*The Separation of Polythionates with Anion-Exchange Resins**

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The separation of di-, tri-, tetra- and penta-thionates is very difficult by an ordinary analytical method. In the present study, the author applied the anion-exchange chromatography to this separation. First, the distribution coefficients, K_d, of polythionates to the anion-exchange resin were measured and, by the use of these results, polythionates were separated with satisfactory results.

Experimental

Materials. — Anion-exchange resin, Dowex 1-X2, X4 and X8 of mesh size 50∼100 were used in air dried state and in chloride form.

The following polythionates were synthesized by the usual methods described in text books$^{1,2)}$.

Sodium dithionate was prepared by the reaction of sodium sulfite with silver nitrate$^{3)}$.

Sodium trithionate was obtained by passing sulfur dioxide into a solution containing both sodium thiosulfate and bisulfite with a small amount of sodium arsenite. Potassium salt was obtained by the double decomposition of sodium salt with potassium acetate$^{4)}$.

Sodium tetrathionate was prepared by mixing sodium thiosulfate with iodine in the granular state$^{5)}$.

Potassium pentathionate was prepared by the reaction of concentrated hydrochloric acid with a solution containing sodium thiosulfate and a small amount of sodium arsenite at $-10°C^{6)}$.

Procedure. *Analysis of polythionates.*—Sodium dithionate was oxidized by potassium bromate in acidic solution and the formed sulfate ion was determined by the usual gravimetric method. The purity of this salt was also determined by heating and decomposing it into sodium sulfate. The sodium sulfate was determined gravimetrically$^{7,8)}$.

Potassium trithionate was titrated with potassium iodate$^{9)}$. Its purity was also determined from the decrease of weight on conversion into potassium sulfate by heating$^{10)}$.

Sodium tetrathionate and potassium pentathionate were titrated with potassium iodate as in the case of trithionate$^{9)}$. The purity of these salts was also determined through the reaction with sodium sulfite. The thiosulfate ion thus formed was determined by iodimetric titration after masking the residual sulfite ion with formalin$^{11)}$.

The results of these analyses showed that these salts were pure enough for the purpose of this study.

Measurement of Distribution Coefficients in Various Concentrations of Hydrochloric

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* This paper was presented before the Autumn Meeting of the Chemical Society of Japan held on Nov. 23, 1957 in Tokyo.

1) W. G. Palmer, "Experimental Inorganic Chemistry", Cambridge Univ. Press, England (1954), p. 365.

2) T. Inouye, "Inorganic Preparative Experiments" (Mukikagaku Seizojikken), Shokabo, Tokyo (1956), p. 96.

3) H. Baubigny, *Ann. chim. phys.*, (VIII), **20**, 5 (1910).

4) A. Kurtenäcker and K. Matejka, *Z. anorg. allgem. Chem.*, **193**, 367 (1930).

5) N. v. Klobukow, *Ber.*, **8**, 1871 (1885).

6) A. Kurtenäcker and W. Fluss, *Z. anorg. allgem. Chem.*, **210**, 125 (1933).

7) C. Mayr and I. Szentpaly-Peyfuss, ibid., **131**, 203 (1924).

8) W. C. de Baat, *Rec. trav. chim., Pays-Bas*, **45**, 237 (1926); *Chem. Zentr.*, **97**, (I) 3133 (1926).

9) A. Kurtenäcker et al., *Z. anorg. allgem. Chem.*, **224**, 399 (1935).

10) H. Stamm, K. Goejring and U. Feldmann, ibid., **250**, 226 (1942).

11) F. Forster and K. Centner, ibid., **157**, 45 (1926).

Acid.—The measurement of distribution coefficients K_d was carried out by the column method. The K_d values of the ions were calculated from the volume of the eluant, using the following equation:

$$K_d=(V-i)/M^{12)}$$

where K_d (cc./g.) is the distribution coefficient, V (cc.) the volume of eluant passed through the column until the concentration of solute in the effluent becomes maximum, i (cc.) the interstitial volume of the column and M (g.) the weight of the resin.

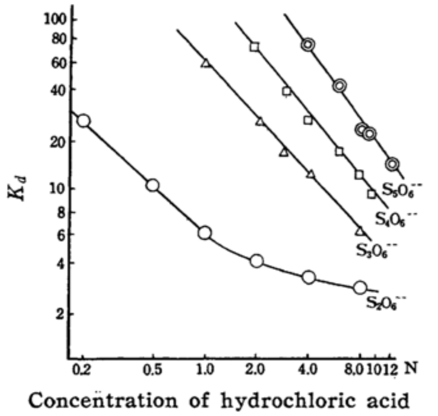

Fig. 1. Relationship between K_d and the concentration of hydrochloric acid in the eluant.

