Binding of Aluminum and Aluminum Alizarin to Alginate

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ABSTRACT: Competitive binding equilibria between the trivalent metal ion Al^{3+} and lower valence ions were studied by dialysis of sodium alginate against $Al_2(SO_4)_3$, $NaAl(SO_4)_2$, $Al_2(SO_4)_3 + Na_2SO_4$, and $Al_2(SO_4)_3 + CaSO_4$ solutions of various concentrations. The results were interpreted in terms of a divalent ion binding site model proposed in ref 2. The alginate sample was low in poly(guluronate) content and high in poly(mannuronate) and alternating copolymer. The $[COO^-]/[Al^{3+}]_b$ ratio approaches 2 at high $Al_2(SO_4)_3$ concentrations, in accord with the divalent site model. The displacement of Na^+ by Al^{3+} is described by $K_{Na}{}^{Al} = [Al^{3+}]_b[Na^+]_x{}^2/[Al^{3+}]_x[Na^+]_b{}^2$, which is understandable if the binding of one Al^{3+} to the polymer disrupts two Na^+-bound sites. Competition between Ca^{2+} and Al^{3+} seems best described by $K_{Ca}{}^{Al} = [Al^{3+}]_b[Ca^{2+}]_x/[Al^{3+}]_x[Ca^{2+}]_b$, where a majority of sites favor Al^{3+} over Ca^{2+}, but a minority, possibly poly(guluronate), favor Ca^{2+} over Al^{3+}. Al^{3+}, bound to alginate, forms distinct complexes with one and 2 mol of the monovalent, bidentate ligand alizarin, but not with three, which is again best reconciled with a site model.

Alginate is an algal polysaccharide and copolymer of mannuronic and guluronic acids which is well known for its metal ion binding properties, and their effects on solution viscosity and gelation. In a recent paper, we interpreted the results of a study of binding competition between Na^+ and divalent metal ions (M^{2+}) to indicate the presence of distinct divalent ion binding sites along the polymer chain.[2] Construction of models suggested that these sites were composed of carboxylate groups of two adjacent mannuronic (Man) or guluronic (Gul) residues and the pyranoside ring oxygen between them. The existence of definite binding sites could go far toward explaining the well-known selectivity of alginate for certain divalent metal ions.[3–5]

It was further learned that binding of divalent ions at these sites is not sufficient to gel alginate solutions; gelation is rather due to cross-linking between carboxylate groups not composing definite divalent ion binding sites.[2] At least 90% of the carboxylate groups could be bound with divalent ions without significant gelation, and the divalent ion Mg^{2+}, though it binds well enough to the polymer, does not cause gelation at all in aqueous solution.[6]

The hypothesis of divalent ion binding sites implies certain consequences when trivalent ions (M^{3+}) are bound to alginate. If it is assumed that one M^{3+} will fit into each site, the bound metal content of the polymer should saturate at one for every two carboxylate groups, instead of one for every three, as would be expected from simple ion exchange. This would tend to reverse the charge on the polyelectrolyte, unless compensated by binding of by-ions to the metal. In either case, the bound metal would retain the capacity, through its third valence uncompensated by the polymer, to bind extraneous anionic ligands including monovalent, bidentate chelating agents. We have observed this capacity in gelled alginates with Fe^{3+} and CNS^-, with Cr^{3+} and aurin tricarboxylic acid or alizarin (1,2-dihydroxyanthraquinone), and with Al^{3+} and alizarin, purpurin (1,2,4-trihydroxyanthraquinone), 8-hydroxyquinoline, or hypericin.

We also found that the exchange equilibrium between Na^+ and divalent ions was better expressed by a constant $K_{Na}{}^{M} = [M^{2+}]_b[Na^+]_x/[M^{2+}]_x[Na^+]_b$, where the subscripts b and x refer to bound and free (external phase) ion concentrations, than by the quantity $Q_{12} = [M^{2+}]_b[Na^+]_x{}^2/[M^{2+}]_x[Na^+]_b{}^2$ usually employed.[2] Equilibrium between Na^+ and trivalent ions would analogously be expressed by $Q_1 = [M^{3+}]_b[Na^+]_x/[M^{3+}]_x[Na^+]_b$, if one Al^{3+} ion displaces one Na^+ ions from a site, rather than by $Q_3 = [M^{3+}]_b[Na^+]_x{}^3/[M^{3+}]_x[Na^+]_b{}^3$ expected on the basis of electroneutrality.

Finally, since each M^{3+} bound to a divalent ion binding site would be a potential locus for cross-linking, we might expect a structure and consistency of gels different from those formed with divalent metals. In this regard, Thiele and Hallich described aluminum alginate gels as more turbid and fragile than those of divalent metals.[7]

The only quantitative study of competitive ion binding to alginate involving trivalent ions to come to our attention is that of Lunde et al.[8] They found that the selectivity of polyguluronate, and to a lesser extent that of polymannuronate, for rare earth ions depended on the ionic radius, maximizing at about 0.95 Å. This suggested that more than simple electrostatic binding was involved. Dolmatova and Panteleeva found that the uptake of trivalent ions by alginic acid decreased in the order $Fe^{3+} > Ce^{3+} > Y^{3+}$.[9] Cozzi et al. have compared R_f values for a number of trivalent ions on alginic acid thin layers.[10,11] Mongar and Wassermann followed the exchange of Ca for Al in alginate fibers.[12]

We decided to examine in detail the binding and exchange behavior of one trivalent ion, Al^{3+}, on alginate, and to try to determine whether the predictions of the divalent ion site binding model would be fulfilled, or whether another basis of description would be more appropriate. Aluminum is perhaps not the ideal metal for such work, because it hydrolyzes at a pH (ca. 5) that is within the useful range for alginate solutions,[13] and it also is known to form stable dimeric ions in solution.[14,15] However, Al is the trivalent metal most often encountered in patented applications of alginate, such as in fibers,[16] textile finishes,[17,18] adhesives,[19] and surgical dressings.[20] The use of alum in the preparation of kelp for pickles is also probably related to the gelling property of the metal.[21] It seems appropriate, therefore, to attempt at least to account for the binding of Al^{3+} within the context of a model.

