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CHROMATOGRAPHIC STUDY OF SOME INORGANIC IONS ON SEPHADEX GEL IN THIOCYANATE MEDIA

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SUMMARY

The adsorption of thiocyanate ion on a Sephadex G-15 gel has been studied. The chromatographic separation of thiocyanate, chloride, bromide and iodide on a Sephadex G-15 column was achieved by elution with 0.25 *M* sodium sulphate solution. Distribution ratios of alkaline earth metal, Zn^{2+} , Cd^{2+} , Mn^{2+} , Co^{2+} and Ni^{2+} on Sephadex G-15 gel were determined. The chromatographic separation of the above metal ions on Sephadex G-15 gel was investigated.

INTRODUCTION

Gel chromatography is one of the useful analytical techniques in liquid chromatography. The mechanism of separation in gel chromatography is based on the molecular sieve effect, and this technique has been applied extensively in biochemistry and organic polymer chemistry.

Since 1966, gel chromatographic studies of inorganic compounds have been undertaken by several workers¹⁻³. It has been reported that side-effects such as adsorption play an important role in the gel chromatographic separation of inorganic compounds⁴⁻⁶, but little information is available on these side-effects.

In this study, we have found that thiocyanate ion is adsorbed on Sephadex gels and have investigated some chromatographic applications of this phenomenon. It has been clarified that the adsorption occurs reversibly and that a relatively short time is required for the establishment of the adsorption equilibrium. The adsorption isotherm of thiocyanate ion on Sephadex G-15 is linear, which explains the symmetric elution curve of thiocyanate ion on a gel column using water as the eluent.

The separation between thiocyanate and halide ions other than fluoride has been examined. As many metal ions form thiocyanate complexes, it was worthwhile investigating the chromatographic behaviour of metal ions on Sephadex gel with adsorbed thiocyanate ion in an aqueous thiocyanate medium in order to ascertain whether any useful separations could be achieved⁷. The metal ions studied were alkaline earth metal ions and several bivalent transition metal ions. Distribution ratios for these metal ions were determined at various metal or thiocyanate ion concentrations.

EXPERIMENTAL

All of the batch and elution experiments were carried out at $20 \pm 1^\circ$.

Materials

All reagents used were of commercially available analytical grade, unless otherwise stated.

Sodium trimetaphosphate was prepared by the method described in the literature⁸.

Gel

Sephadex G-15 gel from Pharmacia (Uppsala, Sweden) was used.

Adsorption of thiocyanate ion on Sephadex G-15

Five grams of Sephadex G-15 gel were placed in a conical flask fitted with a rubber stopper and 40 ml of 0.1 *M* thiocyanate solution were added. The flask was shaken mechanically for various time periods, then the gel was allowed to settle and the thiocyanate ion in the supernatant solution was analysed by the Volhard method.

Solvent uptake by the Sephadex G-15 was determined by a batch method using Blue Dextran 2000, which is considered not to be able to diffuse in the gel phase.

Effect of the presence of electrolytes on the adsorption of thiocyanate ion

The extent of adsorption of thiocyanate ion was determined by similar experiments to those mentioned above. The concentrations of co-existing electrolytes were varied from 0.05 to 1 *M*, while the initial concentration of thiocyanate ion was kept constant at 0.1 *M*.

The concentration of thiocyanate ion was determined by the Volhard method or colorimetry using iron(III) ion.

Measurement of distribution ratios of metal ions

Distribution ratios of a metal ion in the Sephadex G-15–thiocyanate system were measured by changing the metal ion concentration at a constant thiocyanate concentration. About 5 g of gel and 40 ml of solution containing thiocyanate and the metal ion were used. The pH of the aqueous phase in these systems was adjusted to about 2.0 with hydrochloric acid.

Determination of metal ions

Metal ion concentrations in the thiocyanate media were determined by atomic-absorption or atomic-emission spectroscopy using a Nippon Jarrel-Ash Model AA781 instrument.

Elution procedure

A Sephadex G-15 column was prepared as described in the literature⁹. A column of length 60 cm and I.D. 1.0 cm was used for elution with Sephadex G-15 gel. In each elution, the volume of sample solution delivered to the column was 1 ml and the eluents were changed stepwise in order to obtain satisfactory separations. Each

fraction of the effluent was collected with an automatic fraction collector and analysed for each component. The flow-rates in each elution were about 25 ml/h.

