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The Ionisation Constants of Tellurous and Selenous Acids

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The first and second ionisation constants of tellurous and selenous acids at ionic strengths of 0.1, 0.5, 1.0, and 1.5 have been determined by potentiometric titration using the Bjerrum function \bar{n} . Equations relating the ionisation constants to the ionic strength of the solution have been derived. A linear relation has been established between the ionisation constants of the acids H_2EO_3 (E = S, Se, or Te) and the ionisation potentials of the sulphur-subgroup elements.

The available literature values of the first ionisation constant of tellurous acid (Table 1) differ by more than three powers of 10; the differences between the second ionisation constants are smaller but nevertheless fairly substantial. There are no data concerning the effect of the ionic strength of the solution on these constants. For these reasons, the constants cannot be employed for reliable calculations on equilibria involving tellurous acid.

The available ionisation constants of selenous acids are close to one another but in most cases were obtained in solutions with variable ionic strengths: the values of K_2 calculated for $I = 0$ differ markedly (Table 1). In view of this, our aim was to determine the ionisation constants of tellurous and selenous acids over a wide range of ionic strengths and to find criteria of their reliability.

EXPERIMENTAL

The potentiometric titration method was chosen. Selenous acids of "analytical reagent" grade containing

< 0.05% TeO_2 and sodium tellurite were employed as the starting materials. Sodium tellurite was obtained from TeO_2 of "chemically pure" grade freed from selenium by dissolving it in sodium hydroxide solution and precipitating the resulting salt with ethanol¹⁰. The concentrations of sodium tellurite and selenous acid in the initial 0.049 M Na_2TeO_3 and 0.172 M H_2SeO_3 solutions were checked gravimetrically by isolating selenium and tellurium in an elemental state. All the solutions were prepared in carbon dioxide-free water. 0.1 N sodium hydroxide solution was obtained from an 18 N solution free from carbonate. The titration was performed in an atmosphere of nitrogen from a microburette using an LPM-60M potentiometer with a glass electrode and a silver | silver chloride reference electrode. To avoid an appreciable change in the volume of the solution titrated, the titrant solutions were made 30-40 times more concentrated. The ionic strengths of the solutions (0.1, 0.5, 1.0 and 1.5) were kept constant with the aid of $NaClO_4$. The temperature was $20 \pm 0.5^\circ C$.

Table 1. The ionisation constants of selenous and tellurous acids (literature data).

Acid	pK_1	pK_2	Method of determination, t ($^\circ C$), I	Refs.
H_2SeO_3	2.57	7.29	Calorimetric and conductimetric, 25 $^\circ C$, dilute solution	1
	2.31	—	Calorimetric, 25 $^\circ C$, variable I	2
	2.46	—	—	—
	2.40	8.06	Calorimetric, room temp., variable I	3
	2.51	8.05	Potentiometric, 17 $^\circ C$, variable I	4
	2.54	8.02	Potentiometric, 18 $^\circ C$, variable I	5
	2.40	8.00	Potentiometric, 20 $^\circ C$, variable I	6
	2.62	8.32	Potentiometric, 25 $^\circ C$, $I \rightarrow 0$	7
2.57	6.60	Potentiometric, 25 $^\circ C$, $I \rightarrow 0$	8	
H_2TeO_2	2.57	7.70	Calorimetric and conductimetric, 25 $^\circ C$, dilute solution	1, 9, 4
	6.05	8.30	Potentiometric and solubility, 25 $^\circ C$, $I = 1.5$	10
	6.27	—	—	—
	5.37	8.43	Solubility, 25 $^\circ C$, variable I	11
	5.84	—	—	—
	2.46	—	Extraction, 25 $^\circ C$, $I = 0.1$	12
	3.07	—	$I = 3.0$	—

The Bjerrum formation function ${}^{13}\bar{n}$ was calculated from the results of the potentiometric titration of sodium tellurite with 0.100 *N* hydrochloric acid (Fig. 1) using the equation

$$\bar{n} = \frac{H-h}{[\text{Te}]},$$

where *H* is the total analytical concentration of hydrogen ions introduced into the solution, *h* the equilibrium concentration of free hydrogen ions and [Te] the concentration of sodium tellurite calculated for each point on the titration curve.