We have performed the following series of competitive metal ion binding dialysis experiments. (I) Sodium alginate was dialyzed against a series of concentrations of $Al_2(SO_4)_3$ solution, in order to determine the maximum Al content of the polymer. (II) Sodium alginate was dialyzed against a series of concentrations of $NaAl(SO_4)_2$ solutions, to determine the ionic composition of the polymer at a fixed Na^+/Al^{3+} ratio but increasing salt concentration. (III) Sodium alginate was dialyzed against a fixed $Al_2(SO_4)_3$ concentration in a series of Na_2SO_4 concentrations, in order to determine the equilibrium constant for displacement of Na^+ from alginate by Al^{3+}. (IV) Sodium alginate was dialyzed against $Al_2(SO_4)_3$ and $CaSO_4$ in solution together at different ratios, in order to determine the form of the equilibrium constant for competition between Al^{3+} and a divalent metal ion.

In addition to these series, and in order to demonstrate the

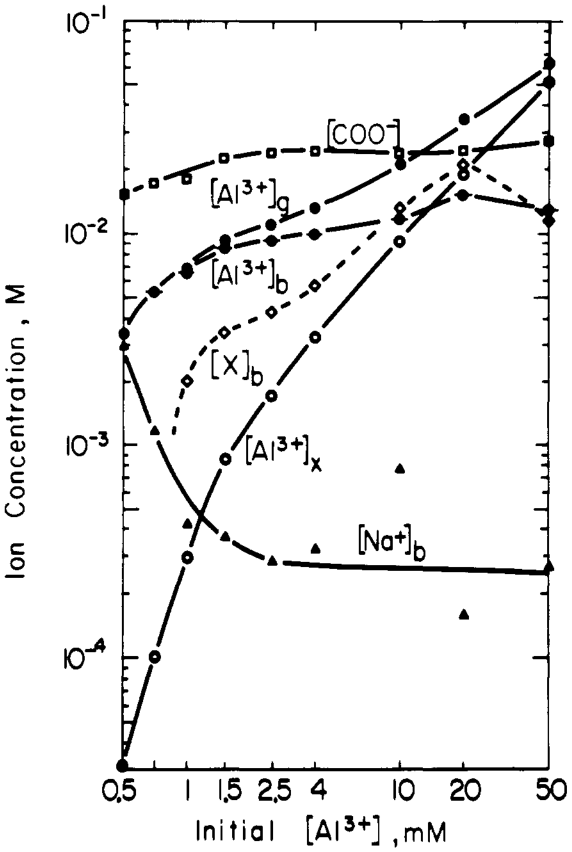

Figure 1. Series I: Equilibrium dialysis of sodium alginate against $Al_2(SO_4)_3$ solutions. Final ion concentrations plotted against initial $[Al^{3+}]$ (based on total volume of system, 100 ml). $[X^-]_b = 3[Al^{3+}]_b + [Na^+]_b - [COO^-]$. $[COO^-]$ calculated from polymer phase or gel volume, and initial alginate concentration (1.95×10^{-2} N).

residual binding capacity of Al^{3+} bound to alginate, we have examined the formation of complexes of alizarin with Al alginate in solution and as a gel. Although Al alizarin has long been regarded as a classic example of a complex between a metal and a bidentate ligand, it was dismaying to find almost no reliable, quantitative information in the literature about its visible spectroscopic properties, or even about its stoichiometry in solution. Some data on alizarin and aluminum alizarin complexes in solution without alginate are therefore reported also.

Experimental Section

For better comparison with previous results, the same sample of sodium alginate was used as before, a commercial material with (Man)/(Gul) = 2.0–2.1, and block distribution of 46% poly(Man), 18% poly(Gul), and 35% alternating copolymer, as very kindly determined for us by Dr. Olav Smidsrϕd. The alginate was dialyzed until free of salt, brought up to pH 7 with NaOH, and made up to a 1.95×10^{-2} N stock solution with triply distilled water. The carboxylate concentration was determined by titration.[2] Alginate titrates almost as a monocarboxylic acid, and at pH 7 is almost entirely in the carboxylate form.[22]

Sodium aluminum sulfate, $NaAl(SO_4)_2 \cdot 12H_2O$, was prepared by crystallization from a solution equimolar in Na_2SO_4 and $Al_2(SO_4)_3$, and the composition checked by analysis.

After some preliminary spectral work, a sample of our commercial alizarin was chromatographed on a column of polycaprolactam (Macherey, Nagel and Co. Polyamid-SC 6) in ethanol with a trace of acetic acid to suppress ionization. The leading brown band was eluted, precipitated with two volumes of water, and reprecipitated from ammoniacal ethanol with acetic acid. The crystals were dissolved in water with the aid of tetraethylammonium (TEA) hydroxide to prepare a stock solution, 1.256×10^{-3} M.

Stock solutions of TEA aluminate, 1.00×10^{-3} M, adjusted to pH 9.3, and a buffer solution of ethanolamine sulfate, 0.1 M, pH 9.3, were also prepared.

Table I
Dialysis of Sodium Alginate Against $Al_2(SO_4)_3$ Solutions[a]

Init $[Al^{3+}]$, $\times 10^{-3}$ M	Gel wt,[b] g	$[COO^-]/[Al^{3+}]_b$	$[Na^+]_b/[COO^-]$	$[X^-]_b$[c]$/[Al^{3+}]_b$
0.5	12.84	4.52	0.192	−0.65
0.7	11.32	3.22	0.068	0
1.0	10.81	2.76	0.024	+0.31
1.5	8.66	2.65	0.016	0.40
2.5	8.23	2.56	0.012	0.465
4.0	8.09	2.46	0.013	0.57
10	8.30	2.04	0.033	1.11
20	8.10	1.62[d]	0.007	1.40
50	7.2	2.14	0.010	0.89

[a] 10 ml of sodium alginate solution, 1.95×10^{-2} N in $[COO^-]$, dialyzed against 90 ml of $Al_2(SO_4)_3$ solution for 4 days at 20.0 °C. Initial $[Al^{3+}]$ based on total volume (100 ml). [b] Weight of polymer phase until gelation complete, at 1.5×10^{-3} M initial $[Al^{3+}]$. [c] $[X^-]_b = 3[Al^{3+}]_b + [Na^+]_b - [COO^-]$. [d] Al content of gel appears to be high; see Figure 1.

