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# Alginate polyelectrolyte ionotropic gels

## Part III *Kinetics of exchange of chelated divalent transition metal ions especially cobalt(II) and copper(II) by hydrogen ions in capillary ionotropic metal alginate polymembrane gels*

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The kinetics and mechanism of exchange of cross-linked $Cu^{2+}$ and $Co^{2+}$ by $H^+$ ions in their alginate gel complexes have been investigated, conductimetrically. The rate of exchange was found to decrease in the order Co > Ni > Cu alginates. The factors affected the rate of exchange such as the ionic radii of metal ions, width of capillaries, strength of chelation and the orientation of the solvent molecules and the macromolecular chains toward the chelated metal ions were discussed. The thermodynamic parameters of exchange have been evaluated and interpreted in terms of gel stability.

## 1. Introduction

Ionotropic gels are formed by diffusion of cations or anions into anion or cation polyelectrolytes, respectively [1]. Alginate anion polyelectrolyte is hence converted into ionotropic gels by the diffusion of polyvalent metal ion electrolytes onto alginate sols. The sol–gel transformation is usually accompanied by a definite structure, and orientation of the solvent molecules and the macromolecular chains toward the interdiffused metal ions. The stoichiometric [2] equation for such gelation process can be expressed as

$$\underset{\text{sol}}{2\text{Na–Alg}} + \underset{\text{electrolyte}}{M^{n+}} = \underset{\text{gel}}{\text{M–Alg}_n} + \underset{\text{electrolyte}}{n\text{Na}^+} \quad (1)$$

where M denotes a polyvalent metal ion and $n$ stands for its valency.

Specker *et al.* [3] have investigated the alginate as an ion exchange material. Takahashi and coworkers [4, 5] examined the affinity and selectivity of alginates as cation exchangers. The kinetics of gelation processes have been investigated in detail by us earlier [6, 7].

In the present work, the kinetics of exchange of chelated $Cu^{2+}$ and $Co^{2+}$ transition metal ions by $H^+$ ions are presented in an effort to gain some information about the stability of the alginate gel complexes in terms of the chelated metal ion reactivities, and to compare the results with that previously obtained for nickel alginate gels [8].

## 2. Experimental procedure

### 2.1. Materials

All materials used were of Analar (BDH) grade. Doubly distilled conductivity water was used in all preparations.

### 2.2. Preparation and analyses of metal alginate pellets

The preparation and analyses were carried out as described earlier [8].

### 2.3. Kinetic measurements

Solutions containing ionotropic copper or cobalt alginates of capillary structures in the form of spherical pellets and aqueous solutions of $H^+$ ions ($HClO_4$) were thermally equilibrated in a constant temperature water bath maintained at the desired temperature to within ± 0.1 °C. When the two reactants had attained the temperature of the thermostat, the required concentrations of both reactants were transferred and mixed into the reaction cell. The course of reaction was followed conductimetrically as a function of time. Some kinetic runs were followed pH-metrically or complexometrically as a function of time to check the producibility of the kinetic results.

The ionic strength of the reaction mixture was maintained constant at 0.1 mol dm$^{-3}$ by adding $NaClO_4$ as an inert electrolyte.

## 3. Results

The rate of exchange depends on the size and shape of ion exchange particles. Strictly spherical gels of uniform size are recommended for the rate measurements to obtain reproducible results since the particle size and shape of alginate pellets are well defined. The change in conductivity as a function of time is a very convenient technique, however, it is restricted to exchange of ions of sufficient different mobilities in the aqueous phase [9, 10].

### 3.1. Stoichiometry

The stoichiometry of these exchange reactions was determined complexometrically and pH-metrically for

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a series of mixtures of different initial concentrations of the reactants at fixed ionic strength and temperature. A stoichiometric ratio of 2.02 ± 0.02 for $[H^+]$: $[M\text{-}Alg_2]$ was observed. The overall exchange reaction can hence be written as

$$\begin{array}{ccccccc} M\text{-}Alg_2 & + & 2H^+ & \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} & 2H\text{-}Alg & + & M^{2+} \\ \text{gel} & & \text{electrolyte} & & \text{gel} & & \text{electrolyte} \end{array} \qquad (2)$$

where $k_1$ and $k_{-1}$ are the rate constants of exchange for the forward and reverse reactions, respectively. The empirical rate law of the exchange is

$$\text{Rate} = -\frac{d[M\text{-}Alg_2]}{dt} = -\frac{1}{2}\frac{d[H^+]}{dt}$$
$$= k_1[M\text{-}Alg_2][H^+] - k_{-1}[H\text{-}Alg][M^{2+}] \qquad (3)$$

