extent of binding. Attempts to include Co-$(NH_3)_6^{3+}$, $Co(NH_3)_3(NO_2)_3$ and $Co(NH_3)_2(NO_2)_4^-$ in this study failed. The first complex, $Co(NH_3)_6^{3+}$, formed a precipitate with PSS^- and the other two underwent some decomposition during the experiment. The threefold difference in binding between the monovalent and divalent cations suggests that electrostatic forces are involved. It should be recalled that for the larger complex ions containing aromatic ligands, $Fe(phen)_3^{2+}$ vs. $Co(phen)_3^{3+}$, there is essentially no difference in binding. This would indicate that the electrostatic contribution to binding becomes relatively less important as the size and/or aromaticity of the complex increases.

A comparison of the data given for the last four complexes in Table III shows the effect that the presence of aromatic ligands in a complex ion has on its degree of binding. The complex $Co(en)_2$-$NH_3NO_2^{2+}$ is not bound to PSS^- under the conditions of these experiments whereas the corresponding complex $Co(en)_2pyNO_2^{2+}$ where pyridine, py, takes the place of NH_3, is definitely bound. Furthermore the monovalent complex $Co(bipy)_2$-$(NO_2)_2^+$, bipy = 2,2'-bipyridine, is bound approximately 2.5 times more than is the pyridine complex. Likewise $Fe(phen)_3^{2+}$, even in a sixteenfold more dilute solution, is bound about 1.5 times more than is $Co(en)_2pyNO_2^{2+}$. It is therefore apparent that the greater the number of aromatic ligands in a complex, the greater the extent of binding of the complex cation by an aromatic polyanion. This would appear to result from an increase in the van der Waals interaction forces.

If the binding of metal complexes containing aromatic ligands is primarily due to van der Waals interaction forces then the similar binding of the $Co(phen)_3^{3+}$ and $Fe(phen)_3^{2+}$ can be accounted for.

The slightly greater binding of cis-$Co(NH_3)_4$-$(NO_2)_2^+$ than the trans-isomer is in agreement with observations on the ion-exchange[15] and chromatographic[16] separation of these isomers. This difference between the cis and trans isomers has been attributed to the unsymmetrical electrical dipole of the cis form giving rise to greater binding or adsorption than does the electrically symmetrical trans isomer. There is one other case where the results of these studies on the binding of complex cations by polyanions agree with the ion-exchange and chromatographic experiments. This is the observation that the replacement of two ammonia molecules in a complex by an ethylenediamine(en) molecule, i.e., $Co(NH_3)_4(NO_2)_2^+$ vs. $Co(en)_2$-$(NO_2)_2^+$ (Table III), is accompanied by a decrease in binding of the complex. Since the complex containing ethylenediamine is larger than that containing ammonia, it may be argued that in these systems the binding is primarily due to electrostatic forces so that the smaller complex cation is bound to the greater extent. One other feature which also changes and may be of some importance is the number and accessibility of the hydrogens on nitrogen atoms in the complex. If hydrogen bonding is a contributing factor to the binding of the complex, then it follows that the ammonia system may be bound more than is the ethylenediamine system.

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(15) E. L. King and R. R. Walters, This Journal, 74, 4471 (1954).

(16) A. Jensen, J. Bjerrum and F. Woldbye, Acta Chem. Scand., to be published.

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Competitive Binding of Cations by Polymethacrylate Ion[1]

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The binding of tris-(1,10-phenanthroline) cationic complexes of iron(II), ruthenium(II) and cobalt (III) by polymethacrylate ion has been studied by a dialysis method. By an extension of the method it was possible to use the distribution of the ruthenium(II) complex to measure the binding of alkali metals. It was found that the alkali metal ions are all bound to approximately the same extent but appreciably more than is the tetramethylammonium ion.

The dialysis method which proved useful in the study of association between complex ions and polystyrene sulfonate[2] has been applied to a study of the association between complexes of (1,10-phenanthroline) and polymethacrylate (PMA^-) ion. Kinetic evidence for association in this latter system already has been presented.[3] By a slight modification of the dialysis conditions the binding of alkali metal ions to the polyelectrolyte also has been measured.

(2) A. Jensen, F. Basolo and H. M. Neumann, This Journal, 81, 509 (1959).

(3) A. Jensen, F. Basolo and H. M. Neumann, ibid., 80, 2354 (1958).

