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# INFLUENCE OF FREQUENCY ON SPECIFIC CONDUCTANCE OF POLYELECTROLYTE GELS WITH SPECIAL CORRELATION BETWEEN STRENGTH OF CHELATION AND STABILITY OF DIVALENT METAL ALGINATE IONOTROPIC GELS

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**Abstract**—A new technique has been used to measure the variation in the specific conductance for metal alginate gel complexes for a wide range of frequencies (0.02–800 kHz). The relationships between the specific conductance and frequency show inflection points at two different frequencies for every metal alginate complex. This behaviour is interpreted as the elimination of the relaxation effects resulting from the cleavage of the coordinate and ionic bonds between the chelated metal ions and the hydroxyl and carboxylate groups of macromolecular chains of alginate polyelectrolyte, respectively. This behaviour is discussed in terms of the strength of chelation and stability of the gel complexes.

## INTRODUCTION

The metal alginate gel complexes are ionotropic [1, 2] differing in nature from the classical type of gels in which the long chain molecules are held together with van der Waal forces; a type of chelation between the metal ions and the functional groups of the macromolecular chains occurs in these gel complexes.

Although many publications and patents have been published [3] on alginic acid and its derivatives, there are few reports on the electrical properties of their metal gels in relation to the strength of the chelate bonds. The equivalent conductances of the alginate sol and some derivatives have been reported [3–6]. Therefore, the present work is of particular interest in an effort to examine the stability of these gel complexes as part of a series of investigations on metal alginate complexes [7–9].

## EXPERIMENTAL PROCEDURES

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

Sodium alginate sols of various concentrations were prepared as described earlier [8]. When a metal ion electrolyte is allowed to diffuse upward, non-capillary gels are formed. This method of gel preparation is known as "ascending technique". Diffusion of the metal ion electrolyte in the downward direction leads to the formation of the capillary structure gels; this method is called the "descending technique". In the present investigation, the former technique is preferred as no pores are formed and gels of homogeneous structure are obtained. Glass columns (2 cm dia and 7 cm high) are chosen. Their internal walls are smeared evenly with a very thin layer of alginate sol and dried in an electric oven at 120° for about 20 min. After cooling, one side of the column is covered with cellophane film and filled with alginate sol of known concentration depending on the degree of hardness and the number of exchange sites required. The column is immersed in the metal ion electrolyte up to two-thirds of its height. The time necessary for the gel growth depends on the concentration of both alginate sol and metal ion electrolyte and the temperature. For example, for 1% alginate sol, the gel grew for a height of 1 cm in about 24 hr, but for 2% sol about 48–60 hr at 25° is needed. The more concentrated the alginate sol, the longer is the time necessary for the same length of growth of the gel. The formed gels are then carefully removed from the internal walls of the columns, washed several times with doubly distilled conductivity water until the washings are free of the metal ions.

### *Conductance measurements*

As shown in Fig. 1a, b, a new technique has been used to measure the specific conductance ($k$) of metal alginate gel complexes for various frequenices. It consists of an outer electrode made of a thin sheet of copper (2 cm width and 5 cm length). The inner electrode consists of thin copper tube (0.5 mm dia) of length sufficient to be inserted right in the middle of the cell parallel to the outer sheet electrode. The tip of the inner electrode was cut so as not to cause any destruction on dipping it inside the gel. The a.c. source was an R.C. generator with a wide range of frequency. A cell of such construction was found to possess a negligible capacitance. By measuring the voltage drops across the fixed pure ohmic resistance (500 ohm) $R_1$, connected in series with the cell and across the cell itself, the resistance $R_2$ of the cell can be calculated thus:

$$\frac{E_1}{E_2} = \frac{R_1}{R_2} = \frac{500}{R_2}. \tag{1}$$

Equation (1) is valid under the condition that:

$$E_{\text{total}} = E_1 + E_2 \tag{2}$$

where $E_{\text{total}}$ is the total voltage drop across the cell and the ohmic resistance, $E_1$ is the voltage drop across the ohmic resistance $R_1$ and $E_2$ is the voltage drop across the cell $R_2$. Thus, the specific resistance of the cell is given by:

$$p = \frac{2L}{2.303 \log a/b} R_2 \tag{3}$$

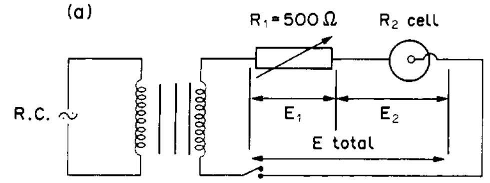


Fig. 1a. The electrical circuit used for measurement of the gel specific conductance.

