BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 1—7 (1968)

Studies on the Liquid-Liquid Partition Systems. VI. Solvent Extraction Study of the Dissociation of Sulfurous, Selenious and Tellurous Acids in Acid Perchlorate Media*1

Tatsuya SEKINE, Hidehiko IWAKI, Mitsuo SAKAIRI and Fumitake SHIMADA
Department of Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo

and Mariko INARIDA
Laboratory of Nuclear Chemistry, Institute of Physical and Chemical Research, Yamatomachi, Kitaadachi-gun, Saitama

(Received May, 4, 1967)

Liquid-liquid distribution behavior of sulfur(IV), selenium(IV) and tellurium(IV) in acid perchlorate media was studied at 25°C. The distribution of sulfur(IV) into carbon tetrachloride was determined by iodometry and that of selenium(IV) into methylisobutyl carbinol or of tellurium(IV) into hexane containing trioctylphosphine oxide was determined by radiometry. The changes in the distribution ratio caused by the changes in the hydrogen ion concentration were explained in terms of the distribution of sulfurous, selenious or tellurous acid as the non-charged form into the organic phase and the dissociation of these acids in the aqueous phase. The distribution constants as well as the dissociation constants of these acids were determined by a graphical method. In acid perchlorate media, sulfurous and selenious acids exist as neutral and mononegative species while tellurous acid exists as monopositive, neutral and mononegative species, and the neutral species exists only in a narrow hydrogen ion concentration range.

Although the dissociation constants of sulfurous and selenious acids have been reported by many authors,1) very few has been known about the dissociation of tellurous acid in acid aqueous solutions.1,2) This may be due to the insoluble nature of tellurous acid in weakly acid aqueous solutions.

In the present paper, the authors have studied the liquid-liquid distribution behavior of sulfur(IV) at low concentration and that of selenium(IV) and tellurium(IV) at tracer concentration in acid perchlorate media at 25°C. From the distribution data given as a function of the hydrogen ion concentration, the acid dissociation constants of sulfurous, selenious and tellurous acids in 0.1 and 3 M perchlorate media were determined by a graphical method.

Statistical Treatment

The dioxide of sulfur, selenium and tellurium in an aqueous solution may be hydrated with unknown number of water molecules. Accordingly the noncharged acids should be described as the general form, $QO_2(H_2O)_m$. Here, m represents zero or any positive integer, while Q represents one of these elements. In the present study, however, they will be always denoted by H_2QO_3. Further it is assumed that only this neutral species can be extracted into the organic phase in a liquid-liquid distribution system.

The stepwise dissociation constants of these acids are described as;

$$K_{a_n}=[H_{2-n}QO_3{}^{-n}][H^+]/[H_{3-n}QO_3{}^{-(n-1)}] \quad (1)$$

The distribution constant of the neutral species is described as;

$$K_D=[H_2QO_3]_{org}/[H_2QO_3] \quad (2)$$

The net distribution ratio, D, may be described as;

$$D=[Q]_{org,total}/[Q]_{total}$$
$$=[H_2QO_3]_{org}/\sum [H_nQO_3{}^{n-2}] \quad (3)$$

In a system where only H_2QO_3 and $HQO_3{}^-$ species exist, Eq. (3) can be written

$$D = K_D/(1 + Ka_1[H^+]^{-1}) \quad (4)$$

On the other hand, in a system where the three species $H_3QO_3{}^+$, H_2QO_3 and $HQO_3{}^-$ are found, Eq. (3) is transformed into;

$$D = K_D/(Ka_0{}^{-1}[H^+] + 1 + Ka_1[H^+]^{-1}) \quad (5)$$

The equilibrium constants in Eq. (4) or (5) can be determined graphically by a curve-fitting

---

[*1] A part of this work was presented to the International Conference on Solvent Extraction Chemistry, Göteborg, Sweden (1966), "Solvent Extraction Chemistry", p. 32, North-Holland (1967).

1) L. G. Sillén and A. E. Martell, "Stability Constants," The Chemical Society, London, spec. pub. 17 (1964).

2) W. A. Dutton and W. C. Copper, *Chem. Revs.*, **66**, 657 (1966).

method. As the details of the graphical treatments were given in the previous work,[3] only the final equations are given in this paper.