Experimental

Materials.—The tris-(1,10-phenanthroline)-ruthenium(II) perchlorate was prepared by the method of Dwyer.[4] The polymethacrylic acid, with a reported mol. wt. of 560,000 as determined by light scattering technique, was supplied by the Monsanto Chemical Company. This polymethacrylic acid was used without further purification. The sodium salt was prepared by the addition of an equivalent amount of sodium hydroxide to a solution of the acid. All of the alkali metal chlorides and the tetramethylammonium chloride are commercially available.

Dialysis.—Dialysis measurements were made by the method described in the accompanying article.[2] All experiments, including blank runs, were performed in triplicate, and the average values are reported.

(4) F. P. Dwyer, J. E. Humpoletz and R. S. Nyholm, J. Proc. Roy. Soc. N. S. Wales, 80, 212 (1947).

Three sets of experiments were performed. In the first set the original solution (0.026 M Na$_2$HPO$_4$ + 0.021 M KH$_2$PO$_4$) was a buffer solution which after dialysis had a pH of 6.8. The polyelectrolyte was added in the acid form, and two different concentrations were used. Tris-(1,10-phenanthroline) complexes of Ru(II), Fe(II) and Co(III) were used in variable concentration and at three different temperatures.

In the second set the original solutions before dialysis contained NaCl of known concentration. The polyelectrolyte was added in the form of the sodium salt; the pH was about 10. The Ru(II) complex was the only complex used.

In the third set the original solutions were buffer solutions of pH $\sim$ 9 (0.0025 M Na$_2$B$_4$O$_7$) which also contained an alkali metal chloride of known concentration. The polyelectrolyte was added as the salt, and again Ru(phen)$_3{}^{+1}$ was the complex used.

Results and Discussion

Binding of 1,10-Phenanthroline Complexes.—
The binding of the complex ions with polymethacrylate ion is different in many respects from the binding with polystyrene sulfonate.[2] The first striking feature is the considerably smaller extent of binding with polymethacrylate. This leads to certain experimental difficulties: relatively high concentrations of polyelectrolyte are needed to get reasonable concentration differences, and Donnan effects are often not negligible under these conditions.

Data collected on the binding of Fe(phen)$_3{}^{2+}$ and Ru(phen)$_3{}^{2+}$ are given in Table I. These

TABLE I

BINDING OF M(PHEN)$_3{}^{2+}$ BY PMA AT pH 6.8

Temp., °C.	[M(phen)$_3{}^{2+}$] blank × 10^5	[M(phen)$_3{}^{2+}$] free outside × 10^5	r	$r/A \times 10^{-5}$
	Fe(phen)$_3{}^{2+}$ and 0.010% PMA			
25.0	4.92	4.81	11	2.3
	4.42	4.33	9	2.1
	4.42	4.33	9	2.1
	4.40	4.29	11	2.6
	4.38	4.28	10	2.3
	4.35	4.25	10	2.4
	Fe(phen)$_3{}^{2+}$ and 0.100% PMA			
25.0	1.17	0.94	2.2	2.2
	2.24	1.77	4.6	2.4
	3.34	2.62	7.2	2.6
	5.39	4.30	10.7	2.3
16.9	1.22	1.00	2.1	2.0
	2.72	2.24	4.6	1.9
	5.66	4.62	10 1	2.1
39.8	1.86	1.62	2.1	1.2
	2.59	2.13	4.4	1.9
	2.80	2.32	4.6	1.9
	Ru(phen)$_3{}^{2+}$ and 0.100% PMA			
25.0	1.11	0.86	2.5	2.7
	1.87	1.44	4.3	2.8
16.9	1.85	1.50	3.4	2.1

experiments were performed in solutions buffered at pH 6.8 and the solutions are 0.073 molar in diffusible cations. In the experiments using 0.010% PMA ("0.0011 N") the Donnan effect is for practical purposes negligible; it can be calculated that the ratio of free complex inside to that outside is 1.004 as a result of the Donnan effect. This calculation takes into account the partial neutralization of the acid at this pH and the fact

that some Na$^+$ and K$^+$ ions are bound to the polyelectrolyte as counterions. The assumption is made that the activity coefficients for any free ion are the same in the two solutions separated by the membrane. In the experiments with 0.10% PMA ("0.011 N"), the Donnan effect is larger. A calculation made on the basis just described shows that the ratio of complex inside to that outside should be 1.06 as a result of the membrane effect.

The ratios 1.004 and 1.06 have been used to calculate the amount of free complex inside the bag, and from this the amount of bound complex has been calculated. The results are expressed in terms of r, the number of moles of complex bound per mole of polyelectrolyte, and A, the concentration of free complex ion in the solution with the polyelectrolyte. The fact that comparable experiments, differing only in PMA concentration, give the same value of r/A suggests that corrections for the membrane effect cannot be greatly in error. In fact, for all experiments with Ru(II) and Fe(II) complexes at 25° the values of r/A are the same within experimental error.

