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Note

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Chromatographic behaviour of some divalent metal ions in sodium chloride, sulphate and nitrate solutions on a Sephadex G-10 column

In recent years, gel chromatography has been applied to the investigation of inorganic compounds[1–12]. Although the sieving effect in the gel phase is the main factor controlling the behaviour of inorganic species in gel chromatography, other side effects, such as adsorption[4–6,13], exclusion[6,14,15] and effects of counter ions and background electrolytes[1,4,6,16], must be considered.

The present paper describes the effects of the type and the concentration of the background electrolytes on the chromatographic behaviour of divalent metal ions, and the evaluation of the contribution of the side effects, such as adsorption, by a batch method. Solutions of sodium chloride, sodium sulphate and sodium nitrate were used as background electrolytes.

Experimental

Sample solutions and reagents. All the reagents used were of analytical grade. Sample solutions for divalent metal ions were prepared by dissolving their chlorides, sulphates and nitrates in deionized water. The concentration of sample solutions was 0.05 M.

Sephadex column. Sephadex G-10 (40–120 μ) was used after swelling for at least 48 h in deionized water. The column was a 1.5 × 60 cm glass tube with a porous polystyrene disc at one end. The column was wet-packed in the usual manner. A small disc of filter-paper served to reduce disturbances at the top of the gel bed. The total volume of the gel bed was 100 ml.

Procedure for elution. A 0.5 ml volume of the sample solution and 0.5 ml of the eluent were placed on top of the bed just as the last few drops of the eluent soaked into the bed. The eluent was applied when the last portion of the sample solution soaked into the bed. The effluent was collected in 1-ml fractions, at a flow-rate of 20–25 ml/h, with a drop-count fraction collector. The amounts of metal ions in a fraction were determined by complexometric titration with an EDTA solution.

Procedure for batch method. A 1.00-g amount of dry gel powder and 10 ml of a sample solution were mixed in a 10-ml measuring flask with a glass stopper. The gel was allowed to swell with occasional shaking. After 48 h, the gel was allowed to settle and an aliquot of the solution was withdrawn from the flask. The metal ion concentration in this solution was determined titrimetrically with an EDTA solution. Sample solutions of magnesium, zinc and cadmium were prepared by dissolving their salts in a solution of the same composition as that of the eluent used for the column operation. The concentration of metal ions in the sample solution was 0.01 M.

Results and discussion

Fig. 1 shows the relationship between the distribution coefficient, K_{av}, and the concentration of the eluents. The K_{av} value is defined by the following equation[17]:

$$K_{av}=\frac{V_e-V_0}{V_t-V_0}$$

where V_t is the total bed volume, V_0 is the void volume outside the gel particles and V_e is the elution volume of a sample.

The batch method was carried out to examine the side effects arising from solute–gel interactions such as adsorption. The extent of adsorption of a metal ion on the gel phase, D, can be expressed by the following equation:

$$D=\frac{C_i-C_f}{C_i}\times 100$$

where C_f is the concentration of the solute in the solution in equilibrium with a definite amount of Sephadex gel, and C_i is the concentration when no Sephadex is added. If there is no interaction between the metal ion and the gel matrix but the metal ion is larger than a water molecule, the concentration of the metal ion in the gel phase becomes less than that of bulk solution, then $C_i<C_f$, and therefore $D<0$. When the concentration of the metal ion in the gel phase is higher than that of bulk solution, *i.e.*, $C_f<C_i$, the D value is positive, which means that some amounts of the metal ion are adsorbed on the gel matrix.

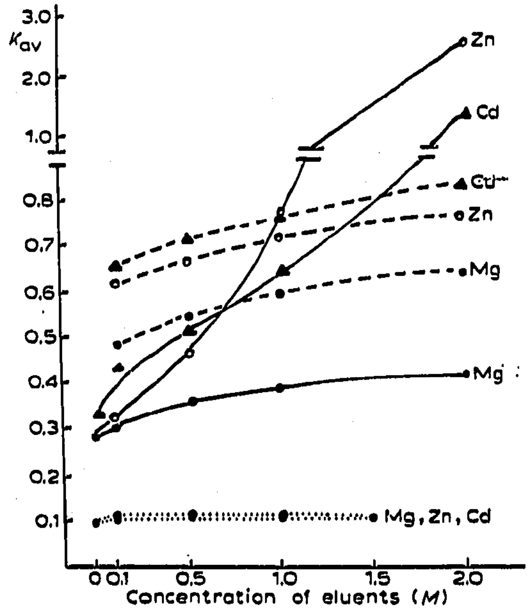

Fig. 1. Relationship between distribution coefficient, K_{av}, and the concentration of eluents. ———, Chloride system; ······, sulphate system; – – – –, nitrate system.

