The Separation of Tellurite, Selenite and Sulfite Ions by Anion-Exchange Resins

By Akira IGUCHI

(Received February 14, 1958)

The separation of tellurite, selenite and sulfite is a difficult problem. A few ion-exchange separations of chloro complexes of tellurium and selenium have recently been reported[1,2]. In this paper the behavior of sulfite, selenite and tellurite towards anion exchange resins is studied in alkaline media. The results give a new successful separation of these oxy-acid anions.

Experimental

Materials. — *Anion-exchange resin.* — Air-dried Dowex 1-X8, 100- to 200-mesh, was used in either the hydroxide or the nitrate form.

Sodium tellurite and sodium selenite.—Guaranteed reagents were used without purification. The ordinary gravimetric analysis of these salts[3] showed that they were pure enough for the purpose of this study. The samples dissolved in water could not be kept for a long time, since the state of these salts in the aqueous solution changes with the lapse of time in a neutral solution; in an alkaline stock solution oxidation may occur, when they are kept too long. Hence the sample solution has been kept for 3 days at the longest, in a glass stoppered Erlenmeyer flask kept in a refrigerator.

Sodium sulfite.—The neutral aqueous solution of this salt decomposes only about 0.5% a day right after dissolution. But the rate of decomposition increases when the solution is kept longer. Thus it is desirable to dissolve the salt right before each experiment. On the anion-exchange resin of the hydroxide form, the sulfite ion seems to be more stable than in a neutral solution; the quantity of sulfite ions eluted from the resin is equal to that expected even after two days' keeping on the resin. The quantity of sulfite is estimated by the iodimetric titration.

Procedures. *Analysis of samples.*—The quantity of tellurite in the solution was determined by the titration of thiosulfate proposed by R. A. Johnson and D. R. Fredrickson[4]. The tellurite in the sample was potentiometrically titrated with standard iodine solution after the addition of hydrochloric acid, potassium iodide and a known quantity of thiosulfate. Ammonium salt did not cause interference even when its concentration was as high as 1.5 mol./l. Since a positive error is expected in a more concentrated solution, the effluent was diluted with a suitable amount of water to keep the concentration of ammonium salts less than 1.3 mol./l.

The quantity of selenite in the solution was determined by the titration method which was proposed by J. F. Norris and H. Fay[5], by the use of standard iodine solution, starch and a definite amount of thiosulfate. Of course the end point was also determined potentiometrically as in the case of tellurite.

The quantity of sulfite in the solution was titrated with standard iodine solution, together with acetic acid and glycerin[6].

The measurement of distribution coefficients of tellurite, selenite and sulfite ions in various concentrations of sodium nitrate and sodium hydroxide.—The distribution coefficient, K_d was measured by the column method. The K_d values of the ion were calculated from the volume of the eluant through the following equation,

$$K_d=(V-i)/M^{7-9)} \qquad (1)$$

where K_d(cc./g.) is the distribution coefficient, V(cc.) the volume of eluant passed through the column until the concentration of the sample in the effluent becomes maximum, i(cc.) the interstitial volume of the column and M(g.) the weight of the resin. The columns were 7.0 mm. in diameter, and contained 1~3 g. of the resin. The flow rate was less than 0.3 cc./min.

Results and Discussion

Relationship between the distribution coefficient of tellurite, selenite and sulfite and the concentration of nitrate or hydroxide ion in the eluant.—The results obtained with the procedure using aqueous solutions of sodium nitrate as eluants are shown in Fig. 1, and those with sodium hydroxide solutions in Fig. 2. The values are the mean values of the two

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[2] Y. Sasaki, ibid., **28**, 89 (1955).

[3] e.g., F. P. Treadwell and W. T. Hall, "Analytical Chemistry" 8th English Ed., John Wiley & Sons, New York, (1935), Vol II, p. 268.

