

## The Affinity of Some Divalent Metals to Different Types of Alginates

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In a series of experiments, Thiele and co-workers have investigated the interaction between divalent ions and polyuronides, in particular alginic acid. They found that gels with a capillary structure were formed if divalent metals under certain conditions were allowed to diffuse into an alginate solution. The diameter of the capillaries depended on the nature of the divalent metal, and increased in the following order:  $Pb < Cu < Cd < Ba < Sr < Ca < Zn, Co, Ni$ <sup>1</sup>. Also other properties of mixtures of alginates and divalent metal salts, such as gel formation<sup>2</sup> and ion exchange<sup>3</sup> varied in the same (or opposite) order. For the precipitation of alginates McDowell<sup>4</sup> found that the amount of divalent metal ions necessary to obtain precipitation increased in the order  $Pb, Cu < Ca < Co, Ni, Zn < Mn$ .

It has recently been shown that the ion exchange properties of alginates depend on the chemical composition of the alginate<sup>5</sup>. Alginates rich in mannuronic acid residues, such as alginates from *Laminaria digitata*, have a lower affinity to calcium in a sodium-calcium ion exchange reaction than alginates rich in guluronic acid residues, such as alginate from *Laminaria hyperborea* stipes. It was therefore of interest to determine if the affinity of alginates to the different divalent metal ions varied in the same order for alginates with different chemical composition.

**Materials and methods.** The preparation of alginate from the algal samples has been described previously<sup>6</sup>. The sodium alginate was washed with 0.1 M hydrochloric acid to transform the alginate to alginic acid, and then carefully washed with water, dried and ground. Samples of 25 mg were suspended in water and sodium hydroxide added in an amount corresponding to half the equivalent amount of alginic acid, the total volume being maintained at 5 ml. The samples were shaken for one hour and the pH determined in a Beckman Zero-matic pH meter furnished with a glass electro-

de. 0.1 M solutions of divalent metal salts were added and the pH again determined after the samples had been shaken for one hour.

The selectivity coefficient for the cadmium-strontium ion exchange reaction was determined by the following method: Samples of 25 mg of sodium alginate were shaken over night with a mixture of 5 ml 0.01 M strontium nitrate, 5 ml 0.01 M cadmium nitrate and 4 ml water. The solution was separated from the alginate by decantation and the alginate washed. The combined solution and wash-water was titrated with 0.01 M EDTA solution at pH 10 with Eriochrome Black T as an indicator. After the endpoint was reached 1 ml of a 0.1 M solution of magnesium EDTA complex was added and the titration continued until the next endpoint was reached. The first endpoint corresponds to the content of cadmium in the solution, while the second corresponds to the total amount of cadmium and strontium. The alginate gel was treated twice with 10 ml 0.2 M hydrochloric acid and the content of cadmium and strontium in the acid determined as described above, after the acid had been neutralized with 1 M sodium hydroxide.

When a metal salt solution is added to a half neutralized sample of alginic acid the pH decreases and the magnitude of the decrease depends on the affinity between the alginate and the metal ion. Table 1 gives the results for two alginate samples produced from *Laminaria digitata* and *Laminaria hyperborea* stipes, respectively. Alginate from *L. digitata* contains more mannuronic than guluronic acid residues while the opposite is usually the case with alginate from *L. hyperborea* stipes. The uronic acid composition of the two alginates used are given in Table 2. The observed difference in pH for half neutralized samples is in agreement with earlier observations<sup>7</sup>. For alginate from *L. digitata* it was found that the magnitude of the decrease of pH depended on the divalent metal used, and that the same order of metals was found as that observed by Thiele for other properties of alginates. For alginate from *L. hyperborea* stipes, however, the order was found to be significantly different, the addition of cadmium salt leading to a smaller pH decrease than addition of barium or strontium salts.

