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Thermochemical Studies of Hydrolytic Reactions

11. Polyselenite Equilibria in Various Ionic Media

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The reactions of H^+ and SeO_3^{2-} have been studied calorimetrically at 25°C in three different ionic media, 3 M $NaClO_4$, 1 M $NaClO_4$, and 3 M $LiClO_4$. The enthalpy and entropy changes for the reactions were calculated using the equilibrium constants determined by Barcza and Sillén.[1] The thermodynamic quantities $\Delta G°$, $\Delta H°$, and $\Delta S°$ in the various media are given in Table 4.

The reactions between the selenite ion, SeO_3^{2-} ($=L^{2-}$), and protons have been studied by emf titrations by Barcza and Sillén.[1] The general reaction can be written

$$pL^{2-}+qH^+ \rightleftharpoons H_qL_p^{(2p-q)-};\quad [H_qL_p]=\beta_{pq}l^ph^q \quad [H^+]=h,\quad [L^{2-}]=l$$

The results from the emf measurements could be explained by assuming the formation of the binuclear HL_2^{3-}, $H_2L_2^{2-}$, $H_3L_2^-$, and H_4L_2 as well as the mononuclear products HL^- and H_2L. The formation constants of the species were determined in nine different ionic media.

Table 1. Logarithms of equilibrium constants $\log(\beta_{pq}\pm 3\sigma)$.

	β_{11}	β_{12}	β_{21}	β_{22}	β_{23}	β_{24}
3 M $NaClO_4$	8.05 ± 0.02	10.66 ± 0.02	7.79 ± 0.07	15.49 ± 0.07	19.02 ± 0.05	20.91 ± 0.10
1 M $NaClO_4$	7.78 ± 0.02	10.05 ± 0.02	8.01 ± 0.12	15.73 ± 0.09	18.70 ± 0.07	20.80 ± 0.07
3 M $LiClO_4$	7.66 ± 0.01	10.18 ± 0.02	–	14.39 ± 0.08	17.99 ± 0.005	19.83 ± 0.08

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Table 2. $\Delta H_{pq}^{\circ} \pm \sigma(\Delta H^{\circ})$ (kcal mol^{-1}).

	3 M $NaClO_4$	1 M $NaClO_4$	3 M $LiClO_4$
ΔH_{11}	-1.26 ± 0.01	-1.20 ± 0.01	-1.85 ± 0.004
ΔH_{12}	0.00 ± 0.02	0.30 ± 0.03	-1.11 ± 0.01
ΔH_{21}	-2.27 ± 0.06	-0.62 ± 0.06	–
ΔH_{22}	-3.41 ± 0.09	-1.24 ± 0.08	-1.27 ± 0.11
ΔH_{23}	-1.98 ± 0.05	0.03 ± 0.06	-2.06 ± 0.05
ΔH_{24}	-2.08 ± 0.16	1.56 ± 0.08	-0.14 ± 0.22
σ_Q, cal	0.068	0.060	0.042

Table 3. Experimental data. Values of v(ml), Q_{exp}(cal), $(Q_{calc}-Q_{exp})$(cal).