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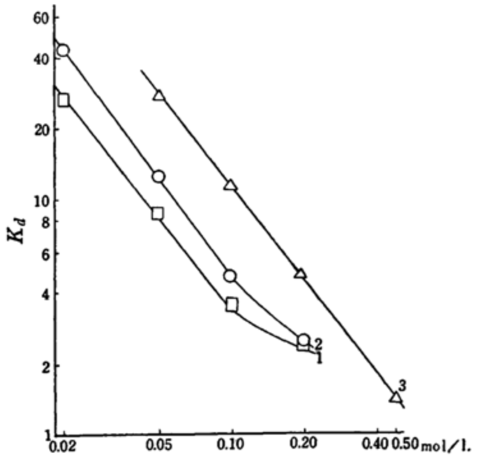
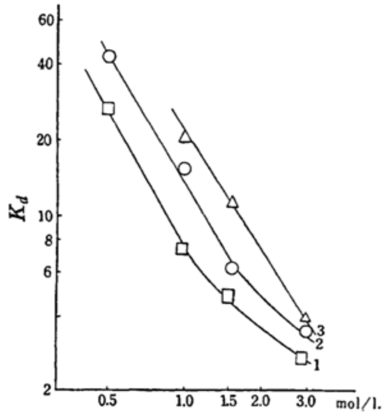


Concentration of sodium nitrate

Fig. 1. Relationship between K_d and the concentration of sodium nitrate in the eluant.
1: Sodium tellurite. 2: Sodium selenite.
3: Sodium sulfite.



Concentration of sodium hydroxide

Fig. 2. Relationship between K_d and the concentration of sodium hydroxide in the eluant.
1: Sodium tellurite. 2: Sodium selenite.
3: Sodium sulfite.

experimental data and the error is less than about 2%.

When the reaction of the ion with the ion-exchanger is supposed to be

$$\nu RX + A^{\nu -} = R_\nu A + \nu X^-$$

the distribution coefficient K_d is given by the equation,

$$K_d = [R_\nu A]/[A^{\nu -}] \tag{2}$$

and the equilibrium constant K_{ex} is given by the equation,

$$K_{ex} = [R_\nu A][X^-]^\nu/[RX]^\nu[A^{\nu -}] \tag{3}$$

From equations 2 and 3 it is seen that

$$K_d = K_{ex} \cdot [RX]^\nu/[X^-]^\nu \fallingdotseq k/[X^-]^\nu \tag{4}$$

where k is a constant.

So the equations 5 and 6 are obtaind:

$$\log K_d = \log k - \nu \log[X^-] \tag{5}$$

or

$$d \log K_d / d \log [X^-] = -\nu \tag{6}$$

Consequently from the slope of the curve, it is possible to induce the charge of the exchanged ion.

From Figs. 1 and 2, linear relationships of $\log K_d$ towards $\log C$ are observed except in the region of high concentrations of the eluants. The linear lines for tellurite, selenite and sulfite in Fig. 1 are almost parallel and their slope is about 1.5 at a low concentration. So they may contain the ions of one negative charge; in other words, $HTeO_3^-$, $HSeO_3^-$ may be present together with anions of two negative charges in these neutral solution.

The straight linesf or these salts in Fig. 2 are also almost parallel and their slope is about 2.0 at a low concentration, so they must exist in the form of anions with two negative charges, that is, TeO_3^{2-}, SeO_3^{2-} and SO_3^{2-} in these strongly alkaline solutions.

As the difference of K_d among these three anions is not very remarkable, and as the tailing part of selenite and tellurite in elution process is not sharp, it is very difficult to separate them by using sodium nitrate or sodium hydroxide solution as an eluant.

The relationship between the concentration of ammonia added and the distribution coefficient.—In the elution process of the column method, these anions are eluted too readily by neutral nitrate solution to be separated from each other, and with too great difficulty by hydroxide solution. Consequently it is necessary to study the intermediate region of pH of the eluant. But aqueous ammonia without salt cannot be used as the eluant, for these anions are not eluted with it in any concentration. Thus the effect of the addition of aqueous ammoia to the eluant containing nitrate or hydroxide was studied. The results are shown in Fig. 3.