In series I–IV, 10 ml of sodium alginate stock solution in a bag of dialysis tubing was dialyzed against 90 ml of the appropriate external phase in a 20.0 °C bath for at least 4 days. The gel within the bag, or the contents of the bag if a firm gel had not formed, was weighed and treated with 0.2 M $HClO_4$ to extract metal ions. After filtration and rinsing with 0.002 M $HClO_4$, the filtrates were diluted to a 50-ml stock solution. This, and the external phase, were analyzed for ion content.

Aluminum was determined by the Solochrome Cyanine R method, standardized against $Al_2(SO_4)_3$ solutions.[23a]

Sodium was determined by atomic absorption spectroscopy in series I, with an average recovery from the two phases within 1% of input. In series II, sodium was measured both by atomic absorption spectroscopy and by a Corning Na electrode. Differences between gel and external phases, determined by the two methods, agreed reasonably well, but atomic absorption recoveries averaged about 6% high, and electrode recoveries were 4% low. An average of the two determinations was usually employed for further calculation.

Calcium in series IV was determined by atomic absorption spectroscopy, with La_2O_3 added to suppress interference by Al.

Sulfate in Series I and II was determined by turbidimetry.[23b] In previous work,[2] where Cl^- was the principal by-ion, little or no difference between the phases was found, and now little was expected with SO_4^{2-}. In series II, analyses of the external phases were quite consistent and averaged 1.2% below the input SO_4^{2-}, but the gel extracts gave unreasonably low values which suggested some kind of interference with the method such as sequestration of SO_4^{2-} by the gel. In series I, external phase concentrations were somewhat high. The sulfate analysis was felt not to be always reliable, but the consistent recovery of SO_4^{2-} from the external phase indicated little retention by the polymer, at least at low salt concentration.

Bound ion concentrations, $[Al^{3+}]_b$, $[Na^+]_b$, and $[Ca^{2+}]_b$, were calculated as the differences between the concentrations in the polymer phase or gel, $[Al^{3+}]_g$, $[Na^+]_g$, and $[Ce^{2+}]_g$, and those in the external phase, $[Al^{3+}]_x$, $[Na^+]_x$, and $[Ca^{2+}]_x$.

The spectra of alizarin, and of Al complexes with alizarin and Solochrome Cyanine R, were recorded on a Cary 14 Spectrophotometer.

Results

Series I. Ion concentrations are plotted in Figure 1; some ratios of them, and weights of polymer phase or gel, are listed in Table I.

The polymer phase appears entirely gelled at 1.5×10^{-3} M initial $[Al^{3+}]$. In contrast to the results with divalent ions, where the gel shrank to about 25% of the original polymer volume, the gel shrinks only to 70–80% of its original volume with Al^{3+}. This probably reflects not a lesser tendency for Al^{3+} to cross-link, but the much larger number of potential cross-linking sites, as already pointed out. The rodlike macromolecules of alginate are not obliged to move very far in order to be bound together.

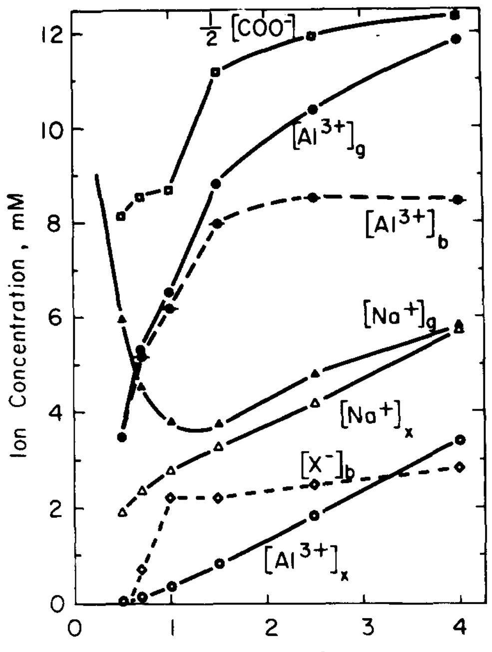

Figure 2. Series II: Equilibrium dialysis of sodium alginate against $NaAl(SO_4)_2$ solutions. Final ion concentrations plotted against initial added salt concentrations, based on total volume of system, 100 ml. Note gel formation and Na^+ expulsion from the polymer between 1.0 and 1.5×10^{-3} M $NaAl(SO_4)_2$.

Table II
Dialysis of Sodium Alginate Against $NaAl(SO_4)_2$ Solutions[a]

Init $[Al^{3+}]$, $\times 10^{-3}$ M	Gel wt, g	$[COO^-]/[Al^{3+}]_b$	$[Na^+]_b$[b]/$[COO^-]$	$[X^-]_b/[Al^{3+}]_b$
0.5	12.03	4.75	0.258	−0.53
0.7	11.46	3.30	0.140	+0.14
1.0	11.20	2.82	0.063	0.36
1.5	8.74	2.80	0.026	0.27
2.5	8.18	2.80	0.033	0.29
4.0	7.88	2.93	0.005	0.33

[a] 10 ml of 1.95×10^{-2} N sodium alginate dialyzed against 90 ml of $NaAl(SO_4)_2$ at 20.0 °C. Initial $[Al^{3+}]$ based on 100 ml of total volume. [b] $[Na^+]_b$ from average of electrode and atomic absorption spectroscopy values.

Nearly all Al^{3+} added is bound until gel formation is complete, which occurs when $[COO^-]/[Al^{3+}]_b \cong 3$. Thereafter, the amount of Al^{3+} bound increases slowly until $[COO^-]/[Al^{3+}]_b$ approximates 2.

The bound sodium content of the gel quickly falls to about 1% of the carboxylate content as gel formation becomes complete, and thereafter remains more or less constant. This contrasts with the results for divalent metal ions, where $[Na^+]_b$ could not be reduced below about 4% even at high $[M^{2+}]_x$. It seems that Al^{3+} is more successful than divalent metal ions in expelling Na^+ from an alginate gel.