Under pseudo first-order conditions where $[M\text{-}Alg_2]$ is present in a large excess over that of $[H^+]$, the observed first-order rate constant of exchange may be expressed by

$$k_{ex} = k_1[M\text{-}Alg_2] + k_{-1} \qquad (4)$$

The values of $k_{ex}$ can be determined from the conductimetric methods [11]

$$\ln(\lambda_t - \lambda_e) = k_{ex}t + \alpha \qquad (5)$$

where $\lambda_t$ and $\lambda_e$ are the conductivities at time $t$ and equilibrium, respectively, and $\alpha$ a constant. The parameter $\alpha$ allows the best fit to the data without the restrictions that the extrapolated value of $\lambda_0$ is used.

### 3.2. Dependence of the exchange rate on $[M\text{-}Alg_2]$ and $[H^+]$ reactants

Plots of $\ln(\lambda_t - \lambda_e)$ against time were fairly linear for more than three half-lives of exchange processes as shown in Fig. 1. This linearity indicates that the exchange reaction is first order with respect to the hydrogen ion concentration. Again, a plot of $k_{ex}$ against $[M\text{-}Alg_2]$ according to Equation 5 should be linear with positive intercept as is observed experimentally (Fig. 2). The values of the exchange rate constants were calculated by using the least-squares method and summarized in Table I. The values of $k_{ex}$ obtained from the pH metric and complexometric kinetic runs were found to be in good agreement with that observed conductimetrically within the experimental errors (± 4%). This fact indicates that the results obtained are reliable.

### 3.3. Dependence of exchange rate on temperature

To determine the thermodynamic parameters of exchange, the reactions were carried out at four temperatures between 2 and 26 °C at constant ionic strength. Plots of the Eyring equation [12] for $k_1$ gave good straight lines from whose, slopes and intercepts the enthalpies and entropies of activations were determined. The thermodynamic parameters were calculated by the least-squares method and are summarized in Table II.

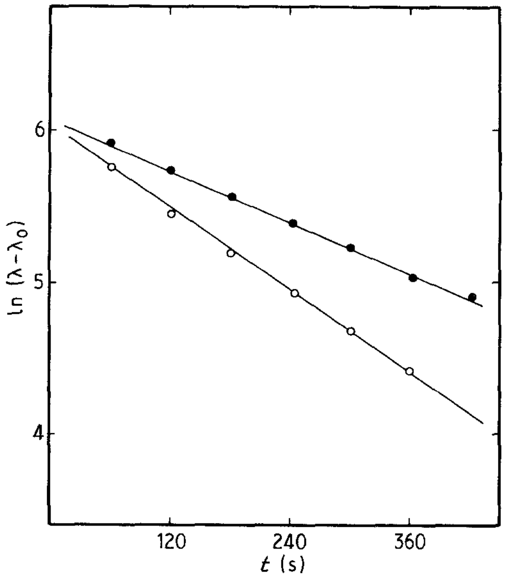

*Figure 1* Plots of $\ln(\lambda_t - \lambda_e)$ against time for exchange of metal ions by hydrogen ions in metal alginate ionotropic gels. $[H^+] = 0.001$ and $I = 0.1$ mol dm$^{-3}$. [●] = $Co^{2+}$ = 0.031 mol dm$^{-3}$ at 8 °C; [○] = $Cu^{2+}$ = 0.041 mol dm$^{-3}$ at 20 °C.

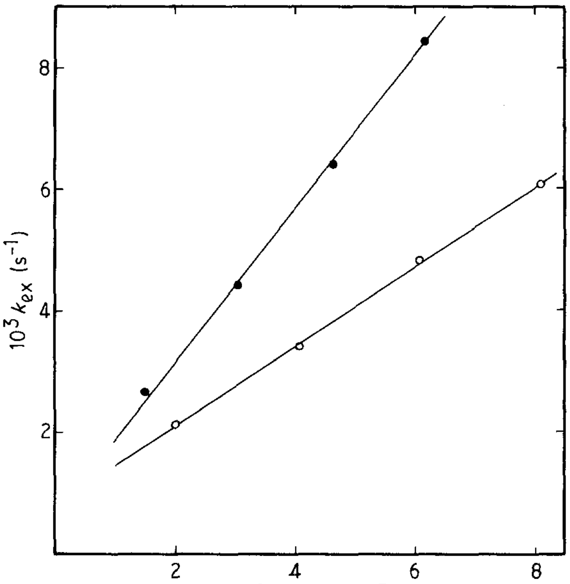

*Figure 2* Plots of $k_{ex}$ against $[M^{2+}]$ for exchange of metal ions by $H^+$ ions in metal alginate ionotropic gels. $[H^+] = 0.001$, $I = 0.1$ mol dm$^{-3}$ and temperature = 20 °C. [●] $Co^{2+}$; [○] = $Cu^{2+}$ alginates.

