 1 gives a survey of the media, with the number of titrations, of experimental points, the range of L used, and the figures where the data are given. Because of the large number of points we have abstained from giving the numerical data, and give only diagrams with a few points marked out.

When the solvent was 0.5 M Na_2SO_4, this means that we kept $[Na^+] = 1$ M and replaced part of the sulfate by selenite or hydrogen selenite ions. In this case, the values for h will depend on the value assumed for the association constant for the reaction

$$H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-; \quad K = [HSO_4^-][SO_4^{2-}]^{-1}h^{-1} \tag{5}$$
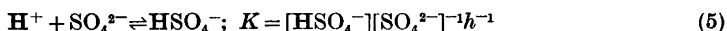
The scale for h is determined by emf measurements with the most acidic solutions; if we denote by h' the $[H^+]$, we would calculate neglecting HSO_4^-, and then we have

$$h' = [H^+] + [HSO_4^-] = h(1 + K[SO_4^{2-}]) \tag{6}$$

We have chosen the value $\log K = -1.02$ (Eichler and Rabideau [16] for 1 M $(Na)ClO_4$). It is easily seen than any other choice for $\log K$ just means a parallel shift in the E_0 and $\log$
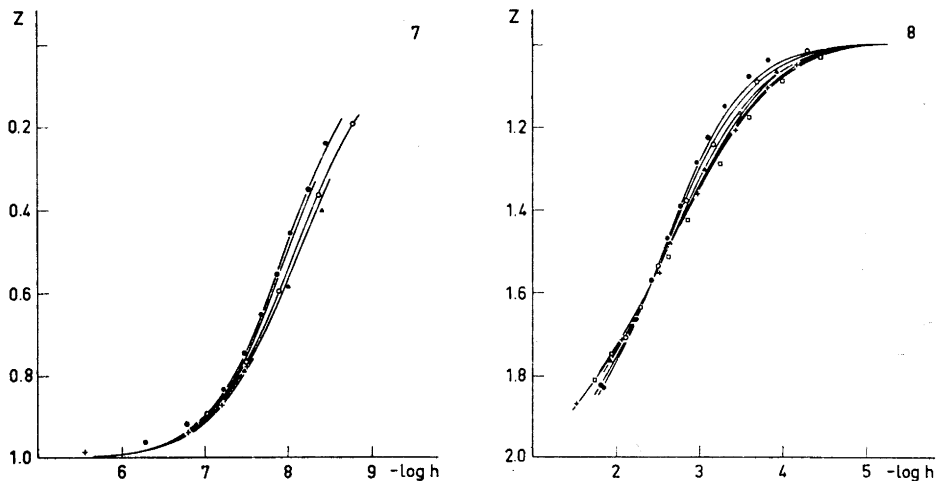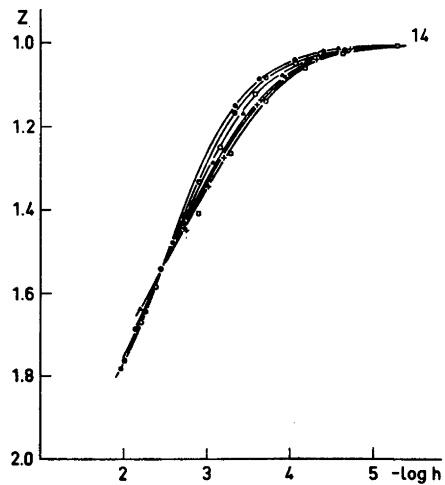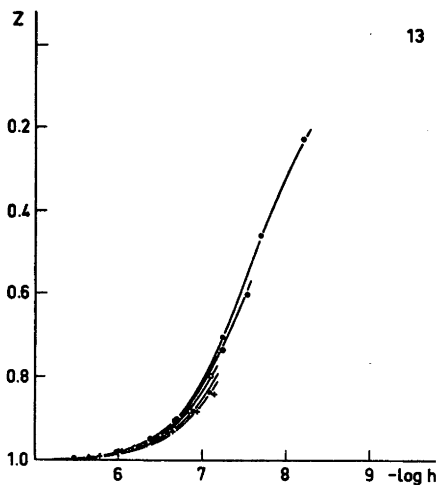
Figs. 7 and 8. Calculated (full drawn curves) and experimental data for selenite in 3 M Na(Cl). ●, 0.1 M. ◑, 0.3 M. ○, 1.0 M. △, 1.8 M + 2.5 M. □, 3.0 M.
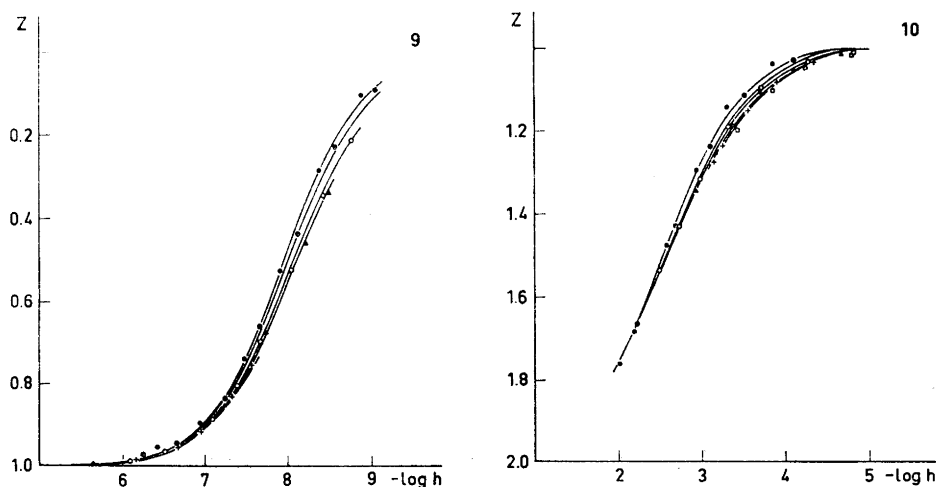
Figs. 9 and 10. Calculated (full drawn curves) and experimental data for selenite in 3 M Na(NO₃). ●, 0.2 M. ◑, 0.6 M. ○, 1.2 M. △, 1.8 M + 2.4 M. □, 3.0 M.
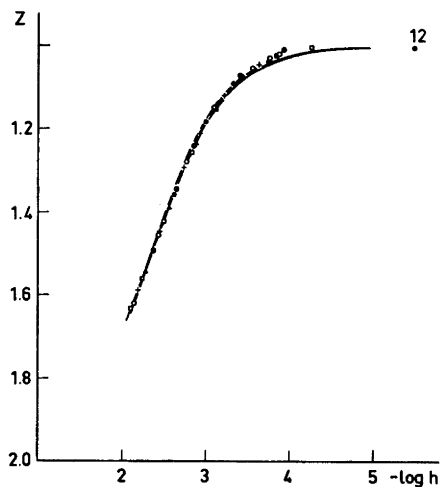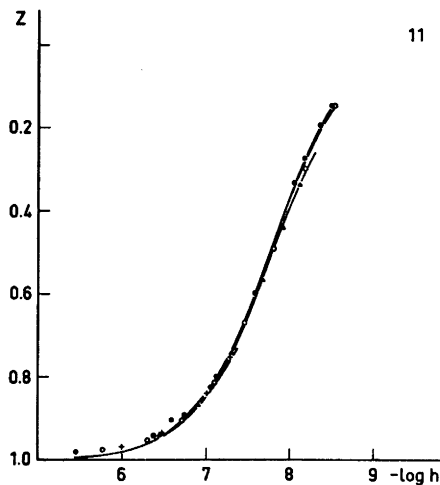
Figs. 11 and 12. Calculated (full drawn curves) and experimental data for selenite in 0.5 M Na$_2$(SO$_4$). ●, 0.1 M. ◐, 0.2 M. ○, 0.4 M. △, 0.6 M + 0.8 M. □, 1.0 M.