The small extent of binding is most apparent when one considers that there are on the average 6,000 carboxylate groups per polyanion, and the number of bound complexes is in the range 2–12. With such a limited occupancy of the binding sites it would be expected that binding at the various sites would be independent of one another, and r/A would have a constant value equal to mK_A, where m is the number of binding sites on the polyanion, and K_A is the intrinsic constant for the binding. In this particular system m is uncertain since a binding "site" may consist of one, two or three carboxylate groups. A value of K_A of the order of 80 is indicated. In the case of polystyrene sulfonate[2] a value of greater than 2 × 10^5 was found for K_A. That the Fe(II) and Ru(II) complexes are bound to the same extent is not surprising since they have the same charge and practically the same size.

Table II shows the results for comparable experiments with Co(phen)$_3{}^{3+}$. Correction for the

TABLE II

BINDING OF Co(PHEN)$_3{}^{3+}$ BY 0.100% PMA AT pH 6.8

Temp., °C.	[Co(phen)$_3{}^{3+}$] blank × 10^5	[Co(phen)$_3{}^{3+}$] free outside × 10^5	r	$r/A \times 10^{-5}$
25.0	2.22	0.86	15	16
	3.59	1.33	25	17
	5.95	2.23	41	17
	7.30	2.77	50	17
	7.51	3.14	47	14
	8.68	3.40	57	16
	8.79	3.95	52	12
16.9	2.42	1.15	14	11
39.8	3.11	1.62	16	9

Donnan effect was made on the basis of a calculated ratio of 1.09 for the ratio of free complex inside to that outside. The greater binding of the Co(III) complex compared to the Ru(II) and Fe(II) complexes is not unexpected in view of its larger cationic charge; its size is almost the same as that of the Fe(II) and Ru(II) complexes.

Although it would appear from the previous observation that binding is primarily caused by electrostatic attraction, experiments in solutions of higher acidity raise some doubt. Experiments with $Fe(phen)_3^{2+}$ could not be carried out at higher acidity because the complex dissociates under these conditions. However, the Co(III) and Ru(II) complexes are stable in acid solution, and it was possible to determine their binding by 0.100% PMA in a solution 0.02 M in HCl and 0.10 M in NaCl. Under these conditions where PMA is almost completely in the acid form, it was observed that $Co(phen)_3^{3+}$ is not bound whereas $Ru(phen)_3^{2+}$ is bound almost to the same extent as it is at pH 6.8. There is no ready explanation for this behavior.

The data at the three temperatures show unusual features. Although the difference in binding over the 23° temperature range is not large, the binding at 25° is clearly greater than at either 16.9 or 39.8°. This effect is most clearly shown with $Co(phen)_3^{3+}$. In order to understand this rather strange temperature dependence, further study is necessary. It should be mentioned that the nature of the polyanion is known to change with temperature.[5]

Effect of Sodium Ions.—The binding of the complex to PMA^- in the presence of simpler cations, e.g., sodium ions, is complicated by the fact that sodium ions themselves will be associated with the polyanion. Varying the concentration of sodium ion will change the nature of the polyanion and cause a consequent change in the distribution of complex. If the experimental conditions are such that the Donnan effect is small, there may be a competition between sodium ions and complex ions for the binding sites on the polyanion, or the configuration of the polyanion might change with the amount of sodium bound and this effect could lead to a change in the extent of binding of the complex. If the binding of the complex is small and the Donnan effect large, the distribution of complex across the membrane will serve as a measure of the distribution of sodium ions across the membrane and hence a measure of the amount of bound sodium.

The calculation of α, the average number of sodium ions associated with each carboxylate group, is accomplished by use of the equation

$$\sqrt{\frac{[C^{++}]_{in}}{[C^{++}]_{out}}} = \frac{[Na^+]_{in}}{[Na^+]_{out}} = \frac{[Na^+]_{total} - \alpha[PMA^-]_{total}}{[Na^+]_{total} - [PMA^-]_{total}}$$

which applies within the approximation that the activity coefficients for a given ion are the same in both solutions. The subscripts "in" and "out" denote the concentrations of free ions inside and outside the dialysis bag, respectively. C^{++} represents the complex ion, and $[PMA^-]_{total}$ is the "normal" concentration of polyanions, i.e., the concentration of anions that would result if the individual anionic sites could be dispersed homogeneously in 10 ml. of solution. The symbol $[Na^+]_{total}$ is used to represent the sum of the concentrations of Na^+ in various parts of the system. It is the concentration that would result if all the sodium ions in the system were present in 10 ml. of

(5) F. T. Wall, J. Phys. Chem., 61, 1344 (1957).

solution. Obviously, there is in fact no part of the system that has such a concentration.