By adding ammonia to a nitrate eluant, the values of the distribution coefficients, K_d, for tellurite and selenite increase rapidly, but the difference among the ions becomes smaller; therefore this combination is not suitable for the purpose of

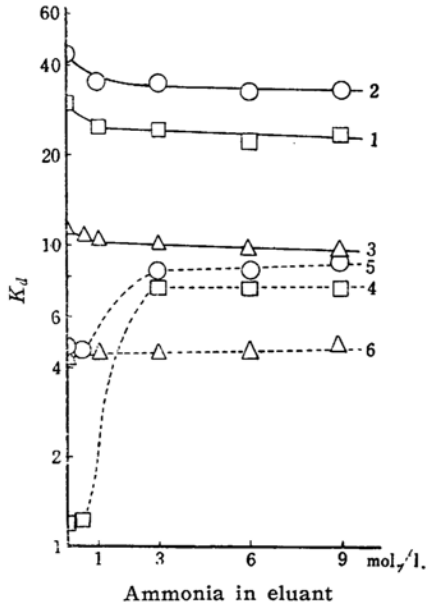


Fig. 3. Relationship between K_d and the concentration of added ammonia in eluant.
1: Sodium tellurite eluted with 0.4 N sodium hydroxide. 2: Sodium selenite eluted with 0.4 N sodium hydroxide. 3: Sodium sulfite eluted with 1.5 N Sodium hydroxide. 4: Sodium tellurite eluted with 0.1 mol./l. sodium nitrate. 5: Sodium selenite eluted with 0.1 mol./l. sodiumnitrate. 6: Sodium sulfite eluted with 0.2 mol./l. sodium nitrate.

separation. On the contrary, although the addition of ammonia to a hydroxide eluant causes only a small decrease of K_d, the difference of K_d for each anion remains unchanged and fortunately the tailing part of selenite and tellurite in the elution process is much shortened. Therefore the eluant containing 0.5 mol./l. of sodium hydroxide and 3.0 mol./l. of ammonia may be the most suitable for the separation of selenite and tellurite.

The effect of an organic solvent on the distribution coefficient.—In order to study the effect of an organic solvent on the distribution coefficient of these anions, the relationship between K_d and the percentage of added ethanol was examined. The concentration of nitrate and ammonia are kept constant, i.e. 0.1 mol./l. of sodium nitrate and 0.5 mol./l. of ammonia for tellurite and selenite, and 0.2 mol./l. of sodium nitrate and 0.5 mol./l. of ammonia for sulfite. Results are shown in Fig. 4A.

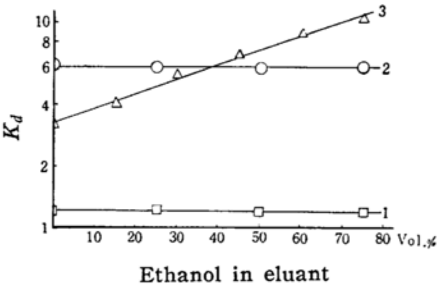


Fig. 4A. Relationship between K_d and the percentage of added ethanol. The eluants contained also 0.5 mol./l. of ammonia.
1: Sodium tellurite eluted wilh 0.1 mol./l. sodium nitrate. 2: Sodium selenite eluted with 0.1 mol./l. sodium nitrate. 3: Sodium sulfite eluted with 0.2 mol./l. sodium nitrate.

From the results thus obtained considerable differences are recognized among selenite, tellurite and sulfite. The distribution coefficient of sulfite increased with the increase of the concentration of ethanol, while the coefficients of the other two ions remain almost constant even up to 75% of ethanol.

These results seemed to suggest a promising method of separating sulfite from selenite or tellurite, but the tailing part of tellurite or selenite is not sharp in the elution process, and no satisfactory result was obtained even with fairly long columns containing up to 5.0 g. of resins. This separation may be completed, when a much longer column is used.