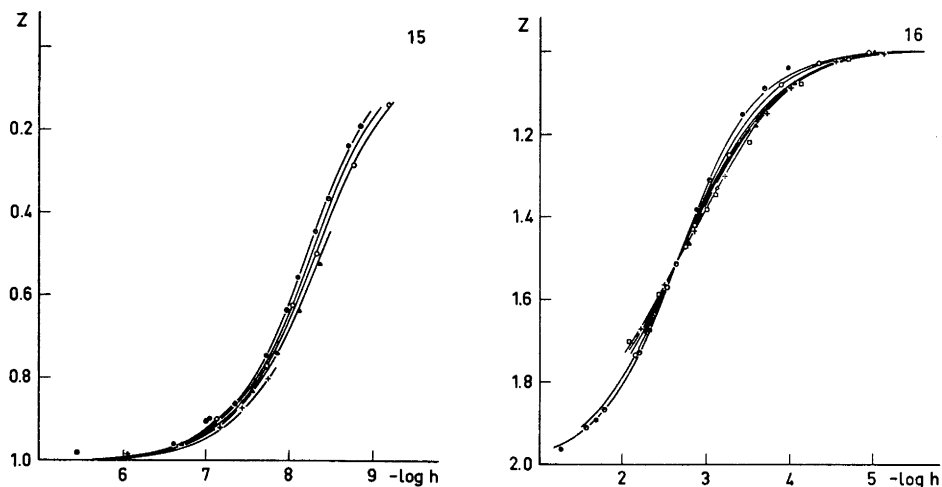*Figs. 13 and 14.* Calculated (full drawn curves) and experimental data for selenites in 3 M Li(ClO$_4$). ●, 0.07 M. ◐, 0.50 M. ○, 1.00 M. △, 1.80 M + 2.50 M. □, 3.00 M.

h scales, and does not affect our conclusions on the species in the solution. Only the calculated β_{pq} values will be shifted correspondingly.

The treatment of the data

The law of mass action, and the mass balance, give the relationships

$$L = l + \sum p\beta_{pq}l^p h^q \qquad (7)$$

Figs. 15 and 16. Calculated (full drawn curves) and experimental data for selenites in 3 M K(Cl). ●, 0.1 M. ◐, 0.3 M. ○, 1.0 M. △, 1.8 M+2.5 M. □, 3.0 M.
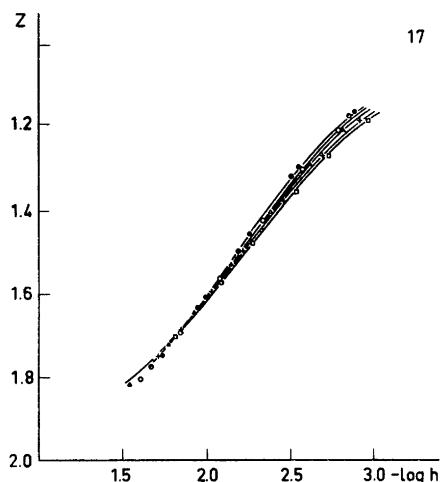

Fig. 17. Calculated (full drawn curves) and experimental data for selenites in 0.5 M Ca((ClO$_4$)$_2$). ●, 0.05 M. ◐, 0.10 M. ○, 0.20 M. △, 0.40 M+0.60 M. □, 0.80 M.

$$LZ = \sum q \beta_{pq} l^p h^q \qquad (8)$$

If a certain set β_{pq} is assumed, one may use the measured values for L and h, and eqn. (7) to calculate the free selenite concentration l in any solution, and hence use (8) to calculate the value for Z.

The data were inserted into the computer program LETAGROP,[17] and those equilibrium constants were searched for which gave a minimum in the error square sum

$$U = \sum (Z_{calc} - Z_{exp})^2 \qquad (9)$$

As a matter of fact, in all the systems studied, minima in U were found when it was assumed that the solution contains the mononuclear species (1,1), and (1,2), and also the

Table 2. Logarithms of equilibrium constants.

Medium $\sigma(Z)$	$\beta_{11}=K_1$	β_{12}	β_{21}	β_{22}	β_{23}	β_{24}	K_{12}
				$\log\ (\beta_{pq} \pm 3\sigma)$			
3 M Na(ClO$_4$) 0.010	8.05±0.02	10.66±0.02	7.79±0.07	15.49±0.07	19.02±0.05	20.91±0.10	2.51
1 M Na(ClO$_4$) 0.0099	7.78±0.02	10.05±0.02	8.01±0.12	15.73±0.09	18.70±0.07	20.80±0.07	2.27
0.3 M Na(ClO$_4$) 0.0078	7.94±0.04	10.29±0.08	8.54±0.14	16.52±0.13	19.32±0.13	21.71±0.15	2.35
3 M Na(Cl) 0.0112	7.94±0.01	10.49±0.02	7.88±0.08	15.71±0.04	19.06±0.03	21.03±0.09	2.55
3 M Na(NO$_3$) 0.0105	7.87±0.02	10.37±0.03	7.84±0.08	15.62±0.07	18.85±0.06	20.89±0.12	2.50
0.5 M Na$_2$(SO$_4$) 0.0081	7.73±0.01	10.08±0.02	7.51±0.16	14.92±0.18	17.58±0.21	19.64±0.22	2.35
3 M Li(ClO$_4$) 0.0096	7.66±0.01	10.18±0.02	–	14.39±0.08	17.99±0.005	19.83±0.08	2.52
3 M K(Cl) 0.0125	8.17±0.02	10.83±0.03	8.10±0.11	16.13±0.08	19.59±0.06	21.50±0.10	2.66
S and C[18] recalc. 0.0055	8.22±0.03	10.92±0.03	8.52±0.07	16.47±0.10	19.89±0.07	21.87±0.14	2.70
0.5 M Ca(ClO$_4$)$_2$ 0.0072	8.46±0.17	10.63±0.005	–	14	18.80±0.08	20.6±0.8	2.17

