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Functionalized Polymers

Oxochloromolybdenum(V) Tetraphenylporphyrin Complex-Containing Polymer as a Phosphate Ion Exchanger

Etsuo Kokufuta*, Toru Sodeyama, and Shoji Takeda

Institute of Applied Biochemistry, University of Tsukuba, Sakura-mura, Niihari-gun, Ibaraki, 305 Japan

Summary

Oxochloro(5,10,15,20-tetraphenylporphyrinate)molybdenum(V) was physically entrapped into poly(styrene) by lyophilizing a benzene solution including both complex and polymer. The functional ability of the obtained complex-containing resin to adsorb $H_2PO_4^-$ from an aqueous solution was investigated in the presence of various anions. It was found that the selectivity of the resin for $H_2PO_4^-$ is superior to those of conventional anion exchangers.

Introduction

Although there are numerous reports (1) on polymeric chelating or complexing compounds known as specific and selective ion exchange resins, their utilities are limited to metal cations. Little attention has been paid to selective anion exchangers. Previous publications (2) from this laboratory have described the syntheses and properties of polymer-bound ferri-protoporphyrin IX chloride able to function as a cyanide ion exchanger. Here we report a phosphate ion exchanger which can be easily prepared by physical entrapment of oxochloromolybdenum(V) tetraphenylporphyrin complex [MoO(Cl)TPP] into poly(styrene) (PSt).

Experimental

MoO(Cl)TPP was prepared from meso-tetraphenylporphyrin and $MoCl_5$ according to the literature (3). Full elemental analysis for the obtained complex gave results consistent with the formulation $C_{44}H_{28}ClMoN_4O$. Additionally, both IR spectrum in KBr disk and UV-visible spectrum in CH_2Cl_2 agreed with those already reported (3,4). MoO(Cl)TPP was physically entrapped within the body of PSt (weight-average molecular weight = 1.76×10^5) by lyophilizing a benzene solution (about 500 ml) including the complex (1.90 g) and the polymer (8.10 g). The extraction test (40 days; 30 °C) with 1 M HCl

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* To whom offprint requests should be sent

or NaOH showed no dissolution of MoO(Cl)TPP from the complex-containing polymer, i.e., MoO(Cl)TPP/PSt.

The selectivity of MoO(Cl)TPP/PSt for $H_2PO_4^-$ was investigated by adsorption and column experiments, and compared with those of the conventional anion exchangers. Amberlite IRA-458 and IRA-35 were converted to the chloride form to use, which are respectively known as representative strongly and weakly basic anion exchangers. In the adsorption experiments, each of the resin was dispersed into aqueous KH_2PO_4 solution (500 ml) containing various anions and then stirred at 25 °C for 12 h. The concentration of ion-exchange groups (C_i) was hold at a constant value (0.01 mM), while that of KH_2PO_4 (C_p) was varied in such a way that $C_p/C_i = 1$ to 20. The amount adsorbed was expressed as the degree of binding (Y) of $H_2PO_4^-$ to ion-exchange groups. The column experiments were made by using a glass column packed with the resins having total 0.25 mmol ion-exchange groups. This quantity corresponds to 1 g of MoO(Cl)TPP/PSt or to ca. 50 mg of Amberlite IRA-458 or IRA-35, as calculated from their ion-exchange capacities in mol/g.

Results and Discussion

The present authors have reported that in organic solvents such as dichloromethane, the ligand exchange reaction between MoO(Cl)TPP and $H_2PO_4^-$ ion is reversible (5):

$$\mathrm{MoO(Cl)TPP} + H_2PO_4^- \rightleftharpoons \mathrm{MoO}(H_2PO_4) + Cl^-$$

In this study, first, we attempted to compare two experimental results (No 1 and 2 in Table I) for the $H_2PO_4^-$ extraction with a dichloromethane solution of MoO(Cl)TPP and for the $H_2PO_4^-$ adsorption onto MoO(Cl)TPP/PSt, in order to elucidate how the ligand exchange reaction is influenced by entrapping the complex into the polymer. There is no pronounced difference between the Y values from both experiments, indicating that the reaction is not affected by whether the complex is dissolved in the organic solvent or entrapped into the polymer.

