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THE MECHANISM OF ION EXCHANGE WITH ALGINIC ACID

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SUMMARY

The exchange mechanism which determines the retention capacity of alginic acid has been investigated. Chromatographic, pH, and viscosity measurements, performed with several metal ions, have permitted us to show that ion exchange is not the only mechanism but that the influence of the two vicinal hydroxyl groups on the retention capacity of alginic acid is also important.

INTRODUCTION

In previous papers[1,2] the characteristics of alginic acid as a new stationary phase for TLC and the chromatographic behavior of most elements on alginic acid thin layers were described. However, in these studies, the retaining mechanism of alginic acid for different metal ions was not investigated. Alginic acid is regarded by some workers[3,4] as a pure ion-exchanger which cross-links with carboxyl groups of different macromolecules, while SCHWEIGER[5,6] suggests that most divalent metal ions form complexes involving two carboxyl groups of one macromolecule and two vicinal hydroxyl groups of the same or another macromolecule.

Therefore we investigated the retaining mechanism of alginic acid to see whether ion-exchange is the essential parameter which determines the retention capacity of the alginic acid or whether the influence of other parameters such as the formation of chelate complexes and absorption, independent of the ionic groups of the polymer, is also important.

EXPERIMENTAL

Chromatographic studies

The chromatographic work on alginic acid was performed as described in a previous paper[1]. To prepare acetylated alginic acid thin layers, 6 g of the exchanger (D.A. = 1.7) were dispersed in 20 ml of a water–isopropanol mixture (1:1 by volume).

pH studies

Solutions. 0.1 *M* solutions, neutral or weakly acid of the following metal salts were prepared:

$Ba(NO_3)_2$, $Pb(NO_3)_2$, $Sr(NO_3)_2$, $Ca(NO_3)_2 \cdot 4H_2O$, $CuSO_4 \cdot 5H_2O$, $BeSO_4 \cdot 4H_2O$, $CoSO_4 \cdot 7H_2O$, $MgSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 7H_2O$, $MnSO_4 \cdot H_2O$, $ZnSO_4 \cdot 7H_2O$, $HgCl_2$, $AgNO_3$, $InCl_3$, $CrCl_3 \cdot 6H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, NaCl, LiCl, KCl and CsCl. Owing to the low solubility of Tl_2SO_4, an 0.05 *M* solution of this salt was employed.

The solutions were titrated according to customary analytical procedures.

Apparatus. pH measurements were performed with a Methrom Herisau Compensator E 388 pH-meter.

Method. 50 mg of alginic acid are dispersed in 10 ml of distilled water. The suspension is shaken for 1 h and the pH measured. 0.1 *M* solutions of the metal salts are added and the pH again determined after the samples have been shaken for at least 1 h. When acetylated alginic acid (D.A. = 1.7) was employed, 65 mg was weighed out in order to have the same concentration of carboxyl groups.

In the case of carboxymethylcellulose, 200 mg of the exchanger in the acid form are necessary because, as shown from curves (a) and (b) in Fig. 1, relative to 100 mg of alginic acid and 100 mg of carboxymethylcellulose, the exchange capacity of the latter is four times smaller than that of alginic acid.

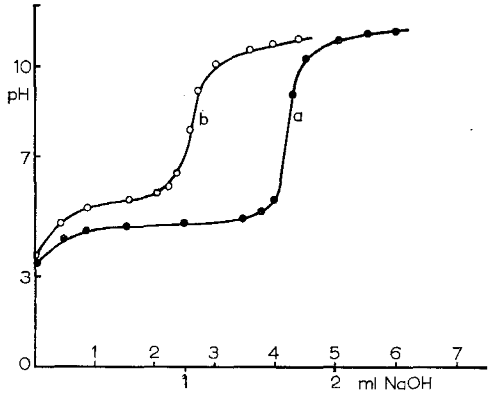


Fig. 1. Titration curves of alginic acid (a) and carboxymethylcellulose (b) with 0.1 *N* sodium hydroxide solution. The expanded scale is referred to carboxymethylcellulose.

