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# Alginate polyelectrolyte ionotropic gels

## Part II *Kinetics and mechanism of exchange of chelated nickel (II) by hydrogen ions in capillary ionotropic nickel alginate polymembrane gel complex*

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The kinetics and mechanism of exchange of $Ni^{2+}$ by $H^+$ ions in ionotropic nickel alginate polymembrane gels of capillary structure have been studied by pH-metric and conductimetric techniques. The rate of exchange conforms to; rate = $k_1$ [nickel alginate] $[H^+] - k_{-1}$ [alginic acid] $[Ni^{2+}]$ with $k_1 = 6.34 \times 10^{-2}$ $dm^3 mol^{-1} s^{-1}$ and $k_{-1} = 8.83 \times 10^{-4}$ $s^{-1}$ at 20 °C, respectively. The activation parameters have been evaluated and a mechanism consistent with the kinetic data is discussed.

## 1. Introduction

Alginates as anion polyelectrolytes possess high affinities for divalent transition metal ions [1–6]. The diffusion of such metal ion electrolytes into alginate sols form capillary ionotropic metal alginate gel complexes. These gel complexes differ from the classical type of gels in which the long-chain molecules are held together by simple van der Waal's forces, the macromolecular chains being chelated by the divalent metal ions.

The kinetics of the sol–gel transformation have been investigated in detail earlier [7–9]. The gel complexes showed an appreciable tendency to exchange their cross-linked divalent metal counter ions with another equivalent cations. The selection of $H^+$ as exchanging counter ion in the present study was based on the relative stability of the formed alginic acid [10] and the distinct different mobilities between the exchanging ions [11, 12].

The main object of this work was to examine the selectivity of nickel alginate gel complex for hydrogen ions in terms of the influence of the exchange process on the properties of nickel alginate ionotropic gels.

## 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 of metal alginate pellets

Ionotropic metal alginate pellets were prepared by dropping sodium alginate sols into $Ni^{2+}$ electrolyte solution using a special syringe. After completion of the sol–gel transformation, the formed pellets were carefully removed and washed with deionized water until the water was free from $Ni^{2+}$ ions. The pellets were then kept in doubly distilled conductivity water until use. For each alginate sol and nickel (II) ion electrolyte, the following precautions were taken into consideration to maintain the size and shape of the sol droplets constant as far as possible: (a) the volume of the alginate sol inside the syringe and the distance from the tip of the syringe to the surface of the nickel (II) ion electrolyte were kept constant; (b) the force exerted upon the piston of the syringe was maintained fixed; (c) the same syringe was used as a dropper.

### 2.3. Analytical determination of the species

The analysis and standardization of the species were carried out as recommended elsewhere [13]. The concentration of $Ni^{2+}$ ions was determined complexometrically and gravimetrically, while that of $H^+$ ions was evaluated by pH-metric and titrimetric techniques. The reproducibility of the analyses were found to be in a good agreement with each other within experimental error (± 3%).

### 2.4. Kinetic measurements

Solutions containing nickel alginate pellets and $H^+$ ions ($HClO_4$) were thermally equilibrated in a constant-temperature water bath maintained at the desired temperature within ± 0.1 °C. When the two reactants had attained the temperature of the thermostat, they were transferred in the required concentrations and mixed into the reaction cell. The course of reaction was followed by monitoring the change of conductance as a function of time.

Some kinetic runs were followed pH-metrically or complexometrically as a function of time to check the

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reproducibility of the kinetic data obtained. The fact that the various methods gave rate constants in good agreement with each other indicates that the results obtained were reliable.

### 2.5. Temperature dependency

To determine the thermodynamic parameters of exchange, the kinetics of the exchange reaction were investigated at temperatures from 2–26 °C. The enthalpies and entropies of activation were evaluated from the Eyring equation [14]. The activation parameters were calculated using the least squares method.

All kinetic measurements were carried out under pseudo first-order conditions where [nickel alginate] was present in a large excess over that of $[\text{H}^+]$ except for the complexometrical runs.

The ionic strength of the reaction mixture was maintained constant at 0.1 mol $\text{dm}^{-3}$ by adding $\text{NaClO}_4$ as a non-complexing agent.