Chloride system. The K_{av} value of the magnesium ion increases gradually as the sodium chloride concentration increases. The result obtained by the batch method (Fig. 2) shows that there is no interaction between magnesium ions and the gel matrix in any concentration of sodium chloride solution. As magnesium has less ability to form the chloro-complex in sodium chloride solution[18], the species of magnesium ion in sodium chloride solution may be hydrated even at higher concentrations of sodium chloride. The behaviour of magnesium ion in sodium chloride solution on the gel chromatography is due mainly to the sieving effect and the gradual increase of the K_{av} value of magnesium as the concentration of sodium chloride increases is due to the partial dehydration of the hydrated magnesium ion. The behaviour of manganese(II), cobalt(II) and nickel ions on the gel was the same as that of the magnesium ion.

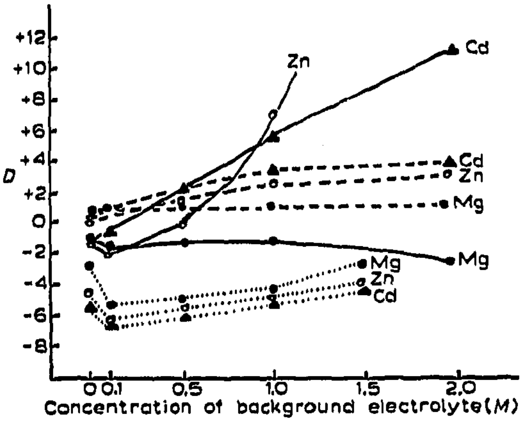

Fig. 2. Relationship between extent of adsorption of metal ions, *D*, and the concentration of background electrolytes. ———, Chloride system; ······, sulphate system; – – – –, nitrate system.

On the other hand, the K_{av} values of zinc and cadmium ions increase steeply with an increase in the concentration of the eluent. Zinc and cadmium ions in sodium chloride solution have a tendency to form their chloro-complexes[18]. The results obtained by the batch method (Fig. 2) show that zinc and cadmium ions have positive *D* values in concentrated sodium chloride solution. A positive *D* value means that the metal ion is adsorbed on the gel matrix. An abrupt increase of the K_{av} values of zinc and cadmium ions is due to the effect of adsorption of their chloro-complexes on the gel matrix, because the chloride ion seems to have no direct interaction with the gel matrix.

Sulphate system. The K_{av} value of metal ions in the sulphate system is small and constant, *i.e.*, about 0.1. The results are quite different from those in chloride and nitrate systems. The results obtained by the batch method show that metal ions are not adsorbed on the gel phase and are excluded from the gel to a considerable extent.

Sulphate ion, as sodium sulphate, was eluted with pure water and with 0.1 *M* sodium chloride solution. The K_{av} value of 0.1 was obtained for the sulphate ion, which is a much smaller value than that expected from the radius of the hydrated sulphate ion given by NIGHTINGALE[19], and this suggested that the sulphate ion is excluded from the gel to a considerably greater extent. The gel chromatographic behaviour of metal ions is controlled by the incomplete penetrating ability of the sulphate ion into inner part of the gel phase.

Nitrate system. The K_{av} values of magnesium, zinc and cadmium ions are greater than those of their ions in the chloride system, except for zinc and cadmium in concentrated sodium chloride solution. The D values of magnesium, zinc and cadmium ions are positive in any concentration of sodium nitrate solutions. These metal ions have no tendency to form complexes with the nitrate ion in sodium nitrate solution[18]. It is suggested that the chromatographic behaviour of their ions on the gel is controlled by adsorption, but the adsorption mechanism is different from that explained for the chloride system. UENO *et al.*[4] have explained the mechanism of the gel chromatographic behaviour of the metal ion in the nitrate system, *i.e.*, sodium nitrate is adsorbed on the gel matrix and then part of the sodium ion is exchanged for the metal ion in question. The present results seem to support the conclusion of UENO *et al.*[4].

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