Each column contains 0.5～2.0 g. of the resin, Dowex 1-X2 in chloride form. The flow rate is adjusted to less than 0.1 cc./min. The relation between K_d and the concentration of hydrochloric acid (C) in the eluant is shown in Fig. 1. A nearly linear relationship between $\log K_d$ and $\log C$ is recognized. The values of K_d of polythionate ions for the same concentration of hydrochloric acid increase with the increase of the numbers of sulfur atom in the ion. The curves for these polythionates were almost parallel to one another. The gradient of these curves was not so great as two, but almost unity; hence as was studied by M. Honda[13], these polythionate ions may exist in these acidic solutions as $HS_nO_6^-$, n being 2～5.

Results and Discussion

The Effect of pH and the Pore-size of Ion-Exchange Resins on the Distribution Coefficient.

— i) *pH.* — By using sodium chloride solution, or sodium chloride solution containing ammonia as an eluant in place of hydrochloric acid, the values of K_d in different pH** were measured. The concentrations of sodium chloride used were 0.5 mol./l. for dithionate and 4.0 mol./l. for other polythionates. The results are shown in Fig. 2. The K_d was almost independent of pH.

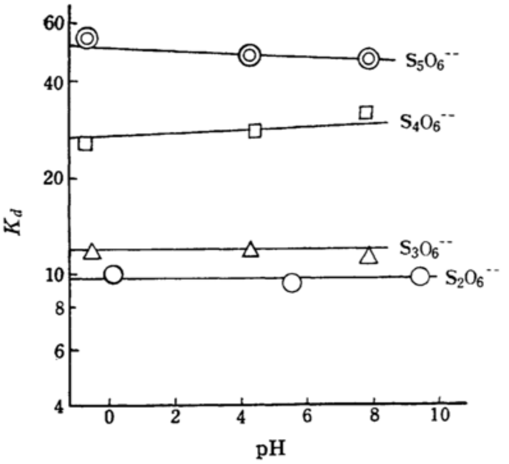

Fig. 2. Relationship between K_d and the pH of eluant. The concentration of hydrochloric acid used as the eluant was 0.5 N for dithionate and 4 N for tri-, tetra- and penta-thionates.

ii) *Pore-size.*—The resins of different X numbers were employed in place of X2 resin to observe the effect of pore-size. The K_d values for dithionate in 1.0 N hydrochloric acid, trithionate in 3.0 N hydrochloric acid, tetrathionate in 6.0 N hydrochloric acid and pentathionate in 9.0 N hydrochloric acid were measured by the elution method using Dowex 1-X2, -X4 and -X8 resins. The results are shown in

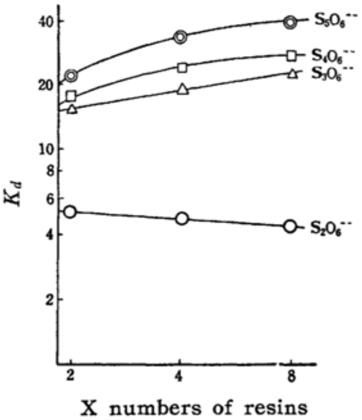

Fig. 3. Relationship between K_d and the X numbers of resins. The concentration of hydrochloric acid used as the eluant was 1 N for dithionate, 3 N for trithionate, 6 N for tetrathionate and 9 N for pentathionate.

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[12] M. Honda, *Japan Analyst (Bunseki Kagaku)*, **2**, 155 (1953).

[13] M. Honda, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zassi)*, **72**, 361 (1951).

** pH of the solution was measured with a glass electrode pH-meter, Type 43, made by Iio Denki Co..

TABLE I

THE ANALYSIS OF MIXED SAMPLES

Thionates	Sample 1			Sample 2		
	Added	Observed		Added	Observed	
	millimole	millimole	%	millimole	millimole	%
Dithionate	0.124	0.122	98.6±2.0	0.100	0.0987	98.7±2.0
Trithionate	0.0584	0.0560	96.0±5.0	0.0707	0.0690	97.4±4.0
Tetrathionate	0.0650	0.0650	100 ± 2.6	0.0336	0.0328	97.7±2.3
Pentathionate	0.0339	0.0343	101 ± 2.8	0.0338	0.0333	98.6±2.3

TABLE II

THE ANALYSIS OF WACKENRODER'S LIQUID

	Sample A		Sample B	
	Observed value millimole	Mol. %	Observed value millimole	Mol. %
Sulfide, Sulfite, Thiosulfate	0.00	0.00	0.00	0.00
Sulfate	6.77×10^{-2}	23.2	4.90×10^{-2}	20.5
Dithionate	2.58×10^{-3}	0.89	3.75×10^{-3}	1.57
Trithionate	5.82×10^{-2}	19.9	5.63×10^{-2}	23.7
Tetrathionate	9.12×10^{-2}	31.2	4.83×10^{-2}	32.9
Pentathionate	5.40×10^{-2}	18.5	4.59×10^{-2}	19.2
Higher thionates	7.70×10^{-3}	2.63	4.87×10^{-3}	2.04

Fig. 3. Slight increase of K_d with the increase of X number was recognized in cases of tri-, tetra-, and penta-thionates, though the difference is not so great. In the case of higher polythionates, elongation of the tail part was observed in the elution process.