In case of sodium hydroxide eluants,

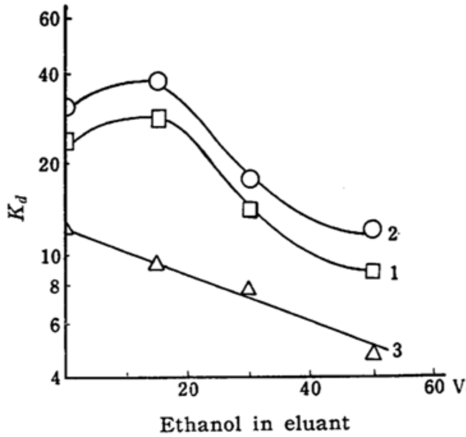


Fig. 4B. Relationship between K_d and the percentage of added ethanol. The eluant contained also 3.0 mol./l. of ammonia.
1: Sodium tellurite eluted with 0.5 N sodium hydroxide. 2: Sodium selenite eluted with 0.5 N sodium hydroxide. 3: Sodium sulfite eluted with 1.5 N sodium hydroxide.

the relationships between K_d and the percentage of ethanol are shown in Fig. 4B. The concentration of sodium hydroxide is 0.5 mol./l. for the tellurite and selenite, and 1.5 mol./l. for sulfite; the concentration of ammonia is 3.0 mol./l. in both cases.

As shown in Fig. 4B, the distribution coefficient of sulfite decreases as the concentration of ethanol increases, and this is a result in contrast to that of nitrate eluant. This fact may be due to the decrease of the dissociation of HSO_3^- ion.

But in cases of tellurite and selenite, the K_d increased up to 20% of ethanol and beyond this value began to decrease. When 50% of ethanol was added to the eluant, tellurite and selenite were eluted more easily, though the separation of selenite and tellurite is not so clear-cut. Therefore, this method can be used only for separating selenite, or tellurite from sulfite by using 5.0 g of Dowex 1-X8 resin column (in Figs. 5A and 5B).

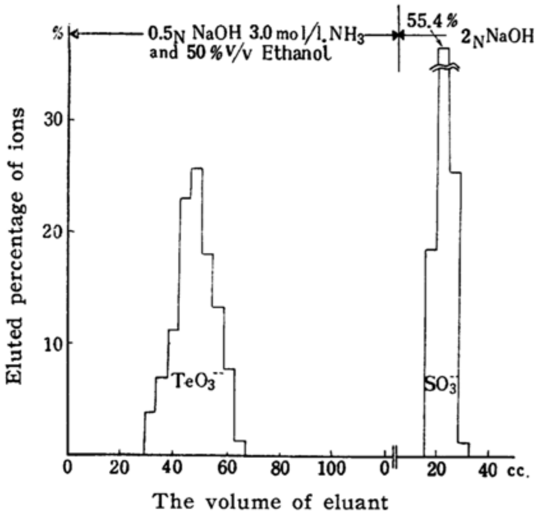


Fig. 5A. Elution curve of mixed sample of tellurite and sulfite. (The flow rate is 0.1 cc./min.)

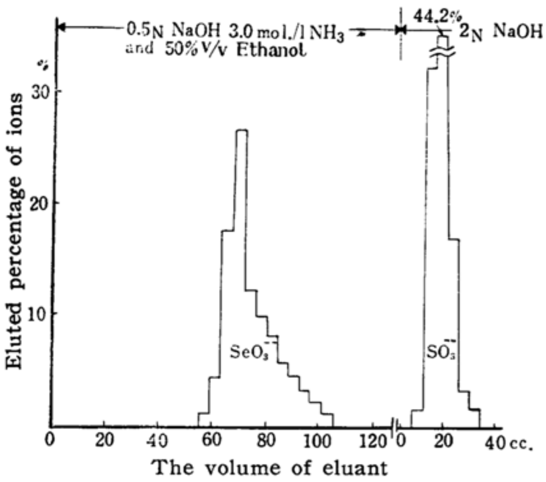


Fig. 5B. Elution curve of mixed sample of selenite and sulfite. (The flow rate is 0.1 cc./min.).