four binuclear species (2,1), (2,2), (2,3), and (2,4). In a few cases, the accuracy of the data was not sufficient to enable calculating all four "binuclear" constants. Attempts were made to introduce also complexes with 3 or 4 L. However, no significant improvement in U was obtained, or (and this is the same thing) the new β_{pq} values were of the same order as their standard deviation $\sigma(\beta)$. For instance, we found in **3 M Na(ClO$_4$)**:

$$\beta_{2,3} = (2.1 \pm 3.2) \times 10^{15}$$
$$\beta_{33} = (2.3 \pm 4.0) \times 10^{22}$$

Hence, it seems, that to explain the data we need not assume larger complexes than binuclear ones.

The results are summarized in Table 2, the values of Sabbah and Carpéni [18] given for reference. We have recalculated their values for KCl medium, and found practically the same values as theirs.

DISCUSSION

From the present data it seems likely that the predominating polynuclear species in selenite solutions are binuclear, although the existence of higher species cannot be excluded. It should be noticed that the concentrations of selenite have been quite high, really up to self-medium without any foreign anion, and

that one might doubt the use of the same equilibrium constants over such a broad range. However, the good fit for all the various solvents seems to make our explanation plausible.

The values for K_1 and K_{12} in Table 2 are of the order expected from earlier measurements. As for the binuclear species, we can compare only with Sabbah and Carpéni's values [18] for 3 M K(Cl) medium, which are systematically lower than ours by $0.3-0.4$ units. However, the relative distances, which indicate the protonation constants for the binuclear species, agree very well.

By comparing the different solvents, we find that dilution of the medium increases the stability of the binuclear species, which might support the view that hydrogen bridges exist. Furthermore, the formation constants of the dimeric species decrease in the order of nitrate, chloride, perchlorate, and sulfate, and in the order of potassium, sodium, and lithium. Calcium ions seem to decrease the stability of all binuclear species, and this may be due to the formation of complexes CaL or CaHL$^+$, although it remains to be proved.

Fig. 18 gives the distribution between species in 1 M (Na)ClO$_4$ for two selenite concentrations.

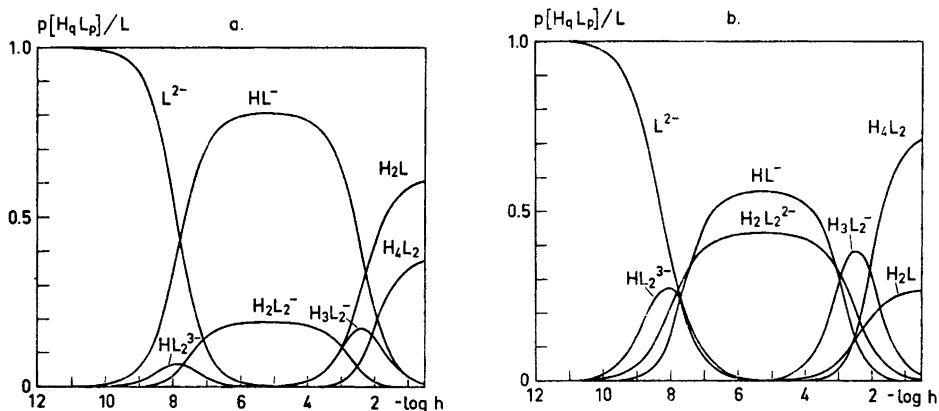*Fig. 18.* Calculated distribution of Se between species in 1 M Na(ClO$_4$) with a) $L=0.1$ M, b) $L=1.0$ M.

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