## 4. Discussion

The stoichiometry of exchange requires that the fluxes of the two exchanging counter ions be equal in magnitude, even though the counter ion mobilities may be quite different, i.e., the ion exchange process is inherently a stoichiometric process [13].

In divalent metal alginate gel complexes, the interdiffused metal ions form a sort of bridge between two carboxylate and one or two pairs of the hydroxyl

TABLE I The values of the exchange rate constants, $[Co^{2+}] = [Ni^{2+}] = 0.62$; $[Cu^{2+}] = 0.61$, $I = 0.1$ mol dm$^{-3}$ and temperature = 20 °C

| Metal–Alginate | $10^3\ k_{ex}$ ($s^{-1}$) | $10^2\ k_1$ ($dm^3\ mol^{-1}\ s^{-1}$) | $10^4\ k_{-1}$ ($s^{-1}$) | $10^{-2}\ K$ ($dm^3\ mol^{-1}$) | $10^{-2}\ K^a$ ($dm^3\ mol^{-1}$) | Reference |
|---|---|---|---|---|---|---|
| $Ni^{2+}$ | 7.75 | 11.40 | 7.17 | 1.59 | 0.40 | [8] |
| $Cu^{2+}$ | 4.82 | 6.34 | 8.83 | 0.72 | 0.15 | This work |
| $Co^{2+}$ | 8.47 | 12.52 | 6.50 | 1.93 | 0.56 | This work |

[a] These values were obtained thermodynamically [22].

TABLE II The thermodynamic parameters for exchange

| | $\Delta S^{\ddagger}$ ($J\ mol^{-1}\ K^{-1}$) | $\Delta H^{\ddagger}$ ($kJ\ mol^{-1}$) | $\Delta G^{\ddagger}$ ($kJ\ mol^{-1}$) | Reference |
|---|---|---|---|---|
| $Ni^{2+}$ | $-145.85 \pm 4.08$ | $34.18 \pm 0.61$ | $77.64 \pm 1.83$ | [8] |
| $Cu^{2+}$ | $-158.42 \pm 4.72$ | $31.93 \pm 0.64$ | $79.14 \pm 2.05$ | This work |
| $Co^{2+}$ | $-138.90 \pm 4.01$ | $35.99 \pm 0.63$ | $77.38 \pm 1.82$ | This work |

groups of the macromolecular chains of alginate polyelectrolyte through partially ionic and partially coordinate bonds, respectively. These chelates may be either intermolecular [14] where the carboxylate and hydroxyl groups belong to different chains, or intramolecular type [15] in which these functional groups belong to the same chain of the macrostructure. The chelated metal ions can be replaced by other cations such as $H^+$ ions to give the corresponding alginic acid. This metal–acid gel transformation will affect the mechanical and optical properties of the ionotropic gels such as rigidity, elasticity, shape, structure anisotropy and birefringence, respectively. This change depends on the nature of the metal ion and strength of chelation.

As shown in Table I, the rate constants of exchange were increased in the order Cu < Ni $\leqslant$ Co alginates. The magnitude depends on the strength of chelation and the width of capillaries. The stronger the chelated metal ion should be, the slower the rate of exchange. The strength of chelation increases in the order Co $\leqslant$ Ni < Cu alginates [16], in good agreement with the experimental observations of decreasing the exchange rate in the same order. The width of capillaries will enhance the exchange process between the exchanging counterions. The diameter of the capillaries lies in the order Cu < Ni $\leqslant$ Co alginates [17], in good accord with the experimental finding of increasing the rate of exchange in the same direction.

The small values observed for $k_{-1}$ (Fig. 2) may be explained in part by the relative stability of alginic acid [18] and the hinderance effect resulting from the large carboxylate group against the penetration power of the dissociated metal ions which tend to replace the small sized interdiffused hydrogen ions. This induced hinderance will slow down the velocity of the metal ions to a great extent as is observed experimentally.