## 3. Results and discussion

Ion exchange is inherently a stoichiometric process [7–9]. Any counter ions which leave their sites in the ion exchanger matrix must be replaced by an equivalent amount of other counter ions. This is a consequence of the electroneutrality requirements. This means that when a chelated $\text{Ni}^{2+}$ ion migrates from the matrix of alginate gel complex into the surrounding electrolyte of aqueous $\text{H}^+$ ions, the alginate exchanger is left with a surplus electric negative charge which must be compensated by taking up two hydrogen counter ions. The total charge remains constant, irrespective of different valencies of the two counter ions. Therefore, the exchange process between $\text{Ni}^{2+}$ and $\text{H}^+$ ions can be expressed by

$$\underset{\text{gel}}{\overline{\text{Alg}_2\text{-Ni}}} + \underset{\text{electrolyte}}{2\text{H}^+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{gel}}{2\overline{\text{Alg-H}}} + \underset{\text{electrolyte}}{\text{Ni}^{2+}} \qquad (1)$$

where $k_1$ and $k_{-1}$ are the rate constants of exchange for the forward and reverse reactions, and $\overline{\text{Alg}}$ denotes the alginate as anion polyelectrolyte matrix. The empirical rate law of exchange is

$$\begin{aligned} \text{Rate} &= -\frac{\text{d}[\overline{\text{Alg}_2\text{-Ni}}]}{\text{d}t} \\ &= -\frac{1\text{d}[\text{H}^+]}{2\ \text{d}t} \\ &= k_1[\overline{\text{Alg}_2\text{-Ni}}]\,[\text{H}^+] \\ &\quad - k_{-1}[\overline{\text{Alg-H}}]\,[\text{Ni}^{2+}] \qquad (2) \end{aligned}$$

Under pseudo first-order conditions where $[\overline{\text{Alg}_2\text{-Ni}}] \gg [\text{H}^+]$, the observed first-order rate constant of exchange for reversible reactions [15–17] can hold under the relationship

$$k_{\text{ex}} = k_1[\overline{\text{Alg}_2\text{-Ni}}] + k_{-1} \qquad (3)$$

The values of $k_{\text{ex}}$ can be determined from the conductimetric methods [15–17]

$$\ln(\lambda_t - \lambda_e) = k_{\text{ex}}t + C \qquad (4)$$

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

According to Equation 4, plots of ln $(\lambda_t - \lambda_e)$ versus $t$ should be linear as is observed experimentally. A typical plot is shown in Fig. 1. Again, plots of $k_{\text{ex}}$ against $[\overline{\text{Alg}_2\text{-Ni}}]$ according to Equation 3 were fairly linear, as shown in Fig. 2.

The values of the rate constants of exchange were calculated by using the least squares method and summarized in Table I together with the equilibrium

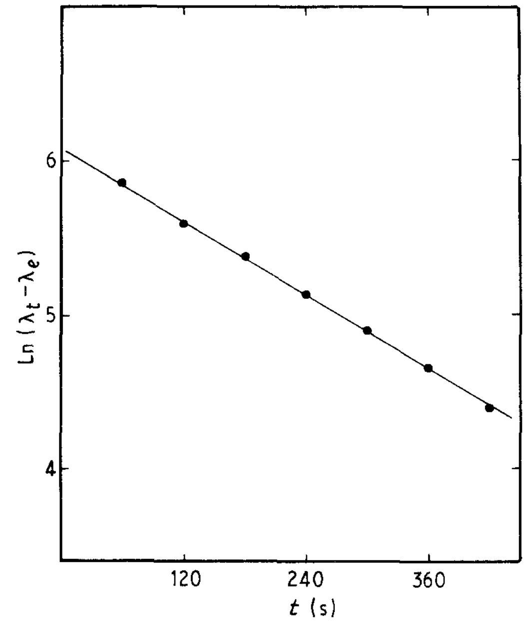

*Figure 1* Plot of ln $(\lambda_t - \lambda_e)$ versus time for exchange of $\text{Ni}^{2+}$ by $\text{H}^+$ ions in nickel alginate ionotropic gels. $[\text{H}^+] = 0.001$, $[\text{Ni}^{2+}] = 0.031$, $I = 0.1$ mol $\text{dm}^{-3}$ and $T = 20$ °C.