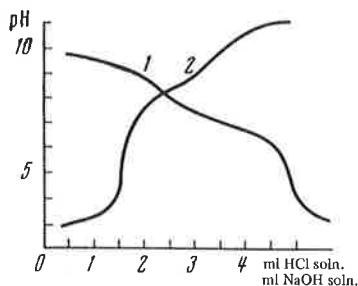


Figure 1. Curves for the potentiometric titration of sodium tellurite solution with hydrochloric acid (curve 1) and of selenous acid solution with aqueous sodium hydroxide (curve 2); $V_{\text{Na}_2\text{TeO}_3} = 90$ ml; $[\text{Na}_2\text{TeO}_3] = 2.4 \times 10^{-3}$ M; $I = 0.1$; $[\text{HCl}] = 0.100$ N; $V_{\text{H}_2\text{SeO}_3} = 48$ ml; $[\text{H}_2\text{SeO}_3] = 3.58 \times 10^{-3}$ M; $[\text{NaOH}] = 0.099$ N; $I = 0.1$.

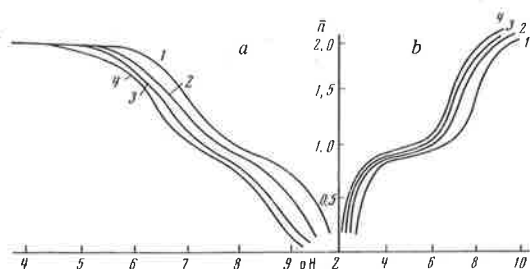


Figure 2. Variation of \bar{n} with pH for different titrations: a) Na_2TeO_3 with HCl solution [ionic strength *I*: 1) 0.1; 2) 0.5; 3) 1.0; 4) 1.5; 2.42×10^{-3} M Na_2TeO_3 ; 0.100 N HCl; $V_{\text{Na}_2\text{TeO}_3} = 90$ ml]; b) H_2SeO_3 with NaOH solution [ionic strength *I*: 1) 0.1; 2) 0.5; 3) 1.0; 4) 1.5; 3.58×10^{-3} M H_2SeO_3 ; 0.099 N; $V_{\text{H}_2\text{SeO}_3} = 48$ ml].

The values of \bar{n} obtained were plotted against pH for each point on the titration curve (Fig. 2a). The Bjerrum method establishes the following relation between K_1 and K_2 on the one hand and $[\text{H}^+]$ on the other for \bar{n} values between 0 and 2:

$$K_1 = \left(\frac{1}{[\text{H}^+]} \right)_{\bar{n}=0.5(1.5)}, \quad \text{for } \bar{n} = 0.5(1.5),$$

$$K_2 = \left(\frac{1}{[\text{H}^+]} \right)_{\bar{n}=1.5(0.5)}, \quad \text{for } \bar{n} = 1.5(0.5).$$

In the titration of the sodium tellurite solution, pK_1 and pK_2 were determined at the points where $\bar{n} = 1.5$ and $\bar{n} = 0.5$ respectively. The ionisation constants of tellurous acid obtained at different ionic strengths are listed in Table 2.

Table 2. The values of pK_1 and pK_2 for tellurous acid at different ionic strengths at 20°C.

<i>I</i>	pK_1	pK_2
0.1	6.90	9.36
0.5	6.56	9.00
1.0	6.36	8.60
1.5	6.18	8.48

The average errors of the determination are ± 0.05 and ± 0.06 for pK_1 and pK_2 respectively.

Fig. 3 shows that at $I = 0.1-1.0$, the variation of the pK 's for the ionisation of H_2TeO_3 with ionic strength is linear and therefore interpolation equations may be fitted by least squares in order to find the constants at any value of *I* in this range: $pK_1 = 6.922 - 0.5875I$; $pK_2 = 9.432 - 0.8375I$.