The law of electroneutrality must apply to the bound ions in the polymer phase as well as to the external phase. It is thereby seen that an apparent bound by-ion concentration increases as $[Al^{3+}]_b$ increases, where the former is designated $[X^-]_b$ and calculated according to eq 1.

$$[X^-]_b = 3[Al^{3+}]_b + [Na^+]_b - [COO^-] \qquad (1)$$

$[X^-]_b$ is also plotted in Figure 1. At the lowest salt concentration, $[X^-]_b$ is negative, which is probably explained by a Donnan exclusion of SO_4^{2-} (i.e., $[SO_4^{2-}]_b = [SO_4^{2-}]_g - [SO_4^{2-}]_x < 0$). At a salt concentration large enough to gel the polymer phase, $[X^-]_b = 0.4\ [Al^{3+}]_b$, and at higher concentrations, as $[COO^-]/[Al^{3+}]_b \rightarrow 2$, $[X^-]_b/[Al^{3+}]_b \rightarrow 1$. There was no counterpart to this bound by-ion in the divalent ion gels. $[X^-]_b$ may be sulfate at high salt concentrations, though sulfate analyses do not support this idea, but it is more likely that bound Al^{3+} is hydrolyzed, and that X^- is OH^-. It is interesting to recall that in an alginate gel formed by precipitation with a solution of $AlCl_3$, Schweiger found a $[COO^-]/[Al^{3+}]_b$ ratio of 2.175, and suggested that a basic salt might have been formed.[24]

Series II. Ion concentrations are plotted in Figure 2, and their ratios are listed in Table II.

Again, the polymer phase appears completely gelled at 1.5×10^{-3} M initial $[Al^{3+}]$, and the size of the gel does not change much thereafter. The bound ion concentrations also stabilize at that point, and their values approximate those at the lower salt concentrations in series I. The $[COO^-]/[Al^{3+}]_b$ ratio of 2.80 and $[X^-]_b/[Al^{3+}]_b$ ratio of about 0.3 suggests that about ¼ of the bound Al^{3+} is hydrolyzed.

Series III. Ion concentrations are plotted in Figure 3, and

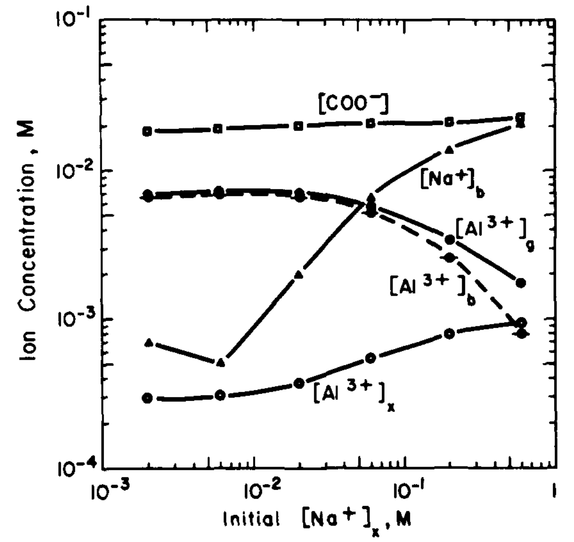

Figure 3. Series III: Equilibrium dialysis of sodium alginate against 1.00×10^{-3} M $[Al^{3+}]$ and excess Na_2SO_4. Final ion concentrations plotted against initial added $[Na^+]_x$. Polymer phase incompletely gelled, shrinks somewhat with increased external ionic concentration.

Table III
Equilibrium Quotients for Competition between Na^+ and Al^{3+} on Alginate[a]

$[Na^+]$ added, M	$[Al^{3+}]_b/[Al^{3+}]_x$	$[Na^+]_b$[b]/$[Na^+]_x$	Q_1[c]	Q_2	Q_3
2×10^{-3}	22.2	0.18	123	686	3 810
6×10^{-3}	22.4	0.063	356	5640	89 500
2×10^{-2}	18.0	0.091	198	2170	23 900
6×10^{-2}	9.52	0.105	91	864	8 220
2×10^{-1}	3.31	0.067	49.5	738	11 000
6×10^{-1}	0.85	0.034	25	735	21 600

[a] 10 ml of sodium alginate, 1.95×10^{-2} N, dialyzed against 1.00×10^{-3} M Al^{3+} as sulfate and added Na^+ as sulfate at the listed concentrations (based on total volume of 100 ml). [b] $[Na^+]_b = [COO^-] - 2.69[Al^{3+}]_b$. [c] $Q_i = [Al^{3+}]_b[Na^+]_x^{\,i}/[Al^{3+}]_x \cdot [Na^+]_b^{\,i}$.

Table IV
Equilibrium Quotients for Displacement of Ca^{2+} on Alginate by Al^{3+} [a]

Init conc $\times 10^{-3}$ M		Gel	$(2[Al^{3+}]_b + 2[Ca^{2+}]_b)$[b]/	$[Al^{3+}]_b/$	$[Ca^{2+}]_b/$			
$[Al^{3+}]$	$[Ca^{2+}]$	wt, g	$[COO^-]$	$[Al^{3+}]_x$	$[Ca^{2+}]_x$	Q_{11}[c]	Q_{23}	Q_{12}
0.5	1.5	6.37	0.84	31.4	7.22	4.34	2.64	0.60
1.0	2.0	5.34	0.86	17.1	3.75	4.55	5.54	1.22
1.0	1.0	5.74	0.88	24.8	5.29	4.69	4.15	0.89
2.0	1.0	5.48	0.82	8.28	3.39	2.43	1.76	0.72
1.5	0.5	6.92	0.82	11.4	4.33	2.63	1.60	0.61

[a] 10 ml of 1.95×10^{-2} N sodium alginate dialyzed against $Al_2(SO_4)_3$ plus $CaSO_4$ at initial concentrations listed (based on 100 ml total volume). Data are tabulated in order of increasing Al^{3+} mole fraction. [b] This quantity would be the fraction of sites occupied, according to the divalent ion binding site model. [c] $Q_{ij} = [Al^{3+}]_b{}^i[Ca^{2+}]_x{}^j/[Al^{3+}]_x{}^iCa^{2+}]_b{}^j$.