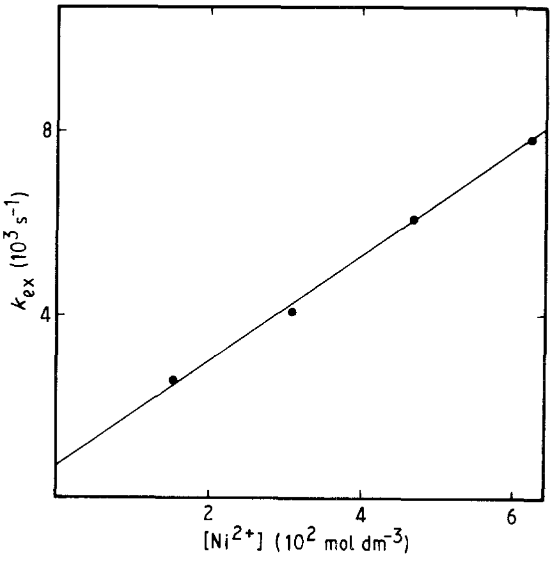

*Figure 2* Plot of $k_{\text{ex}}$ versus $[\text{Ni}^{2+}]$ for exchange of $\text{Ni}^{2+}$ by $\text{H}^+$ ions in nickel alginate ionotropic gels. $[\text{H}^+] = 0.001$, $I = 0.1$ mol $\text{dm}^{-3}$ and $T = 20$ °C

TABLE I. The rate constants of exchange; $[Ni^{2+}] = 0.061$, $I = 0.1$ mol dm$^{-3}$, $T = 20\,°C$

| | |
|---|---|
| $k_{ex}$ (s$^{-1}$) | $6.18 \times 10^3$ |
| $k_1$ (dm$^3$mol$^{-1}$s$^{-1}$) | $11.40 \times 10^2$ |
| $k_{-1}$ (s$^{-1}$) | $7.17 \times 10^4$ |
| $K$ (dm$^3$mol$^{-1}$) | $1.59 \times 10^{-2}$ |
| $K$ (dm$^3$mol$^{-2}$) [18] | $0.40 \times 10^{-3}$ |

constant which was obtained thermodynamically [18]. The values of $k_{ex}$ evaluated from the pH-metric runs were found to be in good agreement with that observed conductimetrically with small deviation of ± 4% indicating that the results obtained were reliable.

The kinetic parameters are summarized in Tables I and II. The magnitude of $K$ which is obtained kinetically, may be attributed to the small $k_{-1}$ values rather than the values of $k_1$. Again, the big difference between the $K$ values observed in Table I may be explained by the different nature of the metal alginates used, where a capillary structure is incorporated within the metal alginate pellets utilized in the kinetic study.

The sol–gel transformation is usually accompanied by the formation of capillaries in the direction of diffusion between $Na^+$ and $Ni^{2+}$ ions. These capillaries are straight, parallel and nearly identical to each other. Under optical microscopic investigations, these capillaries appear as fine pores of the same radius in a transverse section, as shown in Fig. 3. The diffusion process takes place stepwise to form a capillary polymembrane structure. These polymembranes could be separated into very thin layers [19]. The dehydration of solvent waters from these polymembrane gels gives a transparent film of high homogeneity. The capillaries in this film appear to be spiral or cone shaped, as shown in Fig. 4. This fact confirms the capillary polymembrane structure of nickel alginate gel complex. These capillaries will enhance the exchange process between $H^+$ and $Ni^{2+}$ ions. Hence, the equilibrium tends to shift in the forward direction, i.e. towards the formation of stable alginic acid [10] in alginate ionotropic pellets rather than in the solid alginate resinates [18]. On the other hand, when alginic acid is formed, shrinkage occurs in the formed capillaries to some extent. This shrinkage will reduce the velocity of exchange between the interdiffused $H^+$ ions, chelated macromolecular chains and the dissociated $Ni^{2+}$ ions in the external electrolyte, i.e. the reverse reaction of the exchange slows down.

In connection with alginic acid and nickel alginate ionotropic gels, two geometrical coordinations have been suggested being the inter- and intramolecular associations, respectively. In the former geometry, the metal ion chelates the functional groups of alginate macromolecular units of two different chains, whereas the chelation occurs in units of the same chain for the latter type. A discussion for the modes of chelation with respect to the coordination number of chelated metal ion has been described earlier [20]. The divalent metal ions tend to chelate the functional groups via planar-geometry, i.e. an intramolecular association mechanism, whereas the hydrogen ions prefer the chelation of the non-planar intermolecular association type due to the high facility for hydrogen bonding (Figs 5 and 6). This is also confirmed by the electrical