3 M $NaClO_4$

Expt. 1. $B=0.05$ M, $H_S=0.01138$ M, $H_T=0.65$ M, $V_0=228.53$ ml 4.00, 3.42, -0.10; 8.00, 3.40, -0.09; 12.00, 3.35, -0.06;
Expt. 2a. $B=0.05$ M, $H_S=0.05316$ M, $H_T=0.65$ M, $V_0=244.53$ ml 3.00, -1.90, 0.00; 6.00, -1.86, 0.01; 9.00, -1.80, 0.02; 12.00, -1.69, 0.02; 15.00, -1.53, 0.02; 18.00, -1.31, 0.04;
Expt. 2b. $B=0.05$ M, $H_S=0.05316$ M, $H_T=0.65$ M, $V_0=244.53$ ml 1.50, -0.95, 0.00; 4.50, -1.91, 0.03; 7.50, -1.84, 0.02; 10.50, -1.77, 0.04; 13.50, -1.65, 0.05; 16.50, -1.44, 0.04;
Expt. 3. $B=0.05$ M, $H_S=0.005739$ M, $H_T=0.65$ M, $V_0=226.53$ ml 4.00, 3.46, -0.13; 5.00, 0.86, -0.03; 7.00, 1.68, -0.02; 8.00, 0.84, -0.01; 12.00, 3.38, -0.08; 16.00, 3.32, -0.04;
Expt. 4. $B=0.30$ M, $H_S=0.01589$ M, $H_T=1.80$ M, $V_0=226.53$ ml 2.00, 4.90, 0.01; 6.00, 9.62, 0.08; 10.00, 9.55, 0.02; 14.00, 9.44, 0.01; 18.00, 9.18, 0.15;
Expt. 5. $B=0.30$ M, $H_S=0.04685$ M, $H_T=1.80$ M, $V_0=226.53$ ml 4.00, 9.64, -0.01; 8.00, 9.50, 0.00; 12.00, 9.36, 0.02; 16.00, 9.21, 0.07; 20.00, 9.13, 0.05; 24.00, 9.06, 0.03; 28.00, 8.95, 0.06;
Expt. 6. $B=0.60$ M, $H_S=0.1500$ M, $H_T=3.10$ M, $V_0=224.53$ ml 2.50, 10.40, 0.15; 5.00, 10.50, -0.08; 7.50, 10.32, -0.02; 10.00, 10.26, -0.08; 12.50, 10.27, -0.19; 15.00, 9.96, 0.02; 17.50, 9.95, -0.06; 20.00, 9.80, 0.00; 22.50, 9.77, -0.05; 25.00, 9.71, -0.06; 27.50, 9.65, -0.07, 30.00, 9.59, -0.07; 32.50, 9.39, 0.07; 35.00, 9.30, 0.10; 37.50, 9.26, 0.08;
Expt. 7. $B=0.60$ M, $H_S=0.6241$ M, $H_T=3.10$ M, $V_0=224.53$ ml 2.00, -4.36, 0.07; 4.00, -4.35, 0.05; 6.00, -4.34, 0.04; 8.00, -4.33, 0.03; 10.50, -5.36, 0.00; 13.00, -5.35, 0.00; 16.00, -6.37, -0.03; 19.00, -6.33, -0.04; 21.98, -6.20, -0.09; 25.00, -6.26, -0.07; 28.00, -6.21, -0.03; 32.00, -8.20, -0.01; 36.00, -8.05, -0.02; 40.00, -8.00, 0.10;

1 M $NaClO_4$

Expt. 1. $B=0.05$ M, $H_S=0.00857$ M, $H_T=0.65$ M, $V_0=227.53$ ml 3.00, 2.36, -0.07; 6.00, 2.36, -0.09; 9.00, 2.27, -0.01; 12.00, 2.25, 0.00; 15.00, 2.34, -0.11;
Expt. 2a. $B=0.05$ M, $H_S=0.05316$ M, $H_T=0.65$ M; $V_0=244.53$ ml 3.00, -2.22, -0.07; 6.00, -2.16, -0.02; 9.00, -2.02, -0.02; 12.00, -1.88, 0.02; 15.00, -1.67, 0.03; 18.00, -1.44, 0.05;
Expt. 2b. $B=0.05$ M, $H_S=0.05316$ M, $H_T=0.65$ M, $V_0=244.53$ ml 1.50, -1.10, -0.06; 4.50, -2.20, -0.04; 7.50, -2.10, -0.02; 10.50, -1.96, 0.00; 13.50, -1.79, 0.03; 16.50, -1.56, 0.04;
Expt. 3. $B=0.05$ M, $H_S=0.00434$ M, $H_T=0.65$ M, $V_0=226.03$ ml 3.00, 2.33, -0.04; 6.00, 2.27, 0.01; 9.00, 2.27, 0.00; 12.00, 2.26, 0.00; 15.00, 2.27, -0.03;
Expt. 4. $B=0.10$ M, $H_S=0.01148$ M, $H_T=1.30$ M, $V_0=226.53$ ml 3.00, 4.47, -0.02; 6.00, 4.40, 0.01; 9.00, 4.33, 0.05; 12.00, 4.35, -0.01; 15.00, 4.30, 0.01;
Expt. 5a. $B=0.10$ M, $H_S=0.1063$ M, $H_T=1.30$ M, $V_0=244.53$ ml 3.00, -4.81, -0.11 6.00, -4.69, -0.09; 9.00, -4.56, -0.02; 12.00, -4.32, 0.04; 15.00, -3.96, 0.12; 18.00, -3.40, 0.17;

Table 3. Continued.