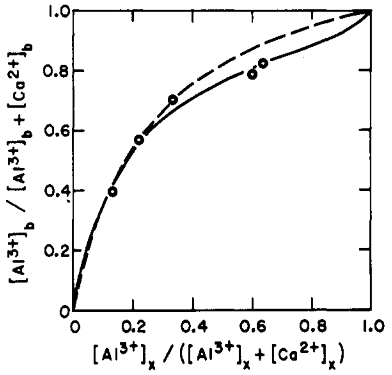

Figure 4. Series IV: Equilibrium dialysis of sodium alginate against $Al_2(SO_4)_3$ plus $CaSO_4$. Mole fraction of bound Al^{3+} plotted against mole fraction of free Al^{3+}. Dashed curve: theoretical dependence for $[Al^{3+}]_b[Ca^{2+}]_x/[Al^{3+}]_x[Ca^{2+}]_b = 4.55$. Solid curve: theoretical dependence for two kinds of sites with different K's; see text.

ion ratios listed in Table III. Only at the three highest Na_2SO_4 concentrations is very much Al^{3+} kept from binding to alginate; therefore, equilibrium constants are significant only when calculated from these data. Except at the highest $[Na^+]_x$ there was a loose gelling of the polymer phase.

Measurement by difference of $[Na^+]_b$ in solutions of such high Na^+ content was not attempted. Instead, $[Na^+]_b$ was calculated from $[COO^-]$ and $[Al^{3+}]_b$, but to do so requires an estimation of $[X^-]_b$. The most nearly comparable values of $[X^-]_b/[Al^{3+}]_b$ are probably those at high ionic strength in Table II. Accordingly, $[X^-]_b/[Al^{3+}]_b$ was assumed equal to 0.31 and $[Na^+]_b$ calculated by eq 2.

$$[Na^+]_b = [COO^-] - 2.69[Al^{3+}]_b \qquad (2)$$

Of the quotients calculated in Table III, Q_2 is most nearly constant at high salt concentration. The equilibrium constant $K_{Na}{}^{Al}$ for competition between Al^{3+} and Na^+ for alginate therefore is best formulated as if one Al^{3+} displaces two Na^+ from the polymer, as in eq 3.

$$K_{Na}{}^{Al} = Q_2 \equiv \frac{[Al^{3+}]_b[Na^+]_x{}^2}{[Al^{3+}]_x[Na^+]_b{}^2} \cong 780 \qquad (3)$$

This result is not sensitive to the value of the numerical factor estimating $[X^-]_b$ and is in accord with the simple expectations of neither the site binding model nor the electroneutrality representation.

Series IV. Data for competition between Al^{3+} and Ca^{2+} are listed in Table IV in order of increasing initial mole fraction of Al^{3+}. Enough of each metal was always present to saturate the polymer so that the results would not be falsified by insufficiency of one or the other ion. The gel weights were all smaller than those obtained with Al^{3+} alone, as though binding of Ca^{2+} were primarily responsible for concentration of the gel. The fourth column represents the fraction of sites occupied, on the assumption of one metal ion for every two COO^-. This fraction appears quite constant, but may decrease slightly as the mole fraction of bound Al^{3+} increases. None of the quotients tabulated is an entirely satisfactory equilibrium constant, though Q_{11} is nearly constant at the lower Al^{3+} mole fractions.

The nature of the situation is better portrayed in Figure 4, where the mole fraction of bound Al^{3+} is plotted against the mole fraction of free Al^{3+}. It appears that the displacement of Ca^{2+} by Al^{3+} could be represented by eq 4

$$K_{Ca}{}^{Al} = [Al^{3+}]_b[Ca^{2+}]_x/[Al^{3+}]_x[Ca^{2+}]_b \qquad (4)$$

except that at high Al^{3+} loading it becomes difficult to add more. It is as though a majority of sites favor Al^{3+} over Ca^{2+} but a minority favor Ca^{2+} over Al^{3+}. The solid curve in Figure 4, calculated with $K_{Ca}{}^{Al} = 6$ for 87% of the sites and $K_{Ca}{}^{Al} = 0.15$ for 13%, fits the data best of a number of similar curves. Considerable variation in the parameters still permits fair representation of the data, but the conclusion remains that there is a difference in ion selectivity among the sites of the polymer.

Alizarin. The un-ionized form of this dye is soluble in ethanol but not in water. The monoanion is present in weakly basic solution, and is characterized by a broad band in the visible, peaking at 524 nm in water, and 542 nm in 90% ethanol. In strong base (e.g. 0.1 M NaOH) the dianion is recognized by its blue color and structured spectrum of two peaks and a shoulder. Absorptivities are listed in Table V; the only literature values with which to compare them are those of Morton and Earlam.[25]

Reaction of $AlCl_3$ with the alizarin monoanion precipitates the 3:1 complex, $Al(aliz)_3$, out of neutral aqueous solution.[26] However, Biryuk et al. found only the 2:1 complex in weakly acidic 40% ethanol.[27] When we added aluminate to alizarin monoanion (pH >9), spectral changes marking complex formation were practically complete at $[aliz]/[Al^{3+}] = 3$. The formation of the presumed 3:1 complex is marked not so much by displacement of the peak as by narrowing of the band and intensification of peak absorptivity. The most characteristic change is in the intensity of the 325-nm band and in its ratio to the peak intensity in the visible, $\epsilon_{325}/\epsilon_m$.

The 3:1 complex appears rather stable to dissociation into lower complexes, but on increasing the excess of Al^{3+}, their formation is indicated by the gradual shift of the band to shorter wavelengths and increase in $\epsilon_{325}/\epsilon_m$. Table V includes spectral data for complexes at three $[Al^{3+}]/[aliz]$ ratios. We have other, less quantitative data, suggesting that in 90%

Table V
Spectral Data for Alizarin and Aluminum Alizarin Complexes[a]

Substance	Medium	λ_m, nm	ϵ_m, M^{-1} cm^{-1}	ϵ_{325}, M^{-1} cm^{-1}	$\epsilon_{325}/\epsilon_m$
Alizarin, un-ionized	90% ethanol + acetic acid	434	5 700[b]	3110	0.55
Monoanion	Water pH 9.3	524	7 630	9760	1.28
Dianion	NaOH soln	567, 609	14 900,[b] 12 900	5080	0.32
[Al^{3+}]/[aliz]					
3.5	pH 9.3[c]	521.5	9 600	4700	0.49
30	pH 9.3	511	7 800	6700	0.86
120	pH 9.3	503	7 400	7500	1.01

[a] Alizarin concentrations [aliz] ca. 10^{-4} M or less. Absorptivities of Al complexes based on alizarin concentration. [b] Morton and Earlam reported 6160 for the neutral molecule and 16 600 at 564 for the dianion in 1% NaOH.[25] [c] A pH ≥9.3 was needed to keep aluminate in solution for preparation of the complex.