Preparation of acetylated alginic acid

50 g of finely powdered sodium alginate are dispersed in 250 ml of 2 *M* HCl. The resulting product is separated, washed with distilled water to complete the removal of chloride ions and activated by washing twice with 250 ml of glacial acetic acid to reduce the water content to a small amount.

Activated alginic acid, glacial acetic acid (300 ml) and acetic anhydride (300 ml) are mixed in a Hobart mixer for 15 min. While mixing, 2 ml of perchloric acid (70 %) are added at such a rate that the temperature does not exceed 40°. This requires about 2 h. After a total reaction time of about 3 h, the mixture is filtered, washed with isopropyl alcohol and dried at room temperature. The yield of partially acetylated alginic acid depends on the reaction time.

Acetyl determination and preparation of ammonium acetyl alginate

The acetyl determination and the preparation of ammonium acetyl alginate were performed according to SCHWEIGER[7]. Products with a D.A. of 0.93 and 1.7 were obtained.

RESULTS AND DISCUSSION

Comparison between alginic acid and acetylated alginic acid

If alginic acid behaves as a chelating agent, its retention capacity with respect to structurally similar ion-exchangers should be greater. So alginic acid has been compared with the acetylated alginic acid (D.A. = 1.7) since the latter cannot form chelates with metal ions.

The acetylation method according to SCHWEIGER[7] is preferred since the degradation of alginic acid is reduced to a minimum.

From the R_F values, reported in Table I, it can be seen that the different ions are retained on alginic acid much more than on acetylated alginic acid. Moreover the differences between the R_F values on acetylated alginic acid are not so marked as on alginic acid, confirming that the selectivity of the latter is due to the hydroxyl groups.

Such behavior confirms the hypothesis of chelate formation by alginic acid with respect to several ions, although the influence of a steric hindrance (due to the acetyl groups) on the bond between the carboxyl groups and the metal cation cannot be excluded.

TABLE I

R_F OF SOME ELEMENTS ON ALGINIC ACID (AA) AND ACETYLATED ALGINIC ACID THIN LAYERS (AAA)
Eluent: 0.01 and 0.05 M HNO_3.

Ion	*AA*		*AAA (D.A. = 1.7)*	
	0.01 M HNO_3	*0.05 M HNO_3*	*0.01 M HNO_3*	*0.05 M HNO_3*
Ag(I)	0.07	0.26	0.39	0.80
Tl(I)	0.05	0.12	0.38	0.80
Cu(II)	0.00	0.16	0.12	0.68
Zn(II)	0.02	0.30	0.24	0.76
Ni(II)	0.03	0.30	0.25	0.77
Pb(II)	0.00	0.00	0.00	0.11
Mg(II)	0.08	0.42	0.30	0.9
Ba(II)	0.00	0.05	0.11	0.67
Ga(III)	0.00	0.06	0.00	0.41
In(III)	0.00	0.00	0.00	0.06

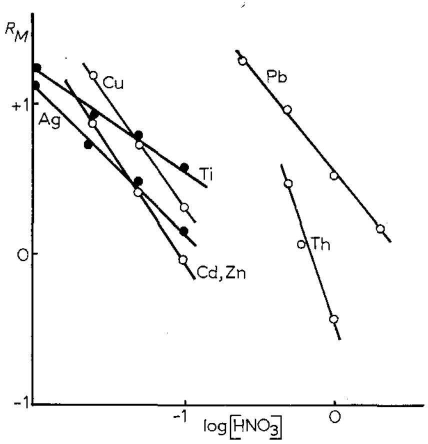
In this connection it would be interesting to know the number of carboxyl groups participating in the exchange reaction with the polyvalent cations in the case of alginic acid and acetylated alginic acid.

By applying the law of mass action to the exchange reaction: $xH_R + M^{x+} = M_R + xH^+$ we obtain, by simple considerations, the relation: $x\text{pH} = R_M + \text{const.}$ (ref. 8).

It is therefore possible to determine the number of carboxyl groups concerned in the exchange reaction through the R_M values, relative to eluents with different mineral acid concentrations.