The results thus indicate that the affinity to these divalent metals is different for alginates with different chemical composition. This point was further investigated by determining the selectivity co-

Table 1. pH of alginate solutions containing metal salts.

| Metal salt                        | mequiv. salt       |      |      | mequiv. alg.               |      |      |
|-----------------------------------|--------------------|------|------|----------------------------|------|------|
|                                   | 0                  | 0.83 | 1.66 | 0                          | 0.83 | 1.66 |
|                                   | <i>L. digitata</i> |      |      | <i>L. hyperborea</i> stipe |      |      |
| Pb(NO <sub>3</sub> ) <sub>2</sub> | 3.90               | 2.60 | 2.40 | 4.48                       | 2.60 | 2.38 |
| Cu(NO <sub>3</sub> ) <sub>2</sub> |                    | 2.85 | 2.75 |                            | 2.95 | 2.65 |
| Cd(NO <sub>3</sub> ) <sub>2</sub> |                    | 2.94 | 2.77 |                            | 3.13 | 2.96 |
| Ba(NO <sub>3</sub> ) <sub>2</sub> |                    | 3.00 | 2.80 |                            | 3.05 | 2.85 |
| Sr(NO <sub>3</sub> ) <sub>2</sub> |                    | 3.05 | 2.95 |                            | 3.10 | 2.92 |
| Ca(NO <sub>3</sub> ) <sub>2</sub> |                    | 3.21 | 2.98 |                            | 3.25 | 3.02 |
| Co(NO <sub>3</sub> ) <sub>2</sub> |                    | 3.24 | 3.11 |                            | 3.41 | 3.31 |
| Ni(NO <sub>3</sub> ) <sub>2</sub> |                    | 3.32 | 3.15 |                            | 3.51 | 3.38 |
| ZnSO <sub>4</sub>                 |                    | 3.32 | 3.22 |                            | 3.49 | 3.40 |
| MnSO <sub>4</sub>                 |                    | 3.32 | 3.31 |                            | 3.74 | 3.72 |
| MgSO <sub>4</sub>                 |                    | 3.39 | 3.36 |                            | 3.80 | 3.70 |

The ionotropic series of Thiele:  
Pb < Cu < Cd < Ba < Sr < Ca < Zn, Co, Ni

Table 2.

| Source of alginate                           | <i>k</i> <sub>Cd-Sr</sub> | Mannuronic acid |  |
|--|---------------------------|-----------------|--|
|  |                           | Guluronic acid  |  |
| <i>L. digitata</i> , Kråkvågøy 3/7           | 1.17                      | 2.10            |  |
| » » Espøvær 8/1                              | 0.98                      | 1.75            |  |
| <i>L. hyperborea</i> stipes, Reine 28/6      | 0.70                      | 1.10            |  |
| » » Hustad 26/2                              | 0.54                      | 0.56            |  |
| <i>Ascophyllum nodosum</i> , Være 2/3        | 1.19                      | 2.45            |  |
| Commercial samples:                          |                           |                 |  |
| Protanal LF ( <i>L. digitata</i> )           | 1.22                      | 2.17            |  |
| Manucol SS/LD ( <i>L. hyperborea</i> stipes) | 0.58                      | 0.70            |  |
| Manucol SA/LM ( <i>A. nodosum</i> )          | 0.95                      | 1.65            |  |

efficient of the cadmium-strontium ion exchange reaction:

$$k = \frac{Cd_g \cdot Sr_s}{Sr_g \cdot Cd_s}$$

where subscripts *g* and *s* refer to gel and solution, respectively. No attempt has been made to determine a true equilibrium constant involving activities. The results for a number of alginate samples of different composition are given in Table 2. The uronic acid composition was determined by hydrolysis of the alginate, separation of the two uronic acids by chromatography on an anion exchange resin<sup>8</sup> and determining the amounts of uronic acid in the two fractions by means of the orcinol method<sup>9</sup> (the detailed procedure will be published later).

The results show that a close correlation exists between the selectivity coefficient for the cadmium-strontium ion exchange

reaction and the chemical composition of the alginate.

The interaction between divalent metals and alginates will be investigated further.

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