Expt. 5b. $B=0.10$ M, $H_S=0.1063$ M, $H_T=1.30$ M, $V_0=244.53$ ml 1.50, −2.42, −0.05; 4.50, −4.81, −0.05; 7.50, −4.66, −0.03; 10.50, −4.47, 0.03; 13.50, −4.18, 0.10; 16.50, −3.72, 0.16;
Expt. 6. $B=0.100$ M, $H_S=0.01995$ M, $H_T=1.30$ M, $V_0=228.03$ ml 3.00, 4.39, 0.04; 6.00, 4.36, 0.03; 9.00, 4.29, 0.07; 12.00, 4.29, 0.04;
Expt. 7a. $B=0.20$ M, $H_S=0.030$ M, $H_T=1.75$ M, $V_0=224.53$ ml 1.49, 2.87, 0.02; 4.50, 5.82, 0.00; 7.50, 5.80, −0.03; 10.50, 5.66, 0.08; 13.50, 5.67, 0.03; 16.50, 5.58, 0.09; 19.50, 5.62, 0.01; 22.50, 5.67, −0.07;
Expt. 7b. $B=0.20$ M, $H_S=0.03$ M, $H_T=1.75$ M, $V_0=224.53$ ml 3.00, 5.83, −0.02; 6.00, 5.80, −0.02; 9.00, 5.77, −0.02; 12.00, 5.72, 0.00; 16.01, 7.66, −0.07; 20.00, 7.50, −0.01;
Expt. 8a. $B=0.20$ M, $H_S=0.2023$ M, $H_T=1.75$ M, $V_0=249.53$ ml 4.00, −8.38, 0.12; 7.00, −6.21, 0.04; 10.00, −6.10, −0.01; 13.00, −6.03, 0.00; 16.00, −5.91, −0.01; 19.00; −5.71, −0.07;
Expt. 8b. $B=0.20$ M, $H_S=0.2023$ M, $H_T=1.75$ M, $V_0=249.53$ ml 2.50, −5.19, 0.03; 5.50, −6.24, 0.05; 8.50, −6.09, −0.05; 12.00, −7.04, −0.03; 16.00, −7.87, −0.05; 20.00, −7.57, −0.10; 23.00, −5.48, −0.02;