The data and results for a series of experiments at pH~10 are given in Table III. The relative contribution of binding and Donnan effect to the observed results cannot be assessed in an absolutely accurate way. A few conclusions resulting from limiting considerations are valid. If one assumes a negligible Donnan effect (this condition could arise from a high Na^+/PMA^- ratio, or because $\alpha = 1$), limiting values for binding by the complex can be calculated. These limiting values are listed in the column r/A. It should be noted that all of these values are smaller than the values obtained in the experiments at pH 6.8.

TABLE III

[Na+]total	[C++]blank × 10^6	[C++]out × 10^6	Limiting values r/A × 10^-6	α	Consistent values r/A × 10^-5	α	[Na+]in
			0.654% PMA⁻ ("0.070 N")				
0.14	1.83	0.96	<1.55	>0.32	0.57	0.7	0.05
.20	1.89	1.35	<0.68	> .36	.29	.7	.08
.28	1.89	1.60	< .31	> .49	.11	.7	.12
.42	1.87	1.69	< .18	> .50	.06	.7	.19
.56	1.88	1.74	< .14	> .44	.05	.7	.26
.70	1.91	1.82	< .08	> .56	.03	.7	.33
			0.100% PMA⁻ ("0.0107 N")				
0.20	1.85	1.76	<0.57	>0.10	0.30	0.7	0.10
0.26	1.84	1.79	<0.31	>0.36	0.15	0.7	0.13

Taking the opposite point of view, a limiting value of α can be calculated assuming there is no binding by the complex. These values of α are listed in Table III also.

An attempt has been made to calculate a consistent set of values of α and r/A that will satisfy the observed results and which also satisfy certain restrictions that appear reasonable. The first restriction applied is that r/A should be a smoothly increasing function of $1/[Na^+]^2_{in}$. This restriction was suggested by the fact that if the polyanion was behaving with a fixed capacity for cations, e.g., like an ion–exchange resin, and there was a simple competition between sodium and complex cations for the binding sites, a linear relationship would be anticipated. Because the polyanion may have a varying capacity, the more stringent restriction of a linear relationship was not applied. The second restriction applied is that α should be either constant or should increase as $[Na^+]_{in}$ increases. Although other values of α and r/A may satisfy the data, the set given appears to be the most probable. These values are listed in Table III under the heading "consistent values."

Wall and Eitel[6] have measured the amount of sodium bound to polyacrylate ion for solutions "0.07 N" in polyelectrolyte and having concentrations of free sodium ion ranging from 0.03 to 0.08 M. They obtained values of α ranging from 0.638 to 0.686. Because of the uncertainty inherent in the "consistent values" of α it is not possible from

(6) F. T. Wall and M. J. Eitel, THIS JOURNAL, 79, 1556 (1957).

these results with polymethacrylate to say which system shows the greater binding at these concentrations. A value of 0.4 has been obtained by Oth and Doty[7] for polymethacrylate at lower sodium ion concentrations. This suggests that the binding of polymethacrylate is slightly smaller than that by polyacrylate for a given sodium ion concentration. This would be consistent with the observation that acrylic resins form stronger complexes than methacrylic resins.[8]

Binding of Other Alkali Metals.—Dialysis experiments were also carried out on buffered (pH 9, 0.0025 M $Na_2B_4O_7$) solutions of 0.0107 "N" PMA and 1.9 × 10^{-5} M [Ru(phen)₃] (ClO₄)₂ in 0.050 M LiCl, KCl, RbCl, CsCl and $(CH_3)_4NCl$, respectively. The same experiment was performed using NaCl instead of the other chlorides and the NaCl concentration was varied from 0.02 to 0.10 M. A comparison of the binding of a particular monovalent cation with that of the sodium ion was then possible by observing the concentration of sodium ion necessary to give the same effect as the 0.050 M solution of the cation. This comparison is valid regardless of whether the observed distribution of complex is caused by the Donnan effect, by competitive binding of the complex or both. Within experimental error it was found that the 0.050 M alkali halides all correspond to 0.050

(7) A. Oth and P. Doty, *J. Phys. Chem.*, **56**, 43 (1952).