Next, we examined the effects of pH and bicarbonate ion on the $H_2PO_4^-$ adsorption (No 3 and 4 in Table I), since they seem to be an important factor affecting the above exchange reaction. No influence of bicarbonate ion was observed under the conditions used. However, an increase in pH hindered the reaction, which could be due to a decrease in the univalent $H_2PO_4^-$ and/or to the preferential coordination of OH^-. The adsorption and column experiments described below were thus made in the pH range (4.92±0.06) where only the univalent $H_2PO_4^-$ arises from the phosphate.

The effect of common ion on the $H_2PO_4^-$ adsorption was investigated in the presence of KCl, KNO_2, KNO_3, $KHCO_3$, and

TABLE I
Adsorption of $H_2PO_4^-$ Ion onto MoO(Cl)TPP/PSt and Conventional Anion Exchangers from Various KH_2PO_4 Solutions

No	Resin[a]	KH_2PO_4 solution[b]	Y			
			C_p/C_i = 1	5	10	20
1	R1	Ia	0.15	0.49	0.66	0.74
2	R1	Ia	(0.16)[c]		(0.61)[c]	
3	R1	Ib	0.14	0.46	0.67	0.72
4	R1	Ic	0.09	0.29	0.36	0.49
5	R1	IIa	0.10	0.31	0.44	0.66
6	R1	IIb	0.08	0.28	0.41	0.56
7	R2	IIa	0.01	0.08	0.20	0.28
8	R2	IIb	0.01	0.04	0.10	0.22
9	R3	IIa	0.01	0.11	0.21	0.33
10	R3	IIb	0.01	0.04	0.11	0.17

[a] Abbreviations used: (R1) MoO(Cl)TPP/PSt; (R2) Amberlite IRA-458; (R3) Amberlite IRA-35. The ion-exchange capacities in mmol/g (dry weight base) were 0.250 for MoO(Cl)TPP/PSt; 4.29 for Amberlite IRA-458; 5.24 for Amberlite IRA-35.

[b] Prepared by dissolving different amounts of KH_2PO_4 into: carbonate-free twice distilled water (Ia); 2.3 mM $KHCO_3$ solution (pH 4.96) (Ib); KOH solution adjusted to pH 9.01 (Ic); equimolar (0.01 mM) solution (pH 4.99) of KNO_2, KNO_3, and K_2SO_4 (IIa); equimolar (0.01 mM) solution (pH 4.93) of KCl, KNO_2, KNO_3, $KHCO_3$, and K_2SO_4 (IIb). The solution Ic contains only the bivalent HPO_4^{2-} because of adjusting pH to 9.01, and the solutions Ib, IIa, and IIb adjusted to pH *ca.* 5 involve the acid(s) resulting from the weakly acidic ion(s) (NO_2^- and HCO_3^-).

[c] Determined from the extracting experiments with CH_2Cl_2 including MoO(Cl)TPP in amount equimolar with the complex in the resin.

K_2SO_4 (No 5 - 10 in Table I). These salts are selected because their constituent anions are known to be usually detectable from the river or lake water (6). The presence of the common ions in the phosphate solutions causes reducing the Y values of all the resins examined. However, Amberlite IRA-458 and IRA-35 are much more subject to such a hindrance effect than MoO(Cl)TPP/PSt. This could suggest that the complex in the resin serves as a selective adsorption site for $H_2PO_4^-$.

The selective adsorption of $H_2PO_4^-$ on MoO(Cl)TPP/PSt was further confirmed by the column experiments (Figure 1). When the phosphate solution IIb (see Table I) containing 4 mg/l phosphorus was effused through a column of the resin, a large portion of $H_2PO_4^-$ ions was adsorbed until the total fraction volume exceed 250 ml. The adsorbed ions, corresponding to 42 mol% of all the complex entrapped, was then almost or entirely eluted with 0.5 M NaCl solution; recovery ca. 98%. Such adsorption and desorption were reproduced reversibly over different runs of the column experiments. In contrast, the column experiments with Amberlite IRA-458 and IRA-35 showed the lack of their selectivities for $H_2PO_4^-$ ion. Therefore, it becomes apparent that the functional capability of MoO(Cl)/PSt as a phosphate ion exchanger is superior to those of conventional anion exchangers.