Separation of Polythinonates by the Column Method.—The polythionates may be separable because they show different K_d values as shown in Fig. 1. The used column contains 2.16 g. of Dowex 1-X2 and the size of the column is about 0.90 cm. in diameter and about 11 cm. in length. First the dithionate is eluted with 1 N hydrochloric acid. When any other oxy-acids of sulfur than polythionates are contaminated in the sampe to be analyzed, they are eluted out at this stage before the dithionate appears in the eluant. Then trithionate was eluted with 3 N hydrochloric acid, tetrathionate with 6 N and pentathionate with 9 N hydrochloric acid successively.

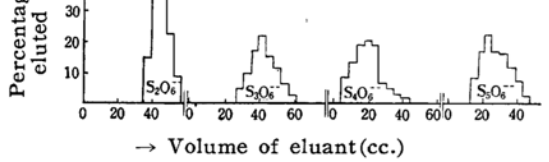

Fig. 4. Elution curve of a mixed sample. The flow rate was 0.5 cc./sec.

The amount of eluted dithionate is determined by gravimetric method and tri-, tetra- and penta-thionates are by the titration with standard potassium iodate solution as described in the experimental part.

One of the typical clean-cut separation of mixed sample is shown in Fig. 4.

Analysis of Mixed Samples. — The method of separation, described above, was applied to the mixture of the known amounts of polythionates and the results are shown in Table I, the mean values of the triplicate experiments being given.

When the sample contains other oxy-acids of sulfur, (e.g., sulfate, sulfite, etc.), they are eluted prior to the elution of dithionate, and are determined separately.

Analysis of Wackenroder's Liquid[14,15]. —This method of separation was applied to the determination of the composition of Wackenroder's liquid. The composition of the liquid, however, may change owing to the preparation method, and further, it contains a large amount of suspended sulfur which interferes with the analytical process. Two samples made by the following methods were analyzed.

i) *Sample A.* — This sample was prepared by dissolving hydrogen sulfide into

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14) H. W. F. Wackenroder, *Ann. chim. phys.*, (III), **20**, 144, (1847).

15) H. Debus, *Ann.*, **244**, 76, (1888).

saturated aqueous solution of sulfur dioxide at 0°C. Hydrogen sulfide was passed twice after an interval of 48 hours, and the solution was left standing 38 days at room temperature (20~15°C). Then the suspended sulfur in the liquid was caused to coagulate by the addition of an equal volume of 1.00 M ammonium chloride solution and filtered off. A portion of the filtrate was titrated with standard iodine solution after being acidified with acetic acid, but the presence of sulfide, sulfite or thiosulfate was not recognized. With another portion of the filtrate, the content of sulfate was determined by the gravimetric method in the form of barium sulfate.

The ion-exchange chromatographic method used for the analysis of Wackenroder's liquid is the same as that used for the known mixed sample, but after the elution of pentathionate with 9 N hydrochloric acid, there remained only a small amount of polythionate which could be eluted only by 12 N hydrochloric acid. Although it was difficult to determine this species, the values in Table II were calculated on the assumption that this species would be hexathionate.

The quantity of dithionate was calculated from the difference between the amount of barium sulfate obtained from the first effluent after oxidation and the amount of the barium sulfate directly from the original sample solution.

ii) *Sample B.*—Sample B was prepared by the same method as that for Sample A, but the solution was left standing only 11 days after passage of hydrogen sulfide. As the suspended sulfur coagulates with difficulty, 1.5 times (by volume) of 1.00 M ammonium chloride solution was mixed before filtration of the sulfur.

The results of the analysis of 1 cc. of the original Wackenroder's liquid are given in Table II.

Summary

1) The distribution coefficient of di-, tri-, tetra-, and penta-thionates between anion-exchange resins and hydrochloric acid solution was measured. The adsorbability of the polythionates increases with the number of sulfur atoms in the ion, i. e. pentathionate> tetrathionate> trithionate> dithionate.

2) The separation of polythionates was accomplished by the anion-exchange chromatography by the use of hydrochloric acid in various concentrations as the eluant.

3) The application of anion-exchange chromatography to the analysis of Wackenroder's liquid was studied.

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