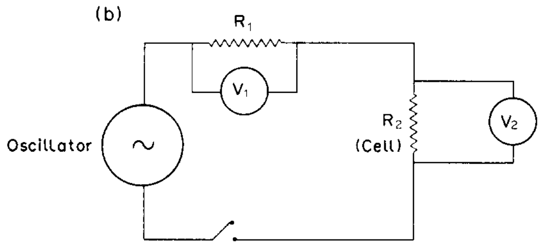


Fig. 1b. Equivalent circuit diagram; where $V_1 = E_1$ and $V_2 = E_2$.

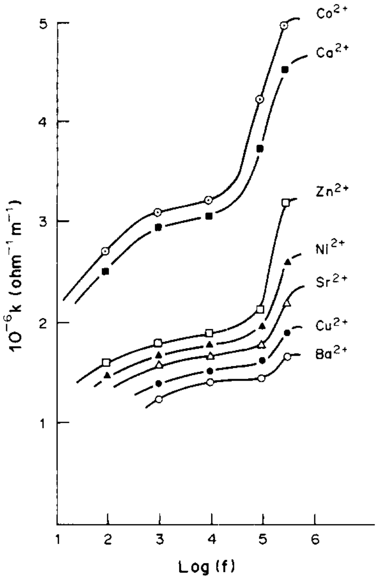


Fig. 2. Plots of log $f$ vs $k$ for divalent metal alginate gels. [Alğ] = 2% and $T = 30°$.

where $p$ is the specific resistance, $R_2$ is the measured resistance, $L$ is the length of the outer electrode (1.5 cm), a is the radius of the inner electrode (0.25 mm) and b is the radius of the outer electrode (0.75 cm). The specific conductance of metal alginate gel is given by

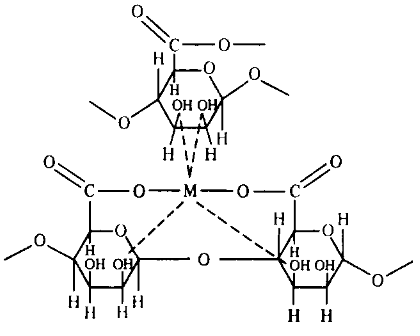
$$k = 1/p. \qquad (4)$$

## RESULTS AND DISCUSSION

The specific conductances for some divalent metal alginate gel complexes were measured for a wide range of frequencies (see Table 1). As shown in Fig. 2, plotting of the specific conductance ($k$) against the logarithm of frequency ($f$) gave curves with two inflection points. This finding indicates the presence of four regions of frequencies. At frequencies up to $\sim 10^3$ Hz, $k$ gradually increases with increasing applied frequency. At frequencies between $10^3$ and $10^5$ Hz, no appreciable change in $k$ is observed. For frequencies $10^5 \sim 10^6$ Hz, a slight increase in the applied field is accompanied by a large increase in $k$. At very high frequencies $> 10^6$ Hz a steady state is attained and the value of $k$ is not affected.

This behaviour seems to be common for all divalent metal alginate complexes. The $f$ values at which the increases in $k$ may be termed the limiting frequency ($l_f$). Every metal alginate complex is characterized by a particular $l_f$ value which depends on the strength of chelation between the metal ion and the functional groups of the macromolecular chains of the alginate polyelectrolyte.

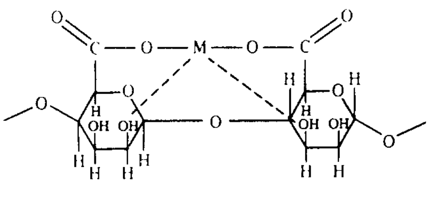
In sol-gel transformation, the $Na^+$ ions resulting from the dissociation of polyelectrolyte in aqueous solution must be replaced by an equivalent amount of divalent metal ions. The interdiffused metal ions chelate the functional groups of macromolecular chains through intermolecular (I) [10] and/or intramolecular (II) [8] mechanisms as follows:



(I)