RESULTS AND DISCUSSION

The rate of adsorption of thiocyanate ion on Sephadex G-15 gel is shown in Fig. 1. Adsorption equilibrium is attained in the first 1-2 h. Although detailed data are omitted here, preliminary experiments indicated that the rate of desorption of thiocyanate ion on Sephadex G-15 is as fast as the rate of adsorption. In batch experiments, therefore, the shaking time of reaction flask was set at 4 h.

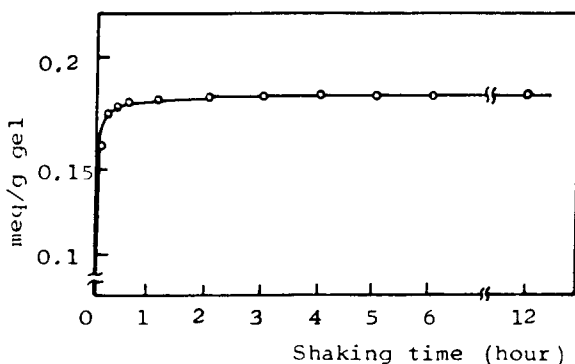


Fig. 1. Rate of adsorption of thiocyanate ion on Sephadex G-15.

In batch experiments, the amounts of thiocyanate ion adsorbed on the gel were determined as a function of equilibrium concentrations of thiocyanate ion in a solution phase. In Fig. 2, the results at 20° are plotted, with milliequivalents of adsorbed thiocyanate ion per gram of the gel on the ordinate and milliequivalents of thiocyanate ion per millilitre of equilibrium solution on the abscissa. A linear adsorption isotherm was obtained for a range of thiocyanate concentration of about 1.5 *M*. The slope of the isotherm is then equal to the distribution ratio, *D*, where

$$D = \frac{\text{mequiv. of SCN}^- \text{ per gram of gel}}{\text{mequiv. of SCN}^- \text{ per ml of solution}}$$

This straight line indicates that the distribution ratio is independent of the solute concentration in the range examined and that the adsorption is not of the chemisorption type, which entails strong, covalent bonding between solute and adsorbent and slow rates of desorption¹⁰. A pH dependence of the amount of thiocyanate adsorbed was not observed.

Sephadex G-15 gel equilibrated with 10 *M* aqueous thiocyanate solution adsorbed 14.8 mequiv. of thiocyanate per gram of gel. Di Gregorio and Sinibaldi¹¹ suggested that the adsorption of thiocyanate ion on Sephadex gel can be attributed to a "hydrophobic interaction".

We investigated the adsorption of thiocyanate ion on Sephadex gel in the presence of several anions such as perchlorate, chloride, nitrate, sulphate and tri-

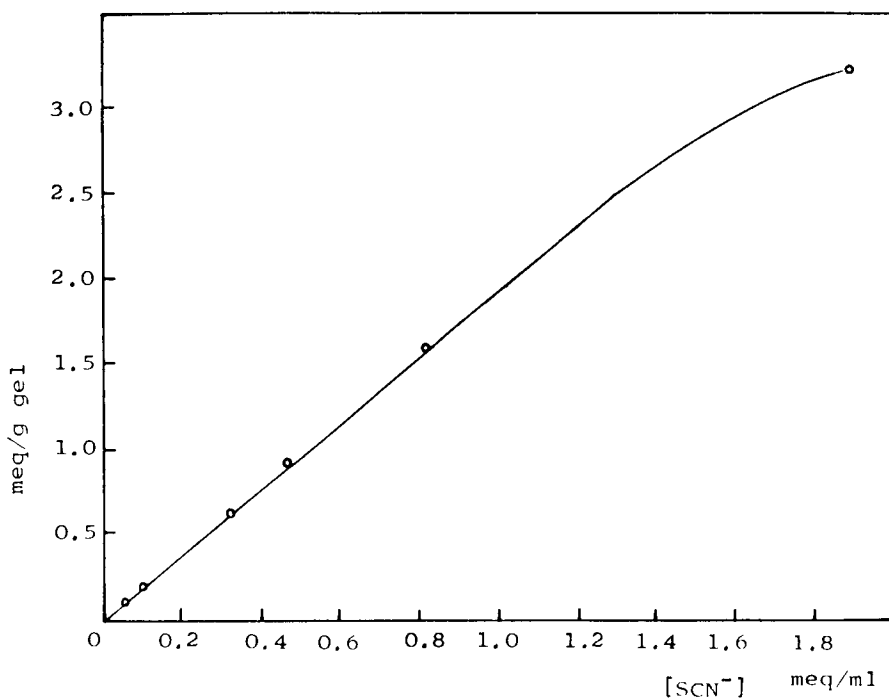


Fig. 2. Adsorption isotherm of thiocyanate ion on Sephadex G-15 at 20°.