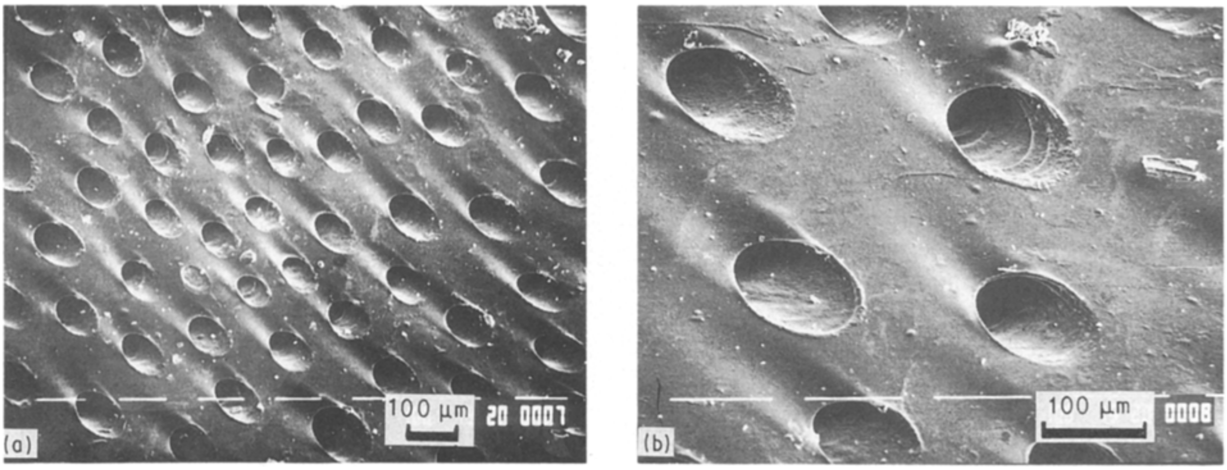

*Figure 3* Scanning electron micrograph of the inside of the pores of nickel alginate membranes.

TABLE II. The thermodynamic parameters for exchange in metal alginate gel complexes

| Metal ion | $\Delta S$ (J mol$^{-1}$K$^{-1}$) | $\Delta H$ (kJ mol$^{-1}$) | $\Delta G$ (kJ mol$^{-1}$) | Reference |
|---|---|---|---|---|
| $Ni^{2+}$ | $-145.85 \pm 4.08$ | $34.18 \pm 0.61$ | $77.64 \pm 1.83$ | This work |
| $Co^{2+}$ | $-138.90 \pm 4.01$ | $35.99 \pm 0.63$ | $77.38 \pm 1.82$ | [21] |
| $Cu^{2+}$ | $-158.42 + 4.72$ | $31.93 + 0.64$ | $79.14 + 2.05$ | [21] |

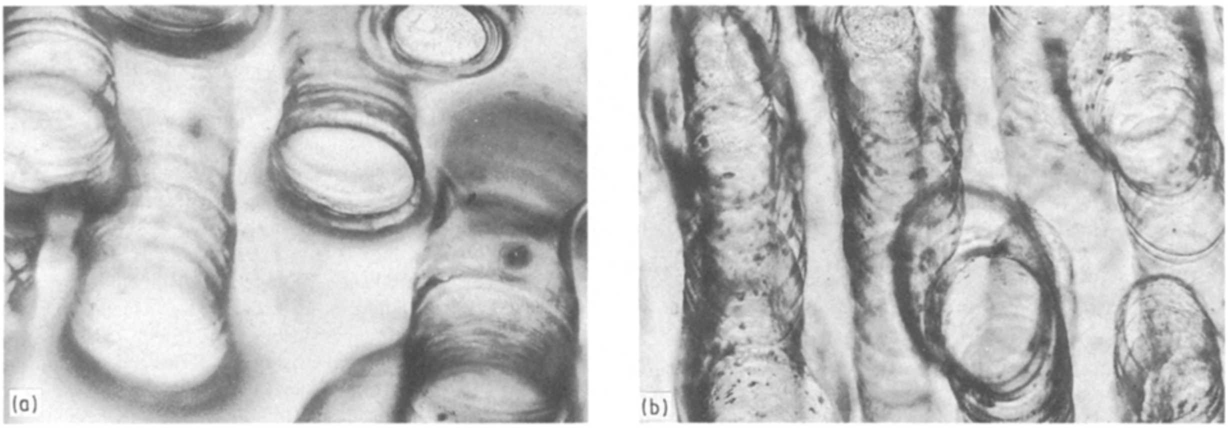

*Figure 4* Optical images of transverse sections in nickel alginate membranes.