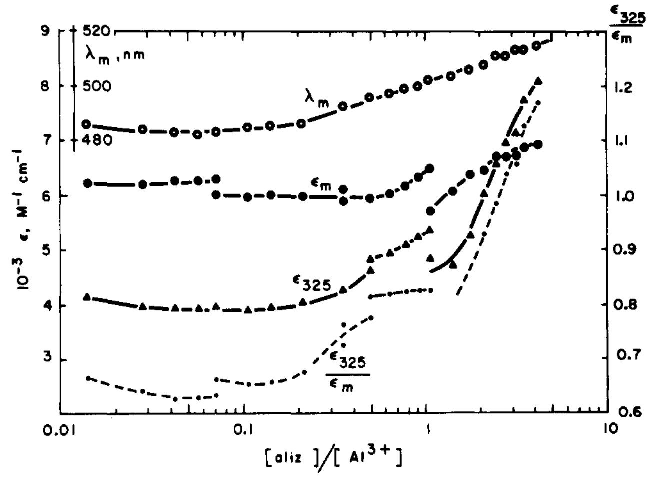

Figure 5. Addition of alizarin to a solution of aluminum alginate, $[Al^{3+}]_b/[COO^-] = 0.086$. Position of visible band peak, λ_m, its molar absorptivity ϵ_m and that at 325 nm, ϵ_{325}, plotted against the left ordinate scales. The ratio $\epsilon_{325}/\epsilon_m$ (dashed line) is plotted against the right ordinate scale. Apparent discontinuities in ϵ occur on changing from 10 cm to 2 cm path length cells, from 2 to 1 cm, and from 1 to 0.1 cm. At $[aliz]/[Al^{3+}] = 0.35$ the pH was readjusted from 6.7 to 5.7.

ethanol a 2:1 complex (515 nm) predominates, in general agreement with Biryuk et al.[27]

When alizarin is added in ethanol to an aluminum alginate gel, the gel takes on the bright red color of an aluminum alizarin complex. The color is not washed from the gel by water. Although this is evidence of a complex between alizarin and Al^{3+} bound to alginate, it does not establish how much Al and alizarin are involved. We have attempted to find a quantitative relation between these amounts.

In one set of experiments, aluminum alginate was prepared by dialysis, washed, and then dialyzed against amounts of alizarin monoanion in amounts 0.2, 0.4, 1, and 2 times that of Al, in ethanolamine buffer with the pH maintained >9.3. The polymer and outer phases were examined spectroscopically. The results indicated a lack of complete equilibration. At the low alizarin concentration, the outer phase contained a small amount of an Al complex (505 nm, absorbance ratio $\rho_{325}\rho_{505} = 1.06$), the polymer phase was virtually colorless, and the rest of the alizarin was in or on the dialysis tubing itself, apparently in the form of an Al complex (508 nm, $\rho_{325}/\rho_{508} = 1.15$). At the largest alizarin concentration, the outer phase contained mostly alizarin monoanion, the dialysis tubing was red but not as much as before, and the polymer phase was also red (512 nm). The polymer phase contained some gel, but about 80% of the alizarin complex passed through a medium sintered glass filter, which showed it to be in the soluble polymer fraction. At intermediate alizarin concentrations, intermediate results were obtained.

This set of experiments showed that amounts of alizarin comparable to those of Al were bound to alginate, but the large retention of dye in the dialysis membrane, apparently in an Al complex form, made it difficult to analyze the system further.

In another approach, a sample of alginate was gelled with excess Al^{3+}, and washed until excess Al^{3+} was removed, at which point $[COO^-]/[Al^{3+}]_b = 2.19$. The gel was then permeated with ethanol, and a solution of alizarin in that solvent added. The alizarin taken up amounted to only 8% of the Al^{3+} bound, but the complex so formed absorbed at the unusually short wavelength of 482 nm.

Finally, a solution of aluminum alginate was prepared without dialysis by adding aluminate to sodium alginate with rapid stirring (2.53×10^{-3} N alginate, $[Al^{3+}]/[COO^-] = 0.086$) and lowering the pH to 5.7 with HCl. Alizarin monoanion solution was added in amounts from 0.014 to 4.2 times that of the Al^{3+} present, and the visible spectrum recorded. The position of the visible band peak, the molar absorptivities at that peak and at 325 nm, and their ratio are plotted in Figure 5. Difference spectra were also calculated as an aid to interpretation.

The first complex formed as alizarin is added absorbs at 484 nm, ϵ_m 6000 and $\epsilon_{325}/\epsilon_m \cong 0.65$. When $[aliz]/[Al^{3+}] > 0.2$, the band begins a gradual shift to longer wavelengths, and the absorptivities to larger values. In the range $0.4 \leq [aliz]/[Al^{3+}] \leq 1.0$, the peaks of the difference spectra are near 508 nm, and the differential molar absorptivities approach 7600 M^{-1} cm^{-1}. Above $[aliz]/[Al^{3+}] = 2$ (where λ_m 508 nm) the 325-nm band increases rapidly, and the peak of the difference spectrum appears at ca. 525 nm.

Without Al^{3+}, there is no interaction between alizarin and alginate, and un-ionized alizarin precipitates at pH ~6.

We interpret these changes as indicating first, the formation of a 1:1 complex Al $(aliz)^{2+}$ bound to alginate (484 nm), then a 2:1 complex (508 nm, *ca.* 7600 M^{-1} cm^{-1}, $\epsilon_{325}/\epsilon_m \simeq 0.85$). Additional alizarin remains as the monoanion ($\lambda_m \simeq 525$ nm, $\epsilon_{325}/\epsilon_m > 1$) in the now weakly basic solution instead of combining with bound $Al(aliz)_2{}^+$ to form the 3:1 complex.