(8) H. P. Gregor, L. B. Luttinger and E. M. Loebl, *ibid.*, **59**, 366 (1955).

M NaCl. The binding of $(CH_3)_4N^+$ is appreciably less as evidenced by the observation that 0.050 M $(CH_3)_4N^+$ is only as effective as is 0.026 M Na^+. Thus the binding tendencies of the monovalent cations with PMA^- are

$$Li^+ \sim Na^+ \sim K^+ \sim Rb^+ \sim Cs^+ > (CH_3)_4N^+$$

This is in agreement with the observation of Wall and Doremus[9] that sodium and potassium ions are bound to the same extent to polyacrylate ion. However, this does not agree with the small differences in the binding of lithium and sodium ions with polyacrylate reported by Hutschneker and Deuel[10] nor to the differences observed with polymethacrylate.[11] Failure to detect a difference in binding in our experiments may result from the technique used not being sensitive enough to show up such small differences. It is also of interest to note that the alkali metal ions are differentiated by ion-exchange resins.[12]

(9) F. T. Wall and R. H. Doremus, THIS JOURNAL, **76**, 1557 (1954).

(10) K. Hutschneker and H. Deuel, *Helv. Chim. Acta*, **39**, 1038 (1956).

(11) H. P. Gregor and M. Frederick, *J. Polymer Sci.*, **23**, 451 (1957); H. P. Gregor, D. H. Gold and M. Frederick, *ibid.*, **23**, 467 (1957).

(12) R. Kunin and R. L. Myers, "Ion Exchange Resins," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 22–25; H. P. Gregor, M. J. Hamilton, R. J. Oza and F. Bernstein, *J. Phys. Chem.*, **60**, 263 (1956).

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Hydrolytic Tendencies of Metal Chelate Compounds. III. Oxometal Ions[1]

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The hydrolysis of a variety of metal chelate compounds of VO(IV), ZrO(IV), UO₂(VI) and MO₂(VI) ions has been studied potentiometrically to determine relative tendencies toward the formation of hydroxo metal chelates. These ions have relatively high affinity for oxygen donor atoms and form the more stable metal chelate systems with ligands containing basic oxygens such as those found in polyphenols and hydroxy acids. Hydrolytic tendencies increase in the order VO(IV) < ZrO(IV) < UO₂(VI) < MoO₂(VI). The most stable soluble aqueous systems are found with Tiron (disodium pyrocatechol-3,5-disulfonate) as a ligand.

This investigation was undertaken to study the nature of the reactions of incompletely coördinated metal chelate compounds and is an extension of investigations already reported on the hydrolysis of metal ions containing no oxo groups. A review of the literature showed that very little work had been reported on the hydrolysis of metal chelates of oxo metal ions. Although the dioxouranium (VI) ion is known to undergo simultaneous hydrolysis and polymerization,[2,3] the reactions seemed to be very complex. It was shown recently by Cabell[4] that aminopolycarboxylic acid ligands containing large numbers of donor groups form uranyl complexes which contain only one metal ion in the

complex anion. On the other hand, potentiometric and spectrophotometric measurements reported by Feldman, Havill and Neuman[5] with such ligands as malate, citrate and tartrate, indicated the formation of polynuclear chelates containing hydroxyl ions or oxo ions as coördinating links between two or more uranyl groups. They interpreted their data on the basis of transitions from binuclear to ternuclear uranyl chelates of α-hydroxy acids.

Experimental

The experimental method consisted of potentiometric titrations of the ligand in the absence of and in the presence of the metal ions being studied in accordance with the detailed procedure previously described.[6] The temperature was regulated at 25 ± 0.1°, and the ionic strength was maintained relatively

(1) This paper reports work done under contract with the Chemical Corps, U. S. Army, Washington 25, D. C.

(2) S. Ahrland, S. Hietanen and L. G. Sillen, *Acta Chem. Scand.*, **8**, 1907 (1954).

(3) J. Sutton, *J. Chem. Soc.*, 5275 (1949).

(4) M. J. Cabell, Atomic Energy Research Estab., Unclassified C/R 813 (1951).

(5) (a) I. Feldman, J. R. Havill and W. F. Neuman, THIS JOURNAL, **76**, 4726 (1954); (b) W. F. Neuman, J. R. Havill and I. Feldman, *ibid.*, **73**, 3593 (1951).

(6) A. E. Martell, S. Chaberek, Jr., R. C. Courtney, S. Westerback and H. Hyytiainen, *ibid.*, **79**, 3036 (1957).