Table 1. Specific conductances of divalent metal alginate gel complexes at 30

| Alg | Frequency (k Hz) | $10^{-5}$(K, ohm⁻¹ m⁻¹) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | $Ba^{2+}$ | $Cu^{2+}$ | $Sr^{2+}$ | $Ni^{2+}$ | $Zn^{2+}$ | $Ca^{2+}$ | $Co^{2+}$ |
| 3% | $10^3$ | 16.52 | 18.63 | 24.01 | 24.95 | 28.55 | 44.55 | 47.85 |
| | $10^4$ | 17.21 | 19.80 | 25.57 | 26.60 | 30.05 | 47.45 | 50.05 |
| | $10^6$ | 22.64 | 27.62 | 37.43 | 42.26 | 53.09 | 71.63 | 78.08 |
| 4% | $10^3$ | 24.15 | 23.30 | 32.12 | 33.43 | 36.01 | 60.14 | 64.66 |
| | $10^4$ | 25.83 | 24.70 | 34.21 | 35.61 | 37.62 | 64.05 | 67.51 |
| | $10^6$ | 32.08 | 33.95 | 49.91 | 56.52 | 65.83 | 95.03 | 102.09 |



**(II)**

where M denotes the divalent metal ions. The detailed mechanism of exchange was discussed earlier [9].

These chelates may account for changing of the specific conductance of metal alginate complexes with the applied frequency. The slight increase in $k$ observed at frequencies up to $\sim 10^3$ Hz may be attributed to the elimination of the relaxation effects resulting from the cleavage of the coordinate bonds between the metal ions and the hydroxyl groups. The frequencies at which the $k$ values increased in this region were found to vary from one metal ion to another. This fact could be attributed to different stabilities of hydroxy complexes of metal ions crosslinking the gel. Copper and barium hydroxy complexes are the most stable, while that of cobalt is the least stable [11, 12]. This is in good accord with the experimental data of conductivity increase at the lower frequencies of these metal alginate complexes.

On the other hand, the large increase in $k$ at frequencies $10^5 \sim 10^6$ Hz can be attributed to the elimination of the relaxation effects resulting from the cleavage of the ionic bonds between the metal ions and the carboxylate groups. The stronger the ionic bonds, the higher is the frequency at which the conductivity increases. Cobalt is known to have the weakest ionic bond [12, 13] and so the conductivity of its alginates starts to increase at a frequency lower than for the other alginates. The slope of the $k$-log $f$ relationship was found to vary from one metal alginate to another. The observed slope may be considered as a measure of the rate of conductance ($R_c$) which explains the electrical properties of a metal alginate gel complex. The value of $R_c$ depends on several factors such as the ionic radius, mobility and polarizability of the metal ion, and on the orientation of the macromolecular chains and solvent molecules toward the chelated metals. It is well known that the mobility of the metal ion increases with decreasing ionic radius and so the corresponding specific conductance is increased. The observed values of $R_c$ for calcium, strontium and barium metal alginate gels are in good agreement with their ionic radii which are in the order $Ca^{2+} < Sr^{2+} < Ba^{2+}$ [14]. Again, barium and copper ions have the highest polarizability [15, 16] and hence the lowest conductivity. The other metal ions such as $Ca^{2+}$ and $Co^{2+}$ possess lower polarizability [15, 16] and higher conductivity.

The orientation of the macromolecular chains and the solvent molecules toward the chelated metals may also play an important role in the electrical behaviour of these metal alginate complexes. Copper and barium are known to be well oriented in their metal alginate complexes and hence have smaller $R_c$ values and higher stabilities than cobalt and calcium of higher $R_c$ values and lower stability. The magnitude of orientation is in the order $Ba^{2+} > Cu^{2+} > Sr^{2+} > Ni^{2+} > Zn^{2+} > Ca^{2+} > Co^{2+}$ [17, 18], in good agreement with the experimental finding of decreasing specific conductance ($R_c$) and increasing the limiting frequency ($l_f$) in the same order. This means that the strength of chelation and hence the stability of the metal alginate gel complexes decreases are in the order $Co^{2+} < Ca^{2+} < Zn^{2+} < Ni^{2+} < Sr^{2+} < Cu^{2+} < Ba^{2+}$. The order of stability agrees well with that reported earlier [19, 20]. The bond energies of the oxygen–metal bonds [21] in these gel complexes also agree with the observed order of stability.

It is well known that increasing the frequency of the applied field makes the oscillation time smaller. As the oscillation time becomes more smaller than that needed for cleaving the chelated bonds, the relaxation effects due to them will disappear and then $k$ will not be affected. This is observed at the frequencies $10^3 \sim 10^5$ and $> 10^6$ Hz at which steady state equilibria are attained.