The separation of tellurite, selenite and sulfite.—From the result of Fig. 3, the eluant containing 0.5 mol./l. of sodium hydroxide and 3.0 mol./l. of ammonia is expected to be suitable for separating tellurite from selenite. Then sulfite can be eluted by 2.0 mol./l. of sodium hydroxide solution.

The column of the size 1.0×13.0 cm. containing 5.0 g. of Dowex 1-X8 (analytical grade) was used. One of the typical examples of the perfect separation is shown in Fig. 6. The collected tellurite, selenite and sulfite are titrated by the methods described before.

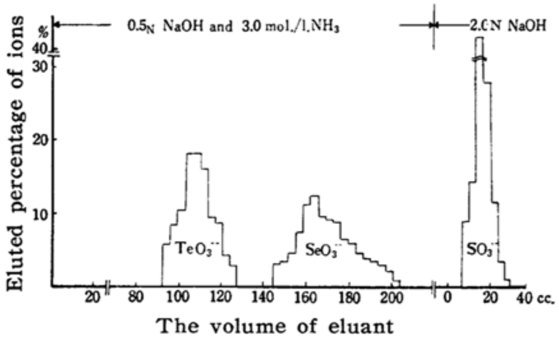


Fig. 6. Elution curve of mixed sample. (The flow rate is 0.1 cc./min.)

The analysis of the mixture of tellurite, selenite and sulfite.—This method of separation was applied to a mixture of known quantities of these salts and the results obtained are shown in Table I. Each value is the mean value of the four repeated experiments.

When the sample solution of tellurite was not fresh or the elution process was too prolonged, the recovery of tellurite was decreased. Therefore, it is desirable to use a newly prepared sample and to shorten the time of analysis. When resins of larger grain size are used, the clear-cut separation is not obtained. Difficulties in handling these intractable materials, for example, the changes of the state in the solution, cause a small discrepancy between the data of recovery and the theoretical values.

TABLE I
THE ANALYSIS OF MIXED SAMPLES

		Sample I		Sample II	
		mmol.	%	mmol.	%
Tellurite	Added values	0.0712_5	100	0.142_5	100
	Observed values	0.0705_5	99.2±0.21	0.141_1	99.0±0.23
Selenite	Added values	0.134_6	100	0.188_5	100
	Observed values	0.123_8	98.0±1.8	0.183_4	97.5±2.5
Sulfite	Added values	0.100_9	100	0.117_8	100
	Observed values	0.0996_9	98.8±1.6	0.116_3	98.7±1.3

Summary

1. The distribution coefficients of tellurite, selenite and sulfite in neutral nitrate solution and alkaline hydroxide solution were measured and the results suggest the presence of an acid salt ion HXO_3^- in neutral solution.

2. By the addition of ammonia to the eluant solution, the distribution coefficient of these salts in nitrate solution was increased, but in hydroxide solution it was decreased.

3. By the addition of ethanol to the eluant solution containing nitrate and ammonia, the distribution coefficient of sulfite increased, but that of tellurite and selenite remained constant even up to 75%. On the contrary, in the addition of ethanol to the hydroxide solution, the distribution coefficient of sulfite decreased, while that of tellurite and selenite increased at first and then decreased.

4. By using these results a complete separation of tellurite, selenite and sulfite was accomplished by the anion exchange chromatographic method using an alkaline eluant.

The author expresses his gratitude to Professor T. Shirai, Dr. Y. Yoshino and his colleagues in the laboratory both for their suggestions and for the discussion helpful in publishing this paper.

Department of Chemistry, College of
General Education, University
of Tokyo, Meguro-ku, Tokyo