The spectrum of the presumed 1:1 complex closely resembles that of alizarin of aluminum alginate gel in ethanol, and the presumed 2:1 complex resembles that seen in the equilibrium dialysis experiments, and of alizarin in the presence of a large excess of Al^{3+} (Table V). It appears, therefore, that Al^{3+} can combine with 1 or 2 mol of alizarin and still remain bound to alginate, presumably as the hexacoordinated, anionic species $[alginate(COO^-)_2Al(aliz)_2]^-$.

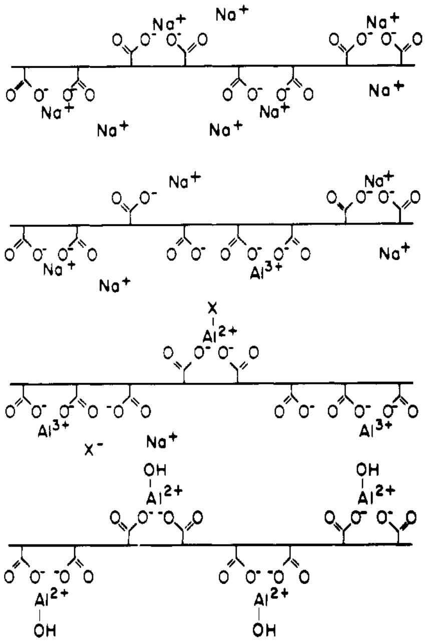

Figure 6. Schematic representations of the state of alginate during replacement of Na^+ by Al^{3+}. From top: (a) sodium alginate, with one Na^+ occupying each site, another in ion atmosphere. (b) At low concentrations of Al^{3+}, Na^+ is released from two sites for each Al^{3+} bound. (c) At $[COO^-]/[Al^{3+}]_b < 3$ all existing sites are occupied by Al^{3+}, and high salt concentration may stabilize this rather disorganized structure. Some Al^{3+} is also bound to X^-. (d) At high Al^{3+} concentration, and low Na^+, all sites are occupied by AlX^{2+}, $X^- = OH^-$ here.

Discussion

It should be evident that the binding of Al^{3+} to alginate is a complex matter. Although a clear pronouncement in favor of one binding model or another cannot be expected, certain results of this work seem to us to be more easily reconciled with a divalent ion binding site model than with any other. These are: the $[COO^-]/Al^{3+}]_b$ ratio approaches 2, not 3, at high $[Al^{3+}]$; the forms of the displacement constants $K_{Na}{}^{Al}$ and $K_{Ca}{}^{Al}$, eq 3 and 4, which can be reconciled with the site model by arguments to follow; and perhaps most persuasive, the ability of Al^{3+}, bound to alginate, to bind firmly 1 or 2 but not 3 mol of alizarin.

The equilibrium constants require some justification if they are to support a site model. With regard to $K_{Ca}{}^{Al}$, no expression of the mass action law is going to be valid unless it is accepted that binding sites with different affinities for Ca^{2+} and Al^{3+} exist; then the first-order exchange quotient Q_{11} applies. As to the plausibility of this argument, we previously pointed out that a small amount of Ca^{2+}, Sr^{2+}, and Ba^{2+} (but not Mg^{2+}), around 10% in fact, appeared to be held by alginate more strongly than the rest.[2] The curve in Figure 4 assumes 13% of the sites prefer Ca^{2+} to Al^{3+}; this together with the 18% poly(Gul) content of the samples, and the established[6,28,29] preference of poly(Gul) over poly(Man) and copolymer for Ca^{2+}, tempts us to identify these sites with that component. Obviously, this could be subject to experimental verification.

The expression for $K_{Na}{}^{Al}$ corresponds neither to the expectations of a conventional ion competition reaction (Q_3 of Table III) nor to a simple site displacement (Q_1) as is valid for Na^+ and Ca^{2+}. A possible rationalization of the equilibrium expression $K_{Na}{}^{Al} = Q_2$, based on the divalent ion binding site model, can be made with reference to the schematic diagram of Figure 6.

We inferred from the Na^+-divalent ion equilibria that the binding sites of alginate in the Na form were each occupied by one, and only one, Na^+, as in Figure 6a. If, when an Al^{3+} displaces a Na^+ from a site, it also disrupts a neighboring site, thereby releasing a second Na^+ (Figure 6b), a two-for-one exchange would take place as long as $[Na^+]_b$ is in reasonable excess. The positive charge on the site containing Al^{3+} would be responsible for the disruption. This process would account for the data of series III as expressed in Table III and in $K_{Na}{}^{Al} = Q_2$. This manner of displacement would continue until $[COO^-]/[Al^{3+}]_b = 3$ and Na^+ is virtually expelled from the polymer. Figure 6c represents the state of the polymer with excess $NaAl(SO_4)_2$, when $[COO^-]/[Al^{3+}]_b \cong 2.8$, and Figure 6d that in excess $Al_2(SO_4)_3$, with $X^- = OH^-$, and $(COO^-)/(Al^{3+})_b \cong 2$. The transition from the state represented by Figure 6c to that of Figure 6d can be traced in the curves of $[Al^{3+}]_b$ and $[X^-]_b$ in Figure 1.

Equation 3 for $K_{Na}{}^{Al}$ and eq 5 reported[2] for the Na^+-Ca^{2+} equilibrium at first sight appear incompatible with eq 4

$$K_{Na}{}^{Ca} = [Ca^{2+}]_b[Na^+]_x/[Ca^{2+}]_x[Na^+]_b = 42 \qquad (5)$$

for $K_{Ca}{}^{Al}$. If $[Na^+]_x/[Na^+]_b$ is eliminated between eq 3 and 5, $K_{Ca}{}^{Al} = Q_{12}$ results, which is not constant (Table IV). It may be that the expressions are simply describing different domains of ion occupation, i.e., of Na^+ loading. Or, the incompatibility may only be apparent. We note that division of eq 3 by eq 5 gives eq 6.

$$[Al^{3+}]_b[Ca^{2+}]_x/[Al^{3+}]_x[Ca^{2+}]_b = (780/42)\ [Na^+]_b/[Na^+]_x \qquad (6)$$

Sodium was not measured in series IV, but $[Na^+]_b/[Na^+]_x$ can be estimated easily enough. If $[Na^+]_b \simeq 0.02[COO^-]$, then $[Na^+]_b \simeq 6 \times 10^{-4}$ M and $[Na^+]_x \simeq 1.9 \times 10^{-3}$ M. Insertion of these values into eq 6 gives $K_{Ca}{}^{Al} = 5.9$, which agrees numerically with the dominant value of $K_{Ca}{}^{Al}$ in the analysis of the curve of Figure 4. An interesting consequence of this line of reasoning is that high salt concentrations should favor binding of Ca^{2+} over Al^{3+} and presumably other trivalent metal ions, a circumstance that conceivably might have some significance for life in a marine environment.