Furthermore, it is seen that $k$ increases with increasing concentration of alginate sol. This behaviour can be explained by the large number of exchange sites present in the more concentrated sols. The order with respect to the sol concentration may be deduced from the empirical relationship

$$\ln k = \ln [C]^n$$

where $C$ denotes the alginate sol and $n$ is the order. As shown in Fig. 3, plotting of $\ln k$ vs $\ln [C]$ gives good straight lines with slopes corresponding to the order of alginate sol. The order of various metal alginate complexes was calculated and found to be $0.95 \pm 0.1$ at all frequency ranges. The magnitude of the order for $Co^{2+}$, $Ni^{2+}$ and $Cu^{2+}$ alginate gel complexes was in good agreement with results [9] of a series of kinetic studies on sol-gel transformation of such gel complexes.

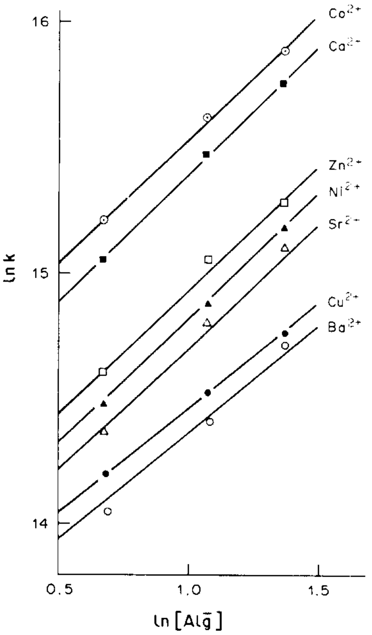


Fig. 3. Plots of ln [Alḡ] vs ln $k$ for divalent metal alginate gels. $F = 10^5$ Hz and $T = 30$ .

## CONCLUSION

The electrical properties of divalent metal alginate ionotropic gels have been examined conductimetrically. A new technique was used to measure the specific conductance of these metal gels for a wide range of frequencies. The results indicate that the electrical behaviour of the gel complexes is related to the strength of chelation between the metal ions and the functional groups of the macromolecular chains. The stronger the chelated bonds, the greater is the stability of the gel complexes. The stabilities of these metal gel complexes are in the order $Ba^{2+} > Cu^{2+} > Sr^{2+} > Ni^{2+} > Zn^{2+}Ca^{2+} > Co^{2+}$.

The order of stability is of great importance for selection of gels which may be used in "column chromatography" for the separation of metal ions from their electrolyte mixtures. Qualitative data for this separation were obtained. Further investigations are in progress to obtain quantitative results.

## REFERENCES

1. H. Thiele. *Z. Natureforeschung* **36,** 778 (1948).
2. H. Thiele. *Koll. 2.* **130,** 80 (1954).
3. R. A. A. Muzzarelli. *Natural Chelating Polymers*, 1st edn. Pergamon Press, Oxford (1973).
4. T. Takahashi and K. Kimoto. *Bull. chem. Soc. Japan* **28,** 519 (1955).
5. M. Nakayuki and S. Kawamura. *J. pharm. Soc. Japan* **84,** 346 (1964).
6. H. Harada. *Seikatsu Kagaku*, Japan **3,** 179 (1971).
7. A. Awad, El-Cheikh and R. Hassan. *Revue roum. Chim.* **24,** 563 (1979).
8. R. M. Hassan, A. Awad and Ahmed Hassan. *J. Polym. Sci.* (in press).
9. R. M. Hassan, M. H. Wahdan and Ahmed Hassan. *Eur. Polym. J.* **24,** 281 (1988).
10. R. G. Schweiger. *J. org. Chem.* **27,** 1789 (1962).
11. A. A. Grinberg and K. B. Yatsuimirski. *Bull. Acad. Sci. USSR Div. chem. Sci.* 239 (1952).
12. R. M. Mahmoud, R. Abdel-Hamid, A. A. Abdel Wahab and H. M. Salman. *Bull. Soc. chim. Belg.* **91,** 11 (1982).
13. H. Irving and R. J. P. Williams. *J. chem. Soc.* 3192 (1953).
14. A. F. Cotton and G. Wilkinson. *Advanced Inorganic Chemistry*, 3rd edn (1972).
15. B. E. Conway. *Electrochemical Data.* Elsevier, London (1952).
16. D. Dobos. *Electrochemical Data.* Elsevier, Budapest (1975).
17. H. Thiele and G. Anderson. *Kolloid Z.* **76,** 140 (1955).
18. K. Plohnke. Dipl. Arbeit, Kiel (1960).
19. R. G. Schweiger. *Kolloid Z.* **196,** 47 (1964).
20. S. Olav. *Acta chem. scand.* **19,** 329 (1965).
21. R. T. Sanderson. *Chemical Bonds and Bond Energy*, 2nd edn. Academic Press, New York (1976).