When the distribution ratio can be represented by Eq. (4), the log$D$ *vs.* $-\log[\mathrm{H}^+]$ plot is fitted with the standard curve;

$$Y = \log(1 + v), \quad X = \log v \tag{6}$$

and when it is represented by Eq. (5), the log D *vs.* $-\log[\mathrm{H}^+]$ plot is found to fit one of the following family of standard curves,

$$Y = \log(v^{-1} + p + v), \quad X = \log v \tag{7}$$

Experimental

Tracers. Selenium-75 was obtained from the Oak Ridge National Laboratory, U. S. A. as a hydrochloric acid solution. It was diluted in 0.1 M perchloric acid or a mixture of 0.1 M perchloric acid and 2.9 M sodium perchlorate and used as the stock tracer solution. Tellurium tracer (a mixture of various radioactive tellurium isotopes) was prepared as follows; tellurium powder (four nine grade) was irradiated with thermal neutrons in JRR-2 reactor at Japan Atomic Energy Research Institute, Tokai, Ibaragi. This was let stand about two weeks and dissolved in a hot 1 : 1 nitric acid. The solution was then shaken five times with 100% tributylphosphate in order to remove radioactive iodine[4] and washed with hexane. This aqueous solution was evaporated to dryness on a water bath and the residue was dissolved in 0.1 M perchloric acid or a mixture of 0.1 M perchloric acid and 2.9 M sodium perchlorate and stored as the stock tracer solution.

Reagents. All of the reagents were of analytical grade. Sodium perchlorate prepared from perchloric acid and sodium carbonate was recrystallized two times from water. Methylisobutyl carbinol was obtained from Tokyo Kasei Co. Trioctylphosphine oxide (TOPO) was obtained from Dijindo & Co. The methylisobutyl carbinol or 0.2 M TOPO hexane solution was washed with 0.1 M perchloric acid, water, 0.1 M sodium hydroxide solution and then several times with water respectively.

Procedures. All of the procedures were carried out in a thermostated room at 25±0.5°C. Two liquid phases were equilibrated in a glass stoppered tube (volume 20 m*l*).

The Experiments for Sulfur(IV). Ten to twenty milligrams of sodium sulfite, various amounts of perchloric acid, sodium perchlorate solution and carbon tetrachloride were placed in the tubes. The two phases in the tubes were agitated vigorously with a mechanical shaker for 5 min and centrifuged. Two milliliter portion was pipetted from each phase and transferred into 120 m*l* Erlenmeyer flasks and the sulfur(IV) content was determined by iodometry.

The Experiments for Selenium(IV) and Tellurium(IV). One tenth milliliter portion of the tracer stock solution, various amounts of perchloric acid and sodium perchlorate solution and then the organic solution were placed in the tubes. The initial concentration of selenium in the aqueous phase was less than 10^{-6} M and that of tellurium was 1.0×10^{-4} M. In some experiments with tellurium(IV), a small amount of sodium sulfanilate or sodium acetate (initial concentration in the aqueous phase was 0.01 M) was added in order to buffer the aqueous phase. No buffer was added to the system containing selenium(IV). The two phases in the tubes containing selenium(IV) were agitated on a mechanical rotating framework usually for one week. The two phases containing tellurium(IV) were shaken 15 min by a mechanical shaker and were then centrifuged for 3 min at 2000 rpm. Two milliliter portion was pipetted from each phase and transferred into small test tubes. The γ-radioactivity of these samples was measured with a well-type (NaI) scintillation counter. Another small portion was also pipetted from the aqueous phase and the hydrogen ion concentration was determined potentiometrically by using a standard solution, 0.0100 M $\mathrm{HClO_4}$ + 0.09 M $\mathrm{NaClO_4}$ or 0.0100 M $\mathrm{HClO_4}$ + 2.99 M $\mathrm{NaClO_4}$ as the standard of $-\log[\mathrm{H}^+]=2.000$. A correction was made for the emf data by using a series of standard solutions when the aqueous phase contained more than 0.01 M hydrogen ion. The ionic media was 0.1 M (H, Na)$\mathrm{ClO_4}$ or 3 M (H, Na)$\mathrm{ClO_4}$ in all experiments. The initial volume of the aqueous phase was always 5.0 m*l* and that of the organic phase was 5.0, 5.0 and 3.0 m*l* respectively for the experiments with sulfur(IV), selenium(IV) and tellurium(IV). In some experiments with tellurium(IV), the tracer was first extracted into the organic phase by similar procedures as described above and then it was back extracted from this organic phase to a fresh aqueous solution and the distribution ratio was determined.