The negative entropy of activation observed in Table II may be interpreted by the necessity of the $H^+$ ions to penetrate the carboxylate groups in order to replace the strongly chelated metal ions. This requires more energy to overcome the energy barrier which in turn needs some rearrangement of the solvent molecules oriented toward the metal ions in the macrostructure. The ordering of the solvent molecules and the macromolecular chains toward the chelated metal ions will, therefore, tend to increase or decrease the entropy of activation. The more oriented the metal ion is the larger the negative entropy of activation. Copper(II) is known to be well oriented in its alginates, and, hence has a large negative value of $\Delta S^{\ddagger}$. The other metal ions are less oriented and possess smaller values of $\Delta S^{\ddagger}$. The magnitude of orientation is in the order Cu > Ni $\geqslant$ Co [19, 21] which agrees very well with the experimental observations for $\Delta S^{\ddagger}$. Again, the differences in $\Delta S^{\ddagger}$ values for these exchange reactions may reflect a different number of water molecules being oriented toward the cross-linked metal ions.

The thermodynamic parameters listed in Table II may throw some light on the stability of these gel complexes. The equilibrium constants ($K = k_1/k_{-1}$) obtained in the present study were compared with that reported in a thermodynamic study and summarized in Table I along with the exchange rate constants. The big difference between the values of K observed in the kinetic and thermodynamic studies may be attributed to the nature of the metal alginates used, in which capillary structures were incorporated in the alginate pellets used in the kinetic study [17].

In the sol–gel transformation, the diffusion process between the counterions of alginate, $Na^+$, and the metal ion electrolytes, $M^{2+}$, is usually accompanied by the formation of capillaries in the direction of the diffusion. These capillaries are straight parallel and are nearly identical. Under optical microscopic investigation, these capillaries appear as fine pores of the same radius in a transverse section as shown in Fig. 3.

The presence of such capillaries in the metal alginate pellets will enhance the exchange process between the $H^+$ and $M^{2+}$ ions in the forward direction, i.e., toward the formation of stable acid alginates [18]. Again, the appreciable shrinkage occurs within the capillaries of the formed acid alginates will affect the rate of exchange for the reverse reaction as is observed experimentally of finding small values of $k_{-1}$. This means that the equilibrium tends to shift toward the