In Figs. 2 and 3 the R_M values of several cations on alginic acid and acetylated alginic acid are plotted *vs.* the log[HNO_3] in the eluent. The R_M/pH ratio increases with increasing valency of the ion and a straight line is observed even if the straight plots can be obtained only in a particular pH range. This is the case for Ag(I) and, particularly, for Ba(II), Sr(II), Pb(II) and Tl(I). Such cations do not travel with the solvent front even for high concentration of mineral acids in the eluent and therefore reveal the presence of a sorption by the thin layer.

Sorption on cellulose ion exchangers has been reported recently by MUZZARELLI[9]. According to this author the sorption is due to the interactions of the cation with the hydroxyl groups of the macromolecule. The values reported in Table II of the slopes



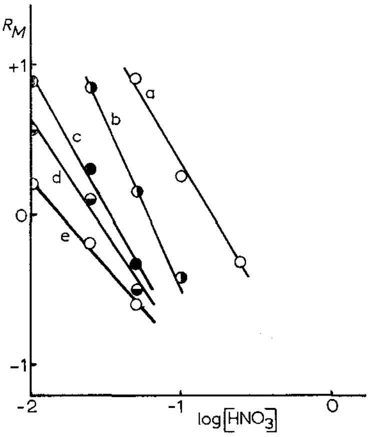


Fig. 2. R_M *vs.* log [HNO_3] in the eluent on alginic acid thin layers.

Fig. 3. R_M *vs.* log [HNO_3] in the eluent on acetylated alginic acid thin layers. (a) = Pb; (b) = Ga; (c) = Cu, Ba; (d) = Cd, Ni, Co, Zn, Ca, Sr; (e) = Ag, Tl.

TABLE II

SLOPES OF THE R_M–LOG [HNO_3] RELATIONSHIP FOR IONS OF VARIOUS IONIC CHARGES ON ALGINIC ACID (AA) AND ACETYLATED ALGINIC ACID (AAA) THIN LAYERS

Ion	*Charge*	*Slope*	
		AA	*AAA*
Ag	1	0.9	1.0
Tl	1	0.7	1.0
Pb	2	1.3	1.6
Ba	2	0.9	1.6
Sr	2	0.9	1.5
Cu	2	1.4	1.6
Cd	2	1.4	1.5
Ni	2	1.5	1.5
Co	2	1.5	1.5
Zn	2	1.5	1.5
Ca	2	1.3	1.5
Mg	2	1.4	1.4
Ga	3	2.4	2.2
In	3	2.4	n.d.
Th	4	3.0	n.d.

of the straight lines, relative to alginic acid and acetylated alginic acid, indicate a number of carboxyl groups equal to the valence of the ion. The difference between the experimental and theoretical values must be attributed, in addition to the sorption phenomena, to the formation of a pH gradient along the thin layer already observed in the case of alginic acid[1] and which is also present in the case of acetylated alginic acid.

pH measurements

On the basis of the above mentioned ion exchange reaction, when a metal salt solution is added to a suspension of alginic acid, the pH decreases and the magnitude of the decrease depends on the affinity between alginic acid and the metal ion.

We have thus decided to use the increase of the acidity, due to the ion exchange reaction, for the following purposes:

(1) to evaluate the affinity of different ions with respect to the acetylated and non-acetylated alginic acid;

(2) to see whether it is possible to correlate the data obtained in such a way with the chromatographic data;

(3) to understand the ion exchange mechanism by the comparison, under the same experimental conditions, of the data obtained on alginic acid with that on the acetylated alginic acid.

The investigation was also extended to carboxymethylcellulose, an ion exchanger widely employed in chromatography and structurally similar to the alginic acid.