Results

Dependence of D on $-\log[\mathrm{H}^+]$. Figures 1a and 2a give the distribution of sulfur(IV) between carbon tetrachloride and the aqueous phase whereas Figs. 1b and 2b give that of selenium(IV) between methylisobutyl carbinol and the aqueous phase as a function of the hydrogen ion concentration. In both cases it is seen that the plot has two asymptotes with a slope zero and minus one. The dependence of D on the $-\log[\mathrm{H}^+]$ is explained by Eq. (4), that is, both of sulfurous and selenious acids exist as $\mathrm{H_2QO_3}$ and $\mathrm{HQO_3}^-$ species in the aqueous phase of this $-\log[\mathrm{H}^+]$ range. By the curve fitting with the standard curve given by Eq. (6), the distribution constant of the acids in the neutral form, K_D, and the dissociation constant, K_{a_1}, were determined as they are listed in Table 1.

Figures 1c and 2c give the distribution ratio of tellurium(IV) between hexane containing 0.2 M TOPO and the aqueous phase as a function of $-\log[\mathrm{H}^+]$. No difference was observed between the results when the tracer initially added to the aqueous phase and those when the tracer was initially added to the organic phase. Figures 1c and 2c contain both kind of the results obtained by the extraction or by the back extraction. Except for the lowest $-\log[\mathrm{H}^+]$ region in 0.1 M

---

[3] D. Dyrssen and T. Sekine, *J. Inorg. Nucl. Chem.*, **26**, 981 (1964).

[4] M. Inarida, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **79**, 721 (1958).

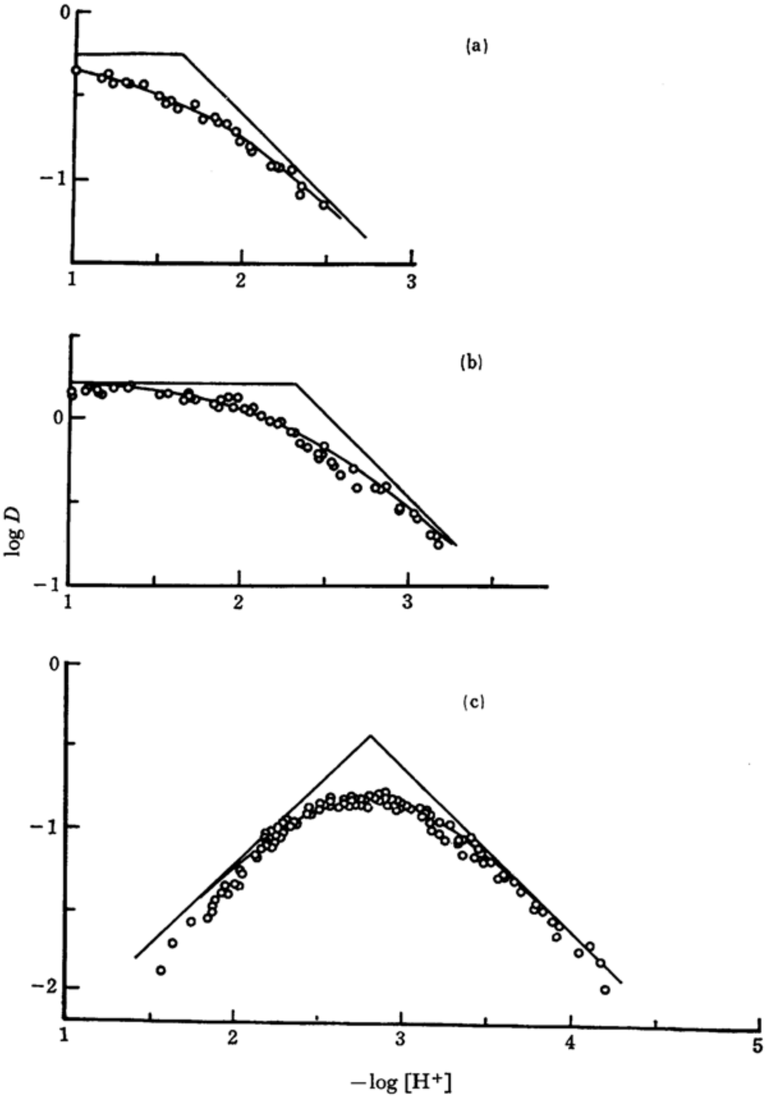

Fig. 1. Distribution of (a) sulfur(IV), (b) selenium(IV) and (c) tellurium(IV) in 0.1 M perchlorate media. The organic phases are described in Table 1. The two asymptotes and the distribution curve were obtained from the constants in Table 1.