3 M $LiClO_4$

Expt. 1. $B=0.10$ M, $H_S=0.01714$ M, $H_T=1.30$ M, $V_0=227.53$ ml 3.00, 6.89, −0.04; 6.00, 6.88, −0.06; 9.00, 6.80, −0.02; 12.00, 6.78, −0.03; 15.00, 6.72, −0.01;
Expt. 2a. $B=0.10$ M, $H_S=0.1063$ M, $H_T=1.30$ M, $V_0=244.53$ ml 3.00, −2.46, −0.03; 6.00, −2.40, −0.02; 9.00, −2.33, 0.00; 12.00, −2.24, 0.03; 15.00, −2.00, 0.00; 18.00, −1.62, −0.07;
Expt. 2b. $B=0.10$ M, $H_S=0.1063$ M, $H_T=1.30$ M, $V_0=244.53$ ml 1.50, −1.23, −0.02; 4.50, −2.45, −0.01; 7.50, −2.42, 0.04; 10.50, −2.32, 0.04; 13.50, −2.17, 0.05; 16.50, −1.83, −0.03;
Expt. 3. $B=0.10$ M, $H_S=0.008627$ M, $H_T=1.300$ M, $V_0=226.03$ ml 3.00, 6.90, −0.03; 6.00, 6.85, −0.02; 9.00, 6.78, 0.02; 12.00, 6.80, −0.03; 15.00, 6.77, −0.03;
Expt. 4. $B=0.30$ M, $H_S=0.12$ M, $H_T=1.20$ M, $V_0=224.53$ ml 2.00, 3.71, 0.00; 4.00, 3.69, 0.01; 6.00, 3.66, 0.03; 8.00, 3.63, 0.05; 10.00, 3.66, 0.01; 13.00, 5.50, −0.01; 16.00, 5.44, 0.03; 19.00, 5.45, 0.01; 22.00, 5.37, 0.07; 25.00, 5.44, −0.01; 29.00, 7.10, 0.11; 33.00, 7.11, 0.08; 37.00, 7.08, 0.08; 41.00, 7.06; 0.06;
Expt. 5. $B=0.30$ M, $H_S=0.3167$ M, $H_T=1.20$ M, $V_0=224.53$ ml 2.46, −1.18, −0.01; 5.00, −1.22, −0.01; 7.50, −1.20, −0.01; 10.00, −1.20, 0.00; 13.00, −1.43, −0.01; 16.00, −1.44, 0.01; 19.00, −1.43, 0.01; 22.00, −1.45, 0.03; 25.00, −1.40, −0.01; 29.00, −1.88, 0.01; 33.00, −1.87, 0.02; 37.00, −1.88, 0.04; 41.00, −1.88, 0.05; 45.00, −1.86, 0.05; 50.00, −2.31, 0.08;
Expt. 6. $B=0.60$ M, $H_S=0.48$ M, $H_T=1.90$ M, $V_0=224.53$ ml 0.99, 2.61, 0.00; 1.99, 2.66, −0.03; 3.00, 2.69, −0.03; 4.07, 2.87, −0.06; 5.00, 2.48, −0.04; 5.98, 2.60, −0.03; 6.98, 2.64, −0.02; 7.96, 2.60, −0.04; 9.00, 2.75, −0.03; 10.01, 2.67, −0.03; 11.50, 3.97, −0.09; 13.00, 3.97, −0.07; 14.50, 3.92, −0.03; 16.00, 3.84, 0.04;
Expt. 7. $B=0.60$ M, $H_S=0.6223$ M, $H_T=1.90$ M, $V_0=224.53$ ml 2.00, −1.07, 0.05; 4.00, −1.08, 0.04; 5.98, −1.06, 0.02; 8.03, −1.10, 0.02; 10.00, − 1.06, 0.02; 13.00, −1.62, 0.02; 16.00, −1.61, 0.01; 18.98, −1.62, 0.02; 22.01, −1.65, 0.02; 25.00, −1.60, −0.02; 29.00, −2.15, −0.02; 33.00, −2.15, −0.03; 37.00, −2.16, −0.02; 41.00, −2.12, −0.07; 45.00, −2.13, −0.06; 50.00, −2.66, −0.09.

In parallel with the emf work some calorimetric measurements were also performed on selenites. These measurements were made in three different ionic media, 3 M $NaClO_4$, 1 M $NaClO_4$, and 3 M $LiClO_4$, in order to obtain some information on the influence of the medium upon the thermodynamic quantities ΔG°, ΔH°, and ΔS°. The results of these calorimetric measurements are reported in the present paper.

Table 4. Thermodynamic quantities

Reaction	$\Delta G°$, kcal	3 M $NaClO_4$ $\Delta H°$, kcal	$\Delta S°$, e.u.
1. $H^+ + SeO_3^{2-} \rightleftharpoons HSeO_3^-$	10.98 ± 0.03	-1.26 ± 0.03	32.6 ± 0.1
2. $H^+ + HSeO_3^- \rightleftharpoons H_2SeO_3$	-3.56 ± 0.04	1.26 ± 0.08	16.2 ± 0.3
3. $H^+ + H(SeO_3)_2^{3-} \rightleftharpoons H_2(SeO_3)_2^{2-}$	-10.50 ± 0.14	-1.14 ± 0.33	31.4 ± 1.2
4. $H^+ + H_3(SeO_3)_2^- \rightleftharpoons H_4(SeO_3)_2$	-2.58 ± 0.16	-0.10 ± 0.50	8.3 ± 1.8
5. $2HSeO_3^- \rightleftharpoons H_2(SeO_3)_2^{2-}$	0.83 ± 0.11	-0.89 ± 0.28	-5.8 ± 1.0
6. $2H_2SeO_3 \rightleftharpoons H_4(SeO_3)_2$	0.55 ± 0.15	-2.08 ± 0.49	-8.9 ± 1.8