The electronic absorption spectra of MoO(X)TPP complexes (where X = various anion ligands) in CH_2Cl_2 have three main peaks; that is, the Soret, α, and β bands. It has been known that the degree of red shifts of the corresponding adsorption maxima increases in the order: $X = OC_2H_5 < BF_4 \cong F < NCO < N_3 < NCS < Cl < Br$ (see ref.3). This was discussed in connection with the electronegativity of ligand X, by considering that the spectral changes are dependent upon the magnitude of donating electrons from a ligand to the porphyrin ring via the central Mo(V) atom (3). Nappa and Valentine (7) studied the influence of axial ligands on the electronic absorption spectra for zinc(II) complex of tetraphenylporphyrin. They reported that the zinc(II) complex preferentially binds hard ligands with donor atoms having relatively high electronegativity and low polarizability, while the ligands with less electronegative and more polarizable donor atoms cause a larger red shift because they allow more negative charge to be transferred to the porphyrin ring. Since no difference was observed in the spectral behavior between the zinc(II) and oxomolybdenum(V) complexes (3), the preferential adsorption of $H_2PO_4^-$ onto MoO(Cl)TPP/PSt can be interpreted by assuming that its electronegativity is considerably large compared to the other anions. In fact, the contribution of $H_2PO_4^-$ to bringing about the red shift are intermediate between BF_4^- or F^- and NCO^-, as indicated by comparing the spectral data for various MoO(X)TPP complexes with that for $MoO(H_2PO_4)TPP$ (see Table II).

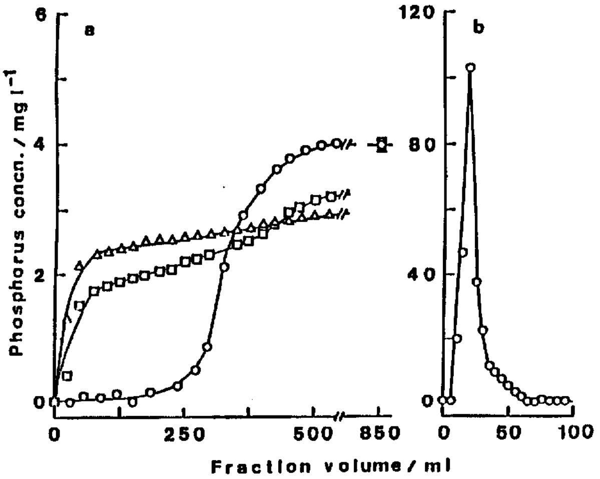

Fig. 1. Column separations (a) of $H_2PO_4^-$ ions with MoO(Cl)TPP/PSt (○), Amberlite IRA-458 (□), Amberlite IRA-35 (△), and elution (b) of the ions absorbed onto the complex-containing resin with 0.5 M NaCl.

TABLE II

Electronic Absorption Spectra of Various Oxomolybdenum(V) Complexes of Tetraphenylporphyrin in CH_2Cl_2 at 25 °C

Complex	λ_{max}/nm (εX10^{-4}/$M^{-1}cm^{-1}$)		
	Soret	β	α
MoO(OEt)TPP[a]	454(15.8)	582(1.51)	622(1.04)
MoO(BF_4)TPP[a]	463(9.82)	591(1.35)	634(1.09)
MoO(F)TPP[a]	463(9.71)	592(1.30)	635(1.04)
MoO(H_2PO_4)TPP[b]	475(4.65)	607(0.98)	649(0.81)
MoO(NCO)TPP[a]	488(4.66)	617(0.85)	664(0.86)
MoO(Cl)TPP[a]	500(4.17)	627(0.85)	674(0.96)
MoO(Cl)TPP[b]	498(4.22)	628(0.89)	673(0.95)
MoO(Br)TPP[a]	508(3.45)	638(0.71)	686(0.86)

[a] Cited from ref. 3.
[b] Obtained in the present study.

In conclusion, the present results indicate that the physical entrapment of MoO(Cl)TPP into PSt gives rise to a phosphate ion exchanger having the selectivity superior to those of conventional anion exchangers. Such functional polymer would be useful for protecting water pollution of rivers or lakes caused by phosphate ions.

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