TABLE 1. DISTRIBUTION AND DISSOCIATION CONSTANTS OF THE ACIDS AT 25°C (*cf.* Eqs. (1) and (2))

	Ionic media M, (H, Na)ClO$_4$	$\log K_D$	$-\log K_{a_0}$	$-\log K_{a_1}$
Sulfurous acid	0.1	−0.25	—	1.62
	3.0	−0.23	—	2.03
Selenious acid	0.1	0.21	—	2.33
	3.0	0.56	—	2.24
Tellurous acid	0.1	−0.08	3.16	2.46
	3.0	0.39	4.17	3.07

Organic phase sulfurous acid: carbon tetrachloride
Selenious acid: methylisobutyl carbinol
Tellurous acid: hexane containing 0.2 M trioctylphosphine oxide

perchlorate media, the plot has two asymptotes with a slope plus one and minus one and has a pronounced maximum between them and this indicates that the monopositive species, $H_3TeO_3^+$, is predominant in the lower $-\log[H^+]$ region while the mononegative species, $HTeO_3^-$, is predominant in the higher $-\log[H^+]$ region. Thus it is anticipated that the proportion of the neutral species, H_2TeO_3, is low all over the $-\log[H^+]$ region because if there were a region where the neutral species is predominant, an asymptote of a slope zero should be seen. The plot was fitted with one of the family of standard curves in Eq. (7) and the distribution constants and the dissociation constants for tellurous acid were determined from the parameters of the best-fit standard

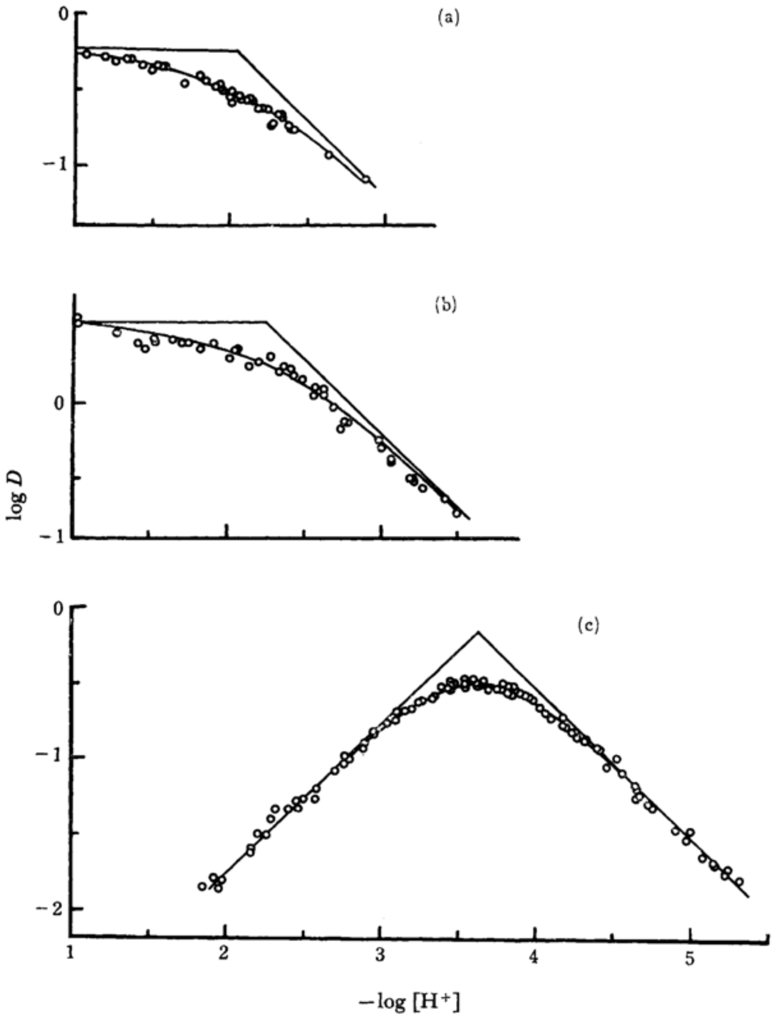

Fig. 2. Distribution of (a) sulfur(IV), (b) selenium(IV) and (c) tellurium(IV) in 3.0 M perchlorate media. The organic phases are described in Table 1. The two asymptotes and the distribution curve were obtained from the constants in Table 1.

curve as they are listed in Table 1.