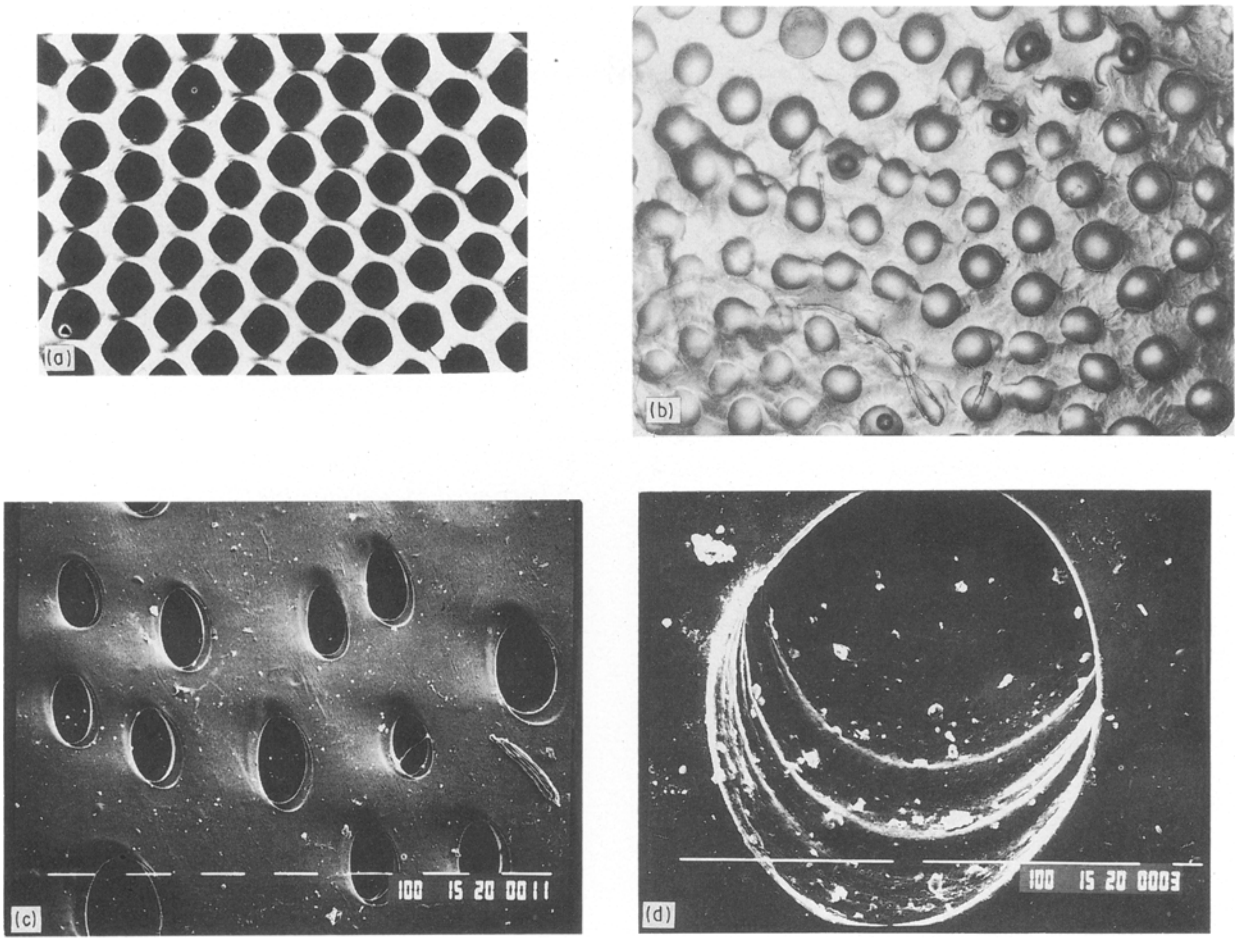

*Figure 3* Optical images of transverse sections in ionotropic metal alginate membranes. Microscopical scanning in the pores of nickel alginate membranes.

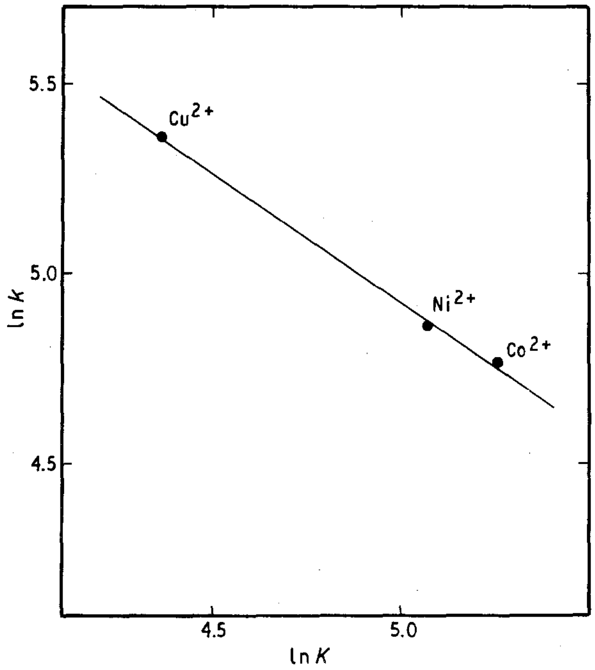

*Figure 4* Plot of ln *K* against ln *k* for exchange of $M^{2+}$ by $H^+$ ions in metal alginate ionotropic gels. $[M^{2+}] = 0.062$, $[H^+] = 0.001$, $I = 0.1$ mol dm$^{-3}$ and temperature = 20 °C.

formation of stable alginic acid [18] in metal alginate gel pellets rather than in solid metal alginate exchangers [22].

Again, a plot of ln $k_{ex}$ against ln *K* was almost linear as shown in Fig. 4. This linear correlation indicates the consistency between these metal ions in their metal alginate complexes based on their corresponding reactivities. The stability of the metal alginate complexes is increased in the order Co < Ni < Cu [23–25], which is consistent with the experimental finding of increasing the magnitude in the same order. In spite of the variety of the transition metal ions incorporated in the alginate gels used, the free energy of activation remained unaltered. This fact may suggest a similar mechanism of exchange between the $H^+$ and $M^{2+}$ counterions.

## 5. Conclusion

The experimental observations showed that the selectivity of metal alginate ionotropic gel complexes for exchange of their chelated metal ions by $H^+$ ions is increased in the order Cu < Ni < Co alginates. This result may be useful in the chromatographic separation of these metal ions from a mixture of them using alginic acid column chromatograph. Qualitative results have been obtained, while the quantitative analyses are in good progress in our laboratory.

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