Finally, it should be emphasized that these results were obtained with one sample of alginate, low in poly(Gul) segments. The conclusions reached with this sample must be considered tentative until they are confirmed by work with alginate samples with other copolymer segment compositions.

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The Synthesis and Solution Properties of Aromatic Polymers Containing 2,4-Quinoline Units in the Main Chain[1]

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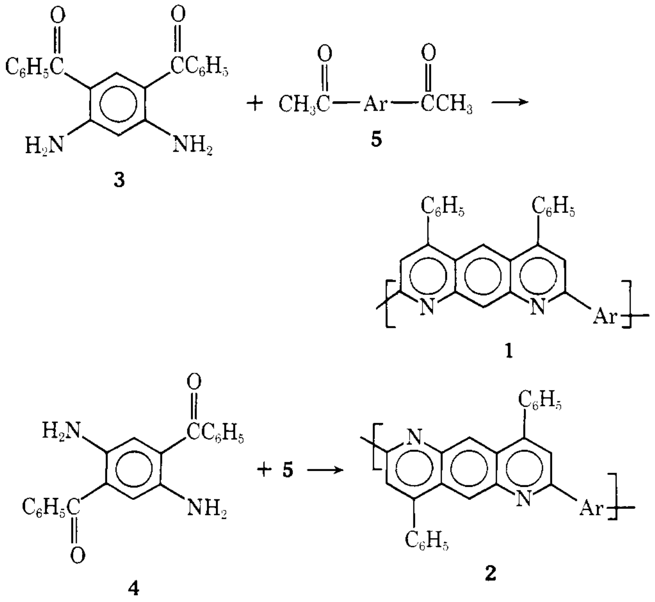
ABSTRACT: The acid-catalyzed polycondensation of 4,4′-bis(2-aminobenzoyl)diphenyl ether with diacetyl or diphenacetyl aromatic compounds afforded polymers containing quinoline groups linked by a variety of aromatic units. The polymers were soluble in phenolic and chlorinated hydrocarbon solvents, and tough, flexible films could be cast from these solutions. Poly[2,2′-(oxydi-*p*-phenylene)-4,4′-(oxydi-*p*-phenylene)diquinoline] showed no weight loss at 300 °C in air after 100 h and a TGA break in air at 510 °C. The polymer could be extruded from the melt at 430 °C through large bore capillaries. These extrudates could be drawn at temperatures above the glass transition temperatures of 251 °C with the resulting material showing an increase in crystallinity by x-ray diffraction. The Mark–Houwink equation for the polymer in chloroform at 20 °C was determined from viscometry and membrane osmometry to be $[\eta] = 5.5 \times 10^{-3}(\bar{M}_n)^{0.44}$. The polymerization followed second-order kinetics and attained number-average molecular weights greater than 25 000 within 15 h of reaction.

The Friedländer quinoline synthesis[2,3] has been utilized under a variety of base- and acid-catalyzed conditions to afford aromatic heterocyclic polymers.[4–6] High molecular weight phenylated polyanthrazolines (**1**) and polyisoanthrazolines (**2**) were prepared[6] by the reaction of 4,6-dibenzoyl-1,3-phenylenediamine (**3**) and 2,5-dibenzoyl-1,4-phenylenediamine (**4**), respectively, with diacetyl aromatic monomers (**5**). These polymers were partially soluble in a number of organic solvents and clear films could be cast from trifluoroacetic acid solutions. The greater solubility of these polymers when compared with the nonphenylated polyanthrazolines[4] was attributed to phenyl substitution on the polymer backbone. In general, polymers **1** which have pseudo-meta catenation due to the 1,9-anthrazoline moiety were found to be more soluble than polymers **2** which have a pseudo-para catenation due to the 1,6-anthrazoline moiety.[6]



Since the thermal transitions of the polyanthrazolines (**1**) and the polyisoanthrazolines (**2**) are all above 360 °C,[7] with decomposition temperatures near 500 °C,[6] processing of these polymers by compression molding or melt extrusion techniques would cause degradation of the polymer chain. The processing temperature for these polymers which affords a low enough melt viscosity is generally 150 °C above T_g. Therefore, a method of decreasing the glass transition temperature to a value to allow fabrication was desirable. In general, an increase in the number of flexibilizing groups per repeating unit in a series of polyquinoxalines led to decreasing glass transition temperatures.[8] Thus, an effort to prepare aromatic polymers via the Friedländer synthesis which were processable by both solution and melt methods by the introduction of an increased number of meta and flexible units was undertaken. Monomers were necessary, therefore, in which the two *o*-aminoketo functionalities were positioned on different rings with the result that the polymer would contain a quinoline rather than an anthrazoline nucleus.

Discussion

Monomer Synthesis. The polyquinoline-forming monomer, 4,4′-bis(2-aminobenzoyl)diphenyl ether (**6**), was synthesized as outlined in Scheme I. The Friedel-Crafts reaction of 2 mol of phthalic anhydride with 1 mol of diphenyl ether afforded either the monoadduct **7** or the diadduct **8** depending on the amount of aluminum chloride and solvent used. Five moles of aluminum chloride in a concentrated solution favored the formation of **8**. The monoadduct **7** was allowed to react further with 2 mol of phthalic anhydride to afford the diadduct 4,4′-bis(2-carboxybenzoyl)diphenyl ether (**8**) in 67% yield. The reaction of thionyl chloride with *o*-benzoylbenzoic acids has been reported to give pseudoacid chlorides.[9,10] Thus, the reaction of **8** with refluxing thionyl chloride gave the bis(pseudoacid chloride) **9**. Treatment of a cold, *N*-methyl-2-pyrrolidinone solution of **9** with anhydrous ammonia gas afforded 4,4′-bis(2-carbamylbenzoyl)diphenyl ether (**10**).

The Hofmann rearrangement of the bis(ketoamide) **10** was