Rate of the Extraction. The extraction of selenium(IV) in aqueous solutions into the methylisobutyl carbinol phase was a slow reaction. Figure 3 gives the increasing D with time when the tracer was initially added to the aqueous phase. The figure shows that the extraction rate is larger in the higher $-\log[H^+]$ range. It was observed that the rate of the back extraction of selenium(IV) from the organic phase to the aqueous phase was very small. No appreciable amount was back extracted into the aqueous phase even after an agitation over one week. On the other hand, the rate of the extraction or the rate of the back extraction of sulfur(IV) and tellurium(IV) was much larger than that of selenium(IV) all over the $-\log [H^+]$ range studied. The distribution equilibrium of these species was attained by an agitation for five minutes.

Effect of the Concentration of the Acids. No change in the distribution ratio or the rate of the extraction of sulfur(IV) was observed when the amount of sodium sulfite initially added was changed from 5 to 20 mg. The distribution ratio of selenium(IV) decreased very much by adding 10^{-4} to 10^{-3} M selenium(IV) carrier to the aqueous phase. It was also observed that an organic solution of selenious acid at macro concentration was not stable. Namely, red precipitates which looked like elementary selenium were formed in methylisobutyl carbinol solutions containing macro amounts of selenious acid. Thus it was concluded that the distribution equilibrium of selenium(IV) is established only when the concentration is

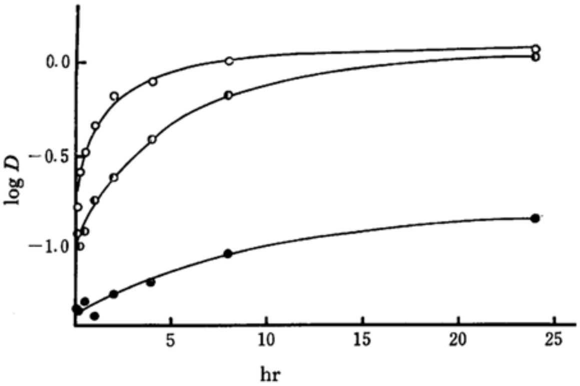

Fig. 3. Increase in the distribution ratio of selenium(IV) in 0.1 M perchlorate media at $-\log[H^+]$ 1.00 (open circles), 1.96 (half-closed circles) and 2.84 (closed cirles) into methylisobutylcarbinol as a function of time.

low and when the tracer is initially added to the aqueous phase. Practically no difference of the distribution ratio of tellurium(IV) was observed when the initial concentration in the aqueous phase was 5×10^{-5}, 1×10^{-4}, 2×10^{-4}, 3×10^{-4} and 4×10^{-4} M in 3 M perchlorate media at $-\log[H^+]$ 3.7 and 4.6. This seems to indicate that no polynuclear tellurium(IV) species are formed in the aqueous phase within the experimental accuracy.

Extraction by Using Other Solvents. The extraction of sulfur(IV) seems to be the lowest when non-polar solvents such as hexane or carbon tetrachloride are used. The distribution of sulfur(IV) increases with increasing the polarity of the solvent. The distribution of selenium(IV) between various organic solvents and an aqueous solution containing 0.1 M perchloric acid and 2.9 M sodium perchlorate was also studied. Most of the solvents like benzene, chloroform, carbon tetrachloride or hexane extracted selenium(IV) only poorly; the *D* value was 10^{-2} or less. Some polar solvents extracted selenium(IV) to some extent. For example, tributylphosphate or methyl isobutyl ketone extracted selenium(IV) with the *D* of arround 10^{-1}. Thus it was concluded that the extraction of selenium(IV) with methylisobutyl carbinol is exceptionally large among the solvents studied.

No organic solvent was found to extract tellurium(IV) to any appreciable amount without TOPO. Some experiments were carried out using different organic solvents as the diluent of TOPO. When the TOPO concentration was the same, the extraction of tellurium(IV) from an aqueous solution at a certain $-\log[H^+]$ into benzene or carbon tetrachloride was one third or one tenth of that into hexane and the extraction was negligibly small when chloroform was used as the diluent of TOPO.