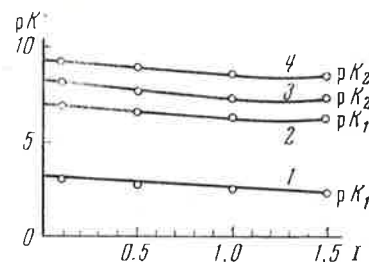


Figure 3. Variation of the ionisation constants of H_2TeO_3 and H_2SeO_3 with ionic strength: 1) and 3) H_2SeO_3 ; 2) and 4) H_2TeO_3 .

If it is assumed that the linear relations between the pK 's and *I* hold down to $I = 0$, then extrapolation to zero ionic strength yields

$$pK_1^0 = 6.92; \quad p_1$$

The potentiometric titration of selenous acid was performed with 0.099 *N* NaOH solution. Fig. 1 presents the titration curve of the H_2SeO_3 solution at an ionic strength of 0.1. The function \bar{n} was evaluated from the same Bjerrum equation as for tellurous acid. The results were expressed in terms of a plot of \bar{n} against pH (Fig. 2b) and pK_1 and pK_2 were determined at the points where $\bar{n} = 0.5$ and 1.5 respectively. Table 3 lists these results. Fig. 3 shows that a linear relation between pK_1 for selenous acid and the ionic strength of the solution is observed up to $I = 1.5$, while that involving pK_2 holds only up to $I = 1$. The following interpolation equation, also fitted by least

squares, can be used to calculate the ionisation constants of selenous acid at the intervening ionic strengths I :

$$pK_1 = 3.097 - 0.5703 I \quad (I = 0.1 - 1.5; 20^\circ \text{C}),$$

$$pK_2 = 8.304 - 1.070 I \quad (I = 0.1 - 1.0; 20^\circ \text{C}).$$

Table 3. The values of pK_1 and pK_2 for selenous acid at different ionic strengths at 20°C .

I	pK_1	pK_2
0.1	3.08	8.28
0.5	2.78	7.62
1.0	2.48	7.30
1.5	2.28	7.30

The average errors of the determination at ± 0.04 and ± 0.05 for pK_1 and pK_2 respectively.

If it is assumed that, as for tellurous acid the linear relations between the pK 's and I hold down to $I = 0$, then extrapolation to zero ionic strength at 20°C yields $pK_1^0 = 3.10$ and $pK_2^0 = 8.30$.

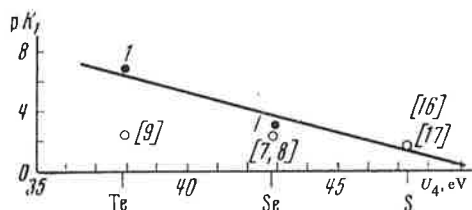


Figure 4. Ionisation constants of the acids H_2EO_3 of the sulphur-subgroup elements with the fourth ionisation potential: 1) this work; the numerals in square brackets represent literature references.

DISCUSSION

Our ionisation constants of tellurous acid at an ionic strength of 1.5 agree satisfactorily with the values found for the same ionic strength by Ganelina and Bogoyarkov¹⁰. Our values of the first ionisation constant of selenous acid differ somewhat from the majority of the literature values, while the second constant agrees satisfactorily with that quoted by Hagiwara⁷. However, the linear relations between our ionisation constants and ionic strength over a wide range of the latter suggests that they are fairly reliable.

To confirm the reliability of our ionisation constants of tellurous and selenous acids, they may be correlated with the ionisation potentials of the elements. Linear relations between the pK 's and the ionisation potentials have already been established for the formation of hydroxo-complexes of Group IV elements¹⁴ and also for the ionisation constants of acids of the type H_2MO_4 ($M = \text{Cr}, \text{Mo}, \text{or W}$) for Group VI elements¹⁵. Our values of pK_1 for tellurous and selenous acids at $I = 0$ fit much better on the linear relation

with the fourth ionisation potentials of the sulphur-subgroup elements^{16,17} than the values available in the literature (Fig. 4). We believe that this serves as adequate confirmation of the reliability of these constants.

Our interpolation equations permit the calculation of the constants at any ionic strength in the range established.

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Received 1st March 1972