metaphosphate. The initial concentration of sodium thiocyanate was kept constant at 0.1 *M* and the concentrations of the above co-existing electrolytes, except trimetaphosphate, were varied from 0.05 to 1 *M*; for trimetaphosphate, the concentration was varied from 0.05 to 0.5 *M*. In Fig. 3, the amounts of adsorbed thiocyanate ion are

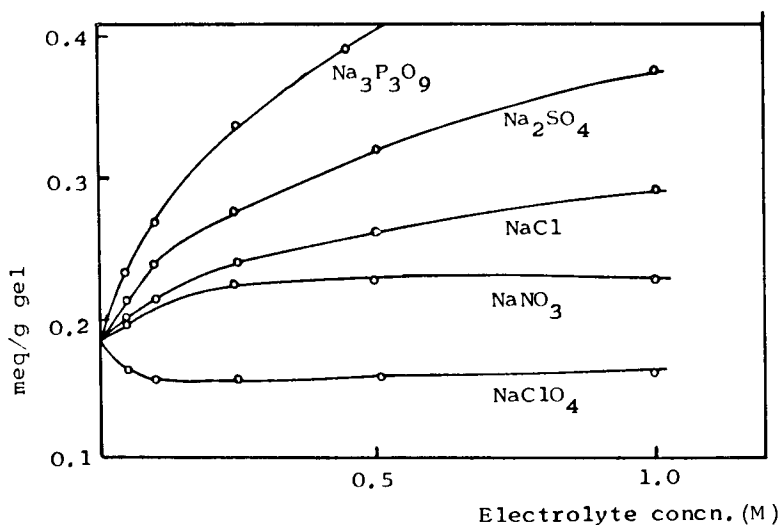


Fig. 3. Effect of various anions on the adsorption of thiocyanate on Sephadex G-15.

plotted as a function of the concentration of electrolyte present. It can be seen that the amount of thiocyanate ion adsorbed decreased when 0.05 *M* of perchlorate was added. However, further addition of perchlorate caused no change in the amount of thiocyanate adsorbed. On the contrary to the above result, the addition of anions other than perchlorate gave an increase of the amount of thiocyanate ion adsorbed on the gel. In every instance, the amount of thiocyanate ion adsorbed increased with increase in the electrolyte concentration, in the order nitrate < chloride < sulphate < trimetaphosphate. This trend is related to the affinity of these anions for Sephadex gel; the anions that interact more strongly with the gel cause a greater decrease in the amount of thiocyanate ion adsorbed.

In adsorption chromatography, when the adsorption isotherm is linear, the band migration rate is independent of the solute concentration and the band shape is of a symmetrical Gaussian type¹⁰. A chromatographic run of thiocyanate ion with Sephadex G-15 using water as the eluent gave a symmetrical elution curve, as expected.

We applied this characteristic adsorption of thiocyanate ion on Sephadex gel to effect the separation between thiocyanate and halide ions (except fluoride), which interfere in the argentimetric determination of thiocyanate ion. Chloride and bromide ions have been considered not to be adsorbed strongly on Sephadex G-15 gel, but it has been pointed out by Deguchi⁴ that iodide ion is adsorbed on the gel. An elution diagram for a mixture of chloride, bromide, iodide and thiocyanate ions using water as the eluent is shown in Fig. 4a. It can be seen that iodide ion is adsorbed on the gel more weakly than thiocyanate ion. The elution volume of Blue Dextran 2000 coincides with the void volume of the gel column. Fig. 4a shows that the separation of thiocyanate ion and chloride and/or bromide ions is almost complete. However, overlapping of the elution curves of iodide and thiocyanate ions also occurs, and we