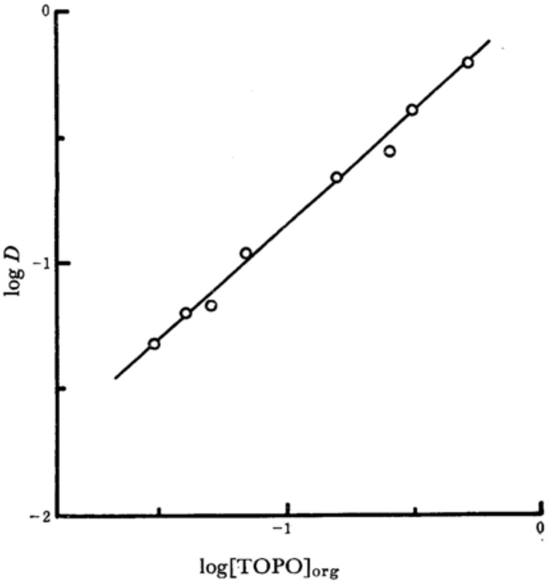

Fig. 4. Distribution of tellurium between hexane containing various amounts of TOPO and 3 M perchlorate media at $-\log[H^+]$ 3.9 as a function of TOPO concentration in the organic phase.

Dependence of Tellurium(IV) Extraction on the TOPO Concentration. The dependence of tellurium(IV) extraction on the TOPO concentration in hexane has been studied. Figure 4 gives the plot log*D* *vs.* $\log[\mathrm{TOPO}]_{\mathrm{org}}$ when the aqueous phase was 3 M perchlorate solution at $-\log[H^+]$ 3.9. The plot falls on a straight line with a slope plus one. This indicates that one molecule of TOPO combines with one molecule of H_2TeO_3 species in the organic phase. This can be described as follows;

$$H_2TeO_3+\mathrm{TOPO(org)} \rightleftharpoons H_2TeO_3\cdot\mathrm{TOPO(org)}$$

Reproducibility of the Results. The recovery of sulfur(IV) from the two phases was almost quantitative. The loss of sulfur(IV) from the two phases as sulfur dioxide after the phase separation was negligible. The recovery of selenium(IV) or tellurium(IV) from the both phases was also quantitative.

An addition of buffering agent such as sulfanilate or acetate to the aqueous phase increased the distribution ratio of selenium(IV) systematically. No effect of the buffer was, however, observed in the extraction of tellurium(IV) when the buffer concentration was less than 0.01 M.

It was necessary to purify the tellurium tracer by a preliminary extraction cycle in order to obtain reproducible results. No purification of the selenium tracer by the extraction method was carried out because the rate of the back extraction was very small. The results of selenium(IV) or of tellurium(IV) extraction seem to be affected by various factors such as the presence of dusts more than many other solvent extraction experiments.

Discussion

It is difficult to compare the dissociation constants of these acids in the present study directly with the previous data which have been determined in ionic media at different concentration. Further, the dissociation constants were calculated by using the stoichiometric concentration ($-\log[H^+]$) in the present study while those have been calculated by using the activity of the hydrogen ion (pH) in most of the previous work.

The first dissociation constant of sulfurous acid, pK_{a_1}, in the previous papers are in the range 1.76 to 1.92¹⁾ when the ionic concentration is low and the present pK_{a_1} values in 0.1 and 3 M perchlorate media is a little smaller and a little larger than those previous values.

The first dissociation constant of selenious acid, pK_{a_1}, in dilute ionic media in the previous papers¹⁾ are in the range 2.46 to 2.62 which are a little higher than the present results in 0.1 and 3 M perchlorate media.

It was observed that the rate of the extraction of selenium(IV) is very small especially when some amounts of carrier was added, that the back extraction was not possible and that the quadrivalent state of selenium in methylisobutyl carbinol at macro concentrations was unstable. Still the distribution ratios of selenium(IV) at tracer concentration in Figs. 1b and 2b are well explained by Eq. (4) and the dissociation constants obtained look reasonable. Thus it may be concluded that selenium(IV) in such a distribution system is enough stable and the rate of the extraction is large enough to achieve the distribution equilibrium by an agitation for one week.