The pH values, obtained after the addition of metal salt solutions to aqueous

TABLE III

pH OF AQUEOUS SUSPENSIONS OF ALGINIC ACID (AA) (INITIAL pH = 2.97), ACETYLATED ALGINIC ACID (AAA) WITH D.A. 0.93 (INITIAL pH = 3.32) AND 1.7 (INITIAL pH = 3.84) AND CARBOXYMETHYLCELLULOSE (CMC) (INITIAL pH = 3.21) AFTER THE ADDITION OF METAL SALT SOLUTIONS (MEQUIV. SALT/MEQUIV. EXCH = 1.43)

Metal salt	*AA*	*AAA (0.93)*	*AAA (1.7)*	*CMC*
$AgNO_3$	2.42	2.67	2.72	2.82
Tl_2SO_4	2.64	2.80	2.86	3.06
CsCl	2.66	2.80	2.82	2.94
KCl	2.72	2.89	—	—
NaCl	2.80	2.90	—	—
LiCl	2.90	2.90	2.91	3.06
$Pb(NO_3)_2$	2.04	2.24	2.53	2.20
$Ba(NO_3)_2$	2.20	2.48	2.77	2.56
$Sr(NO_3)_2$	2.34	2.52	2.78	2.67
$CuSO_4$	2.40	2.47	2.59	2.56
$Cd(NO_3)_2$	2.41	2.46	2.57	2.58
$Ca(NO_3)_2$	2.44	2.68	2.78	2.66
$BeSO_4$	2.60	2.74	2.76	2.88
$ZnSO_4$	2.61	2.76	2.78	2.85
$CoSO_4$	2.61	2.75	2.78	2.84
$NiSO_4$	2.62	2.76	2.78	2.84
$MnSO_4$	2.72	2.78	2.80	2.85
$MgSO_4$	2.74	2.88	2.96	2.88
$InCl_3$	1.98	2.18	2.23	2.28
$Ce(NO_3)_2$	2.12	2.36	2.46	2.54
$CrCl_3$	2.18	2.41	2.48	2.60

suspensions of samples of alginic acid, acetylated alginic acid with D.A. 0.93 and 1.7 and carboxymethylcellulose, are reported in Table III. From the above data it is possible to establish an affinity scale for the ions with respect to the ion exchangers employed (see below). Elements with pH values which differ ± 0.02 are considered to have the same affinity.

Alginic acid
(a) Ag > Tl, Cs > K > Na > Li.
(b) Pb > Ba > Sr > Cu, Cd > Ca > Be, Zn, Co, Ni > Mn, Mg.
(c) In > Ce > Cr.

Acetylated alginic acid (D.A. = 0.93).
(a) Ag > Cs, Tl > K, Na, Li.
(b) Pb > Cu, Cd, Ba > Sr > Ca > Be, Zn, Co, Ni, Mn > Mg.
(c) In > Ce > Cr.

Acetylated alginic acid (D.A. = 1.7)
(a) Ag > Cs > Tl, Li.
(b) Pb > Cu, Cd > Ba, Sr, Ca, Be, Zn, Co, Ni, Mn > Mg.
(c) In > Ce, Cr.

Carboxymethylcellulose
(a) Ag > Cs > Tl, Li.
(b) Pb > Cu, Cd, Ba > Ca, Sr > Zn, Co, Ni, Mn > Be, Mg.
(c) In > Ce > Cr.

In the case of alginic acid we can draw the conclusion that, for ions of the same group of the periodic table, the affinity for alginic acid correlates with the size of the hydrated ionic radius and decreases in the following sequence:

$$\mathrm{Cs^+ > K^+ > Na^+ > Li^+}; \qquad \mathrm{Ba^{++} > Sr^{++} > Ca^{++} > Mg^{++}}; \qquad \mathrm{Cd^{++} > Zn^{++}}$$

These results agree with those for carboxy cellulose[10]. The affinity scale for acetylated alginic acid and carboxymethylcellulose is different from that for alginic acid. On increasing the degree of acetylation the affinity scale changes and the selectivity of alginic acid with respect to several ions decreases. Such results are in agreement with the chromatographic ones.

Characteristics of metal alginates

The data reported have shown that the retention capacity of alginic acid depends, in addition to ion exchange, on other parameters among which the type of chelate involved seems to be important.

Therefore we tried to correlate the data in Table III with that given in Table IV regarding the characteristics of alginates with a variable degree of acetylation.