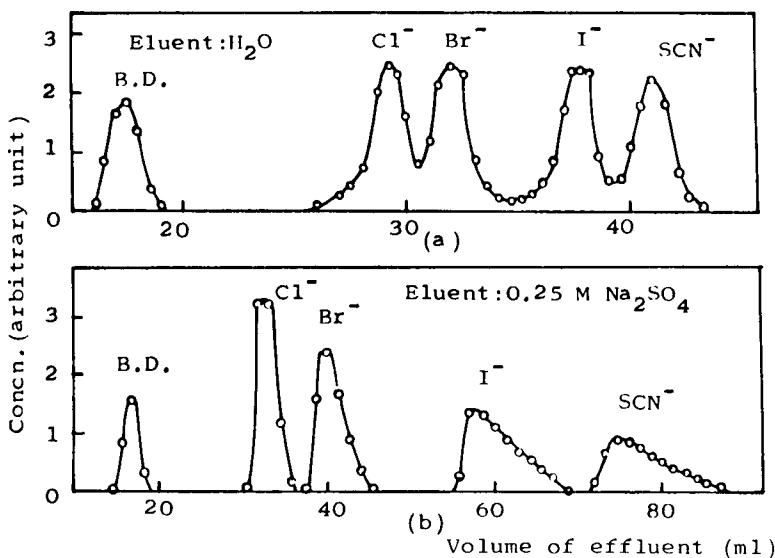


Fig. 4. Gel chromatographic separation of thiocyanate, iodide, bromide and chloride ions by use of a Sephadex G-15 gel column. B.D. = Blue Dextran 2000. Sample concentration: 0.1 *M*. Eluent: (a) water; (b) 0.25 *M* sodium sulphate solution.

used 0.25 *M* sodium sulphate solution as the eluent in order to improve this separation (Fig. 4b). As expected from the data shown in Fig. 3, the elution volume of each ion increased, but the separation of chloride, bromide, iodide and thiocyanate ions could be achieved completely by this procedure.

Sephadex G-15 gel with adsorbed thiocyanate is applicable to the separation of metal ions that have different affinities for thiocyanate in the gel phase. To determine the affinity quantitatively we have defined the distribution ratio for a metal ion, *D*, as (milliequivalents of a metal ion per gram of the gel)/(milliequivalents of a metal ion per millilitre of solution). The distribution ratio would be expected to depend on both the ratio of the concentration of a metal ion to that of thiocyanate ion in the gel or solution phase and the absolute concentrations of the metal or thiocyanate ion in the solution (gel) phase. We then examined the change in the distribution ratio with the metal ion concentration when the initial concentration of thiocyanate ion in solution was kept at 0.1 *M*. The results are shown in Fig. 5. The value of *D* increases with a decrease in the metal ion concentration and reaches a nearly constant value when the metal ion concentration falls below 10^{-3} *M*.

The dependence of the distribution ratios of metal ions on thiocyanate concentration was measured and the results are shown in Fig. 6. The concentrations of the metal ions in this experiment were about 10^{-4} *M*. The distribution ratios tend to increase with increase in the concentration of thiocyanate ion present in the aqueous phase. However, for most of the metal ions, other than Co^{2+} and Zn^{2+} , the magnitude of the increase is relatively small. Although the distribution ratios for Zn^{2+} are not

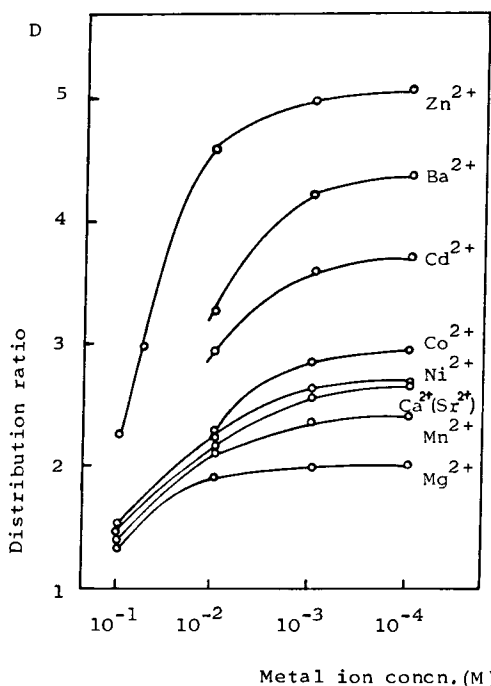


Fig. 5. Distribution ratio of metal ions on Sephadex G-15 at various metal ion concentrations. Ammonium thiocyanate concentration, 0.1 *M*; pH = 2.