There were not many reports on the first dissociation constant of tellurous acid. This may be due to the insoluble nature of tellurous acid in aqueous solutions. The dissociation constants in the previous work were obtained from the analysis of the acid dependence of the solubility of tellurous acid.¹⁾ The existence of the positive charged species of tellurous acid in acid aqueous solutions has been pointed out by some authors from the solubility data,⁵⁻⁷⁾ cation-exchange data⁸⁾ or by the dithizone extraction data.⁹⁾ However, none of them have determined the dissociation constant for the first proton in this positive charged species, $H_3TeO_3^+$ or $TeOOH^+$. Dutton and Cooper²⁾ recommended 3×10^{-3} as K_{a_1} ($=[HTeO_3^-]\,[H^+]/[H_2TeO_3]$) of tellurous acid in the recent review but they did not discuss the dissociation constant of this positive charged species. As is seen in Fig. 5, contribution of the non charged species to the whole tellurium concentration is small over all hydrogen ion concentration region (this corresponds to the fact that there is no region in Figs. 1c and 2c where the slope $d\log D/d\log[H^+]^{-1}$ is zero). It is indispensable to take the dissociation of the positive charged species into the account for the calculation of the K_{a_1} of tellurous acid. Thus although the value given by Blanc,¹⁰⁾ $K_{a_1}=2.7\times10^{-3}$, agrees with the present value in 0.1 M perchlorate media, $K_{a_1}=3.5\times10^{-3}$, still it is necessary to reexamine this previous value.

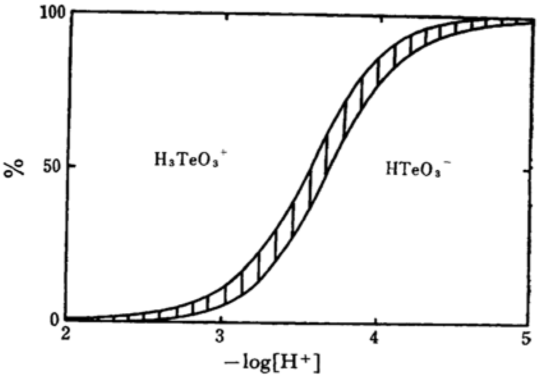

Fig. 5. Distribution of hydrolyzed species as a function of $-\log[H^+]$. The virtically liniated part represents the H_2TeO_3 species.

Figure 1c shows the plot deviates from the asymptote with a slope plus one. The same kind of deviation was also observed in the distribution of vanadium(V), HVO_3, between methylisobutyl carbinol and 0.5 M (H, Na)$ClO_4$³⁾ and Dyressen and Sekine explained this deviation as the change in K_D when sodium ions are replaced by hydrogen ions. The deviation in Fig. 1c seems to be also explained by this explanation, the fact that the deviation does not appear in the experiments in 3 M (H, Na)ClO_4 in Fig. 2c where the change in the cation is not large even in the lower $-\log[H^+]$ region may support the explanation.

Table 1 elucidates that the K_D value in 3 M perchlorate media is larger than that in 0.1 M media. This increase in the distribution constant, the salting-out effect, increases in the sequence sulfurous, selenious and tellurous acids. This sequence also agree with that of the basicity of the necessary extractant for these acid in aqueous solution.

The authors are grateful to Professor Nobufusa Saito, the head of the laboratory of Nuclear Chemistry, Institute of Physical and Chemical

---

5) J. Kasarnowsky, *Z. Phys. Chem.*, **109**, 287 (1924).
6) R. Shuhmann, *J. Am. Chem. Soc.*, **47**, 356 (1925).
7) E. Deltombe, N de Zoubor and M. Pourbaix, Cebelcor Rapp Tech., No 33 (1956).
8) Y. Sasaki, *Japan Analyst*, **4**, 637 (1955).
9) H. Mabuchi and I. Okada, This Bulletin, **38**, 1478 (1965).
10) E. Blanc, *J. Chim. Phys.*, **18**, 28 (1920).

Research where some part of this work was carried out. The authors are also grateful to Professor David Dyrssen of Göteborg University, Sweden and to Dr. Akira Yamasaki of the University of Tokyo for the helpful discussion and Messrs. Takeshi Hamada, Hiroyuki Okamoto and Ichiro Kobayashi of Science University of Tokyo for their experimental aids.