Behaviour of Crosslinked Polyallylamine Resin for the Uptake of Inorganic Anions

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Outline

1. Background of the present work

2. Batch-mode study: Anion selectivity sequence

3. Column-mode study: Phosphate uptake under high flow rates of feeds

1. Background of the present work

Properties of Conventional Anion Exchange Resins Based on Polystyrene Crosslinked with Divinylbenzene

○ **Conventional anion exchange resins prefer lowly hydrated anions to highly hydrated ones (Hofmeister anion selectivity sequence).**

$$F^- < OH^- < H_2PO_4^- < HCO_3^- < Cl^- < Br^- < NO_3^- < I^- < ClO_4^-$$

Lindenbaum et al., *J. Phys. Chem.,* Vol. 62, 995-999(1958).

Wheaton and Bauman, *Ind. Eng. Chem.,* Vol. 43, 1088 -1093 (1951).

○ **Flow rates of feeds in industrial scale columns packed with ion exchange resins with diameters of 0.2 – 1 mm are 20 – 40 h^{-1} in space velocity.**

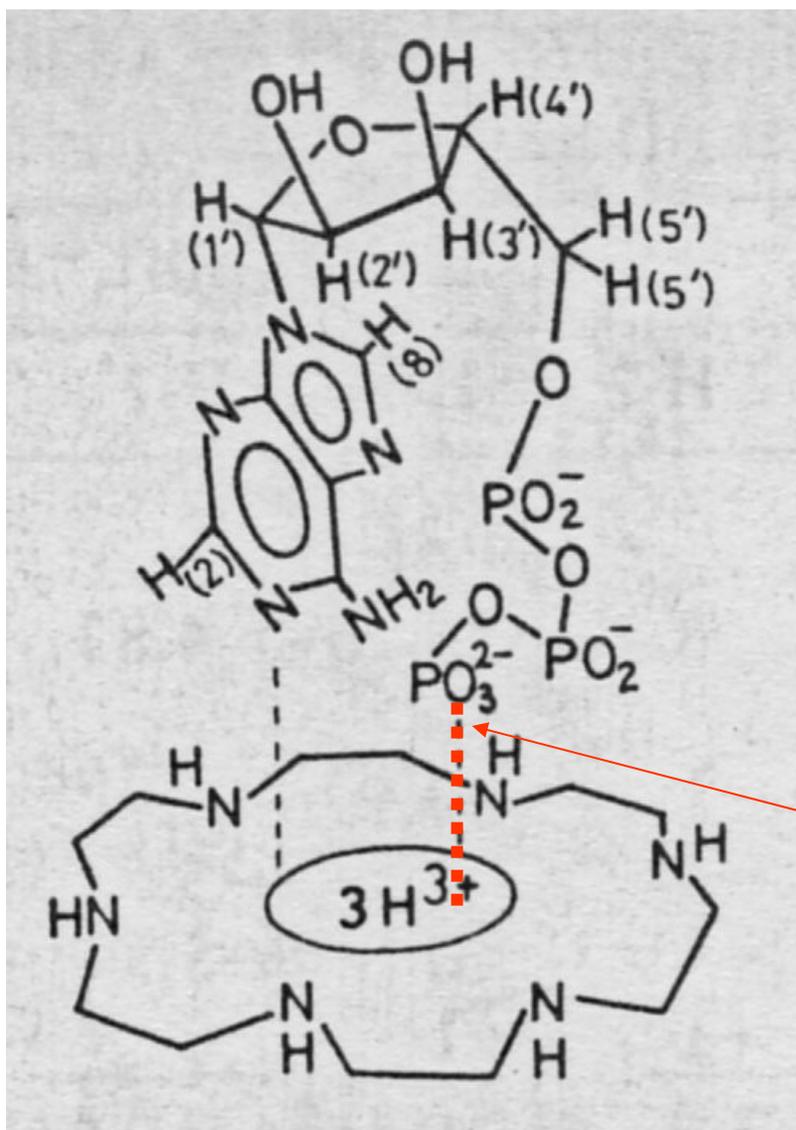Lacour et al., *Water Res.,* Vol. 38, 4045-4054(2004).

Anion Coordination Chemistry

Lehn's groups and Kimura's groups (1980s)

Organic macrocyclic polyammoniums form stable complexes with some anions through both electrostatic interaction and hydrogen bonding.

[15]aneN₄ [16]aneN₄ iso-[16]aneN₄

[17]aneN₄ [15]aneN₅ [16]aneN₅
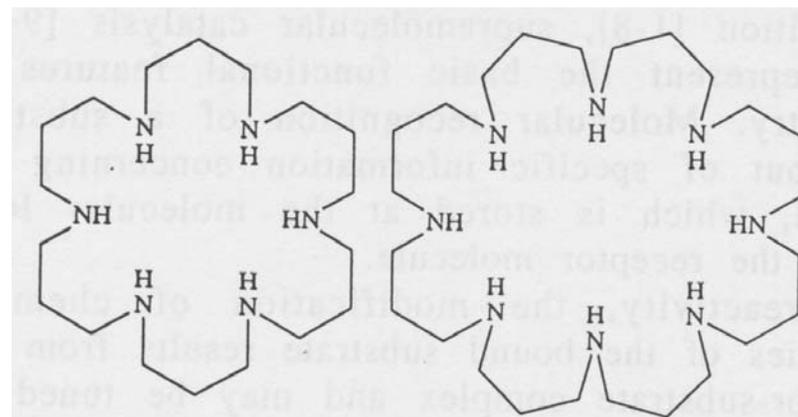