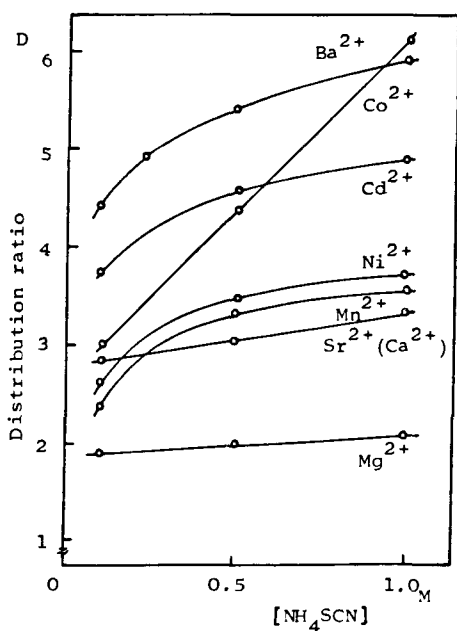


Fig. 6. Distribution ratios of metal ions on Sephadex G-15 at various thiocyanate concentrations. Metal ion concentration = $10^{-4} M$; pH = 2.

shown in Fig. 6, the values are 7.3, 84 and 114 for thiocyanate ion concentrations of 0.1, 0.5 and 1 M, respectively. The distribution ratio of Zn^{2+} depends markedly on the thiocyanate ion concentration.

The separation of mixtures of alkaline earth metal and several transition metal

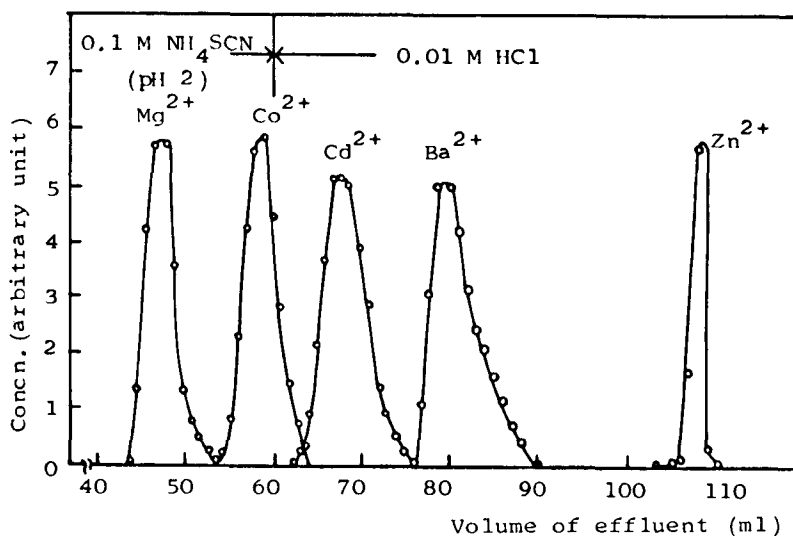


Fig. 7. Separation of several metal ions by use of a Sephadex G-15 column. Sample concentration = $10^{-3} M$.

ions was examined with the Sephadex column using 0.1 *M* ammonium thiocyanate solution of pH 2 as the eluent. This eluent was considered to give a better resolution. Zn^{2+} was expected from the equilibrium data to be adsorbed strongly on the gel column, the eluent was changed to 0.01 *M* hydrochloric acid solution at an effluent volume of 60 ml. A typical elution diagram is shown in Fig. 7. Mg^{2+} , Co^{2+} , Cd^{2+} , Ba^{2+} and Zn^{2+} can be separated almost completely from each other. However, Mn^{2+} , Ni^{2+} , Ca^{2+} and Sr^{2+} were eluted together at the same elution position as that of Co^{2+} .

Although the strong affinity of Ba^{2+} for thiocyanate ion has not been reported, barium is strongly adsorbed on the gel with adsorbed thiocyanate ion. Furthermore, extensive analytical applications using Sephadex G-15 gel with adsorbed thiocyanate ion are to be expected.

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