EXPERIMENTAL

The preparation and analysis of the reagents have been described in the paper on the emf measurements.[1]

The calorimetric technique used has been described previously.[2] The experiments were carried out as enthalpy titrations in which successive additions of v ml of a solution T were made from a thermostated buret to V_0 ml of a solution S contained in the calorimeter vessel. The total selenite concentration, B, was kept constant throughout each experiment. The hydrogen ion excess concentration in the S and T solution is H_S and H_T M, respectively. The values for B, H_S, H_T, and V_0 are given in Table 3 for each experiment ("titration").

RESULTS AND DISCUSSION

The data from the calorimetric titrations have been treated with the generalized least squares computer program LETAGROP/KALLE [3] (calorimetric version of LETAGROP [4,5]). With this program the computer searches for the set of unknown constants, k_i, which minimizes the error square sum

$$U = \sum(Q_{calc} - Q_{obs})^2$$

where Q is the heat effect.

The result is a set of "best" constants with their standard deviations and also the standard deviation in the Q-measurements, σ_Q.

The reactions which have been studied are

$$p SeO_3^{2-} + q H^+ \rightleftharpoons H_q(SeO_3)_p^{(2p-q)-}$$

for which we will write $\Delta H_{pq}°$ for the enthalpy change and β_{pq} for the equilibrium constant. The values for the β_{pq}, determined by emf by Barcza and Sillén,[1] are given in Table 1. Using these equilibrium constants the enthalpy changes $\Delta H_{pq}°$ were calculated by means of the computer program LETAGROP/KALLE. The result is given in Table 2.

In Table 3 the experimental data (v, Q) and the difference ($Q_{calc} - Q_{exp}$) are given. The agreement between experimental and calculated Q-values is satisfactory; no systematic deviations seem to be present. It is to be noted that the calorimetric data could not be satisfactorily interpreted assuming less than six complexes (in 3 M $LiClO_4$ five complexes). This gives some support to the reaction scheme proposed.[1]

for the $H^+ - SeO_3^{2-}$ system.

1 M $NaClO_4$ $\Delta G°$, kcal	$\Delta H°$, kcal	$\Delta S°$, e.u.	3 M $LiClO_4$ $\Delta G°$, kcal	$\Delta H°$, kcal	$\Delta S°$, e.u.
-10.61 ± 0.03	-1.20 ± 0.04	31.6 ± 0.2	-10.45 ± 0.01	-1.85 ± 0.01	28.8 ± 0.03
-3.10 ± 0.04	1.50 ± 0.10	15.4 ± 0.4	-3.44 ± 0.03	0.74 ± 0.04	14.1 ± 0.1
-10.53 ± 0.20	-0.62 ± 0.29	33.2 ± 1.2	–	–	–
-2.87 ± 0.14	1.53 ± 0.29	14.8 ± 1.1	-2.51 ± 0.11	1.92 ± 0.68	14.8 ± 2.2
-0.24 ± 0.13	1.16 ± 0.22	4.6 ± 0.8	1.27 ± 0.11	2.43 ± 0.34	4.0 ± 1.2
-0.96 ± 0.11	0.96 ± 0.27	6.4 ± 1.0	0.73 ± 0.12	2.08 ± 0.66	4.4 ± 2.2

In Table 4 we have given the thermodynamic quantities $\Delta G°$, $\Delta H°$, and $\Delta S°$ for the protonation (1 – 4) and dimerization (5 – 6) reactions in the proton-selenite system. Comparing the values in the different solvents we find that the thermodynamic parameters, especially $\Delta H°$ and $\Delta S°$, are obviously affected by the medium. *E.g.*, for the dimerization reactions (5 and 6), there is a remarkable change in $\Delta H°$ and $\Delta S°$ going from 3 to 1 M $NaClO_4$; the increasing stability of the binuclear species with dilution of the medium seems to be entirely a result of the marked change in the entropy term.

The $\Delta G°$-values for the protonation reactions (1 – 4) are nearly the same in the different media, although the $\Delta H°$ and $\Delta S°$ values are changed; the latter terms apparently counteract each other's influence on the $\Delta G°$ term.

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