Univalent ions

The univalent ions do not cross-link as the viscosity measurements show. Using a Hoeppler viscosimeter, we observed no increase in the viscosity of sodium

TABLE IV

PRECIPITATION REACTIONS WITH METAL IONS[a]

Metal ion	*D.A.*		
	0	*0.93*	*1.7*
Ag(I)	+	+	—
Tl(I)	+	—	—
Cs(I)	—	—	—
Pb(II)	++	++	++
Cu(II)	++	++	++
Cd(II)	++	++	++
Ba(II)	++	++	—
Sr(II)	++	++	—
Ca(II)	++	++	—
Zn(II)	++	++	—
Co(II)	++	+	—
Ni(II)	++	+	—
Be(II)	+	+	—
Mn(II)	+	—	—
Mg(II)	—	—	—
In(III)	++	++	++
Ce(III)	++	++	++
Cr(III)	++	++	++
Th(IV)	++	++	++

[a] ++ = gelatinous precipitate; + = grainy gel; — = no reaction.

alginate solutions resulting from the addition of a thallous sulphate solution. However, unlike the alkali ions, Ag(I) and Tl(I) form insoluble alginates in some cases. Ag(I) forms a precipitate with sodium alginate and ammonium acetyl alginate with D.A. 0.93 but not with the one with D.A. 1.7, although it shows a similar affinity in both cases from the pH values reported in Table III. This behavior indicates that the presence of intramolecular chelates is still possible with alginic acid having D.A. 0.93.

Divalent ions

The divalent ions bind two carboxyl groups. For convenience such ions have been divided into three groups:

(a) Ba, Sr, Ca, Co, Ni, Zn.
(b) Pb, Cu, Cd.
(c) Mn, Mg, Be.

Group (*a*): The behavior of these ions is in agreement with the formation of intermolecular chelates as put forth by SCHWEIGER[6].

Group (*b*): The pH data and the type of precipitate obtained with these elements indicate the presence of cross-linkages between the macromolecules. Such results, which are in agreement with the measurements of viscosity performed by HAUG AND SMIDSROD[11], disagree with those of SCHWEIGER[6] for Pb(II). Furthermore, the chromatographic behavior of Cd(II), which is retained less with respect to the others, cannot be explained as it shows an affinity similar to that of Cu(II).

Group (*c*): For these elements the formation of cross-linkages is excluded. With respect to Be(II), however, the precipitates obtained with sodium alginate and ammonium acetyl alginate with D.A. 0.93 but not with D.A. 1.7, seem to indicate that the formation of basic salts[6] is not the only criterion responsible for the precipitation but it is even possible that intramolecular non-cross-linked complexes are formed.

Tri- and tetravalent ions

In the pH range, at which the chromatographic measurements have been performed, tri and tetravalent ions seem to bind respectively three and four carboxyl groups.

Therefore it is reasonable to assume that carboxyl groups of different chains are participating in the reaction; this is in agreement with the formation of gelatinous precipitates even with high acetylated alginates.

Nevertheless we must consider, in the case of ions with strongly acidic characteristics such as Al(III), Fe(III) and Sn(IV), that the formation of the corresponding alginates may be affected by the presence of hydroxylated species of these ions and that, on increasing the pH, the number of carboxyl groups participating in the reaction may decrease. This behavior is confirmed by the formation of basic alginates and by the lack of a viscosity maximum in their suspensions[6].

CONCLUSION

The chromatographic, pH and viscosity data suggest the presence of mechanisms, different from ion exchange alone, which determine the retention capacity of alginic acid.

These effects are primarily due to the presence of two vicinal hydroxyl groups, and widely influence the tendency of the various ions to coordinate these groups. While for some ions (Ba, Sr, Ca, Zn, Co and Ni) a real chelation is probable, in other cases the great influence of the hydroxyl groups is still evident. In fact, it is sufficient to block the hydroxyl groups in order to decrease the selectivity of alginic acid and to obtain an ion exchanger that does not show substantial differences from exchangers with similar characteristics, such as carboxymethylcellulose. Thus it seems justified that alginic acid should be considered as a new stationary phase in TLC, particularly suitable for analytical purposes.

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