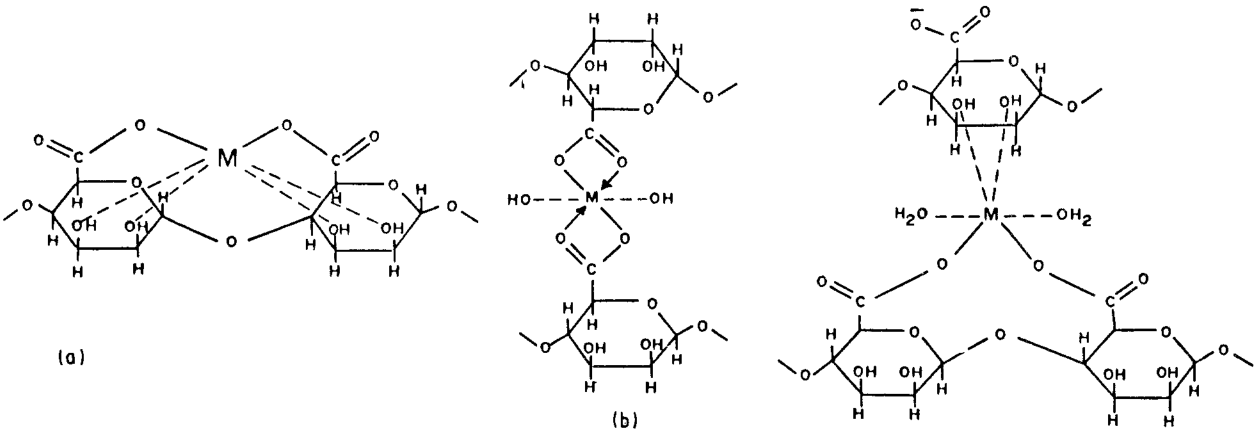

*Figure 5* Chelation in divalent metal alginate complexes. (a) Intramolecular; (b) intermolecular.

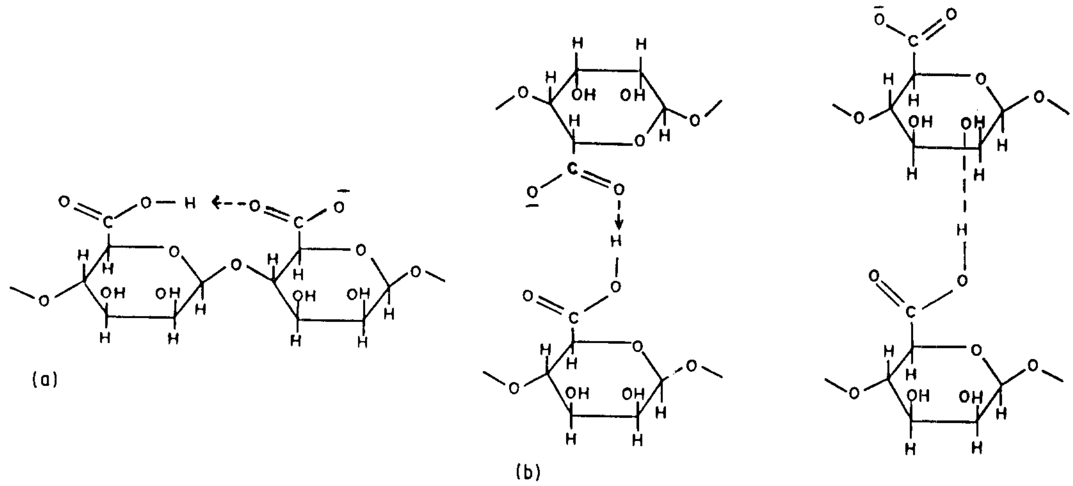

*Figure 6* Chelation in acid alginate complex. (a) Intramolecular; (b) intermolecular.

conductivity measurements under very high frequencies [7–9]. This fact may, in turn, interpret the tendency of this exchange reaction to proceed in the forward direction rather than the reverse reaction.

The observed negative entropy of activation can be attributed to the necessity of $H^+$ ions to penetrate the carboxylate groups in order to replace the chelated $Ni^{2+}$ ions and form the corresponding acid alginate gels. The thermodynamic parameters observed here are in good agreement with those of cobalt (II) and copper (II) alginate gel complexes obtained earlier [21].

## 4. Conclusion

Alginic acid of capillary polymembrane structure is of great importance in the separation of metal ions from their mixtures and to capture the contaminated traces of radioisotopes using alginate membranes or column chromatograph techniques as separation methods.

The separated thin films may be used in electrophotoconductography, photography and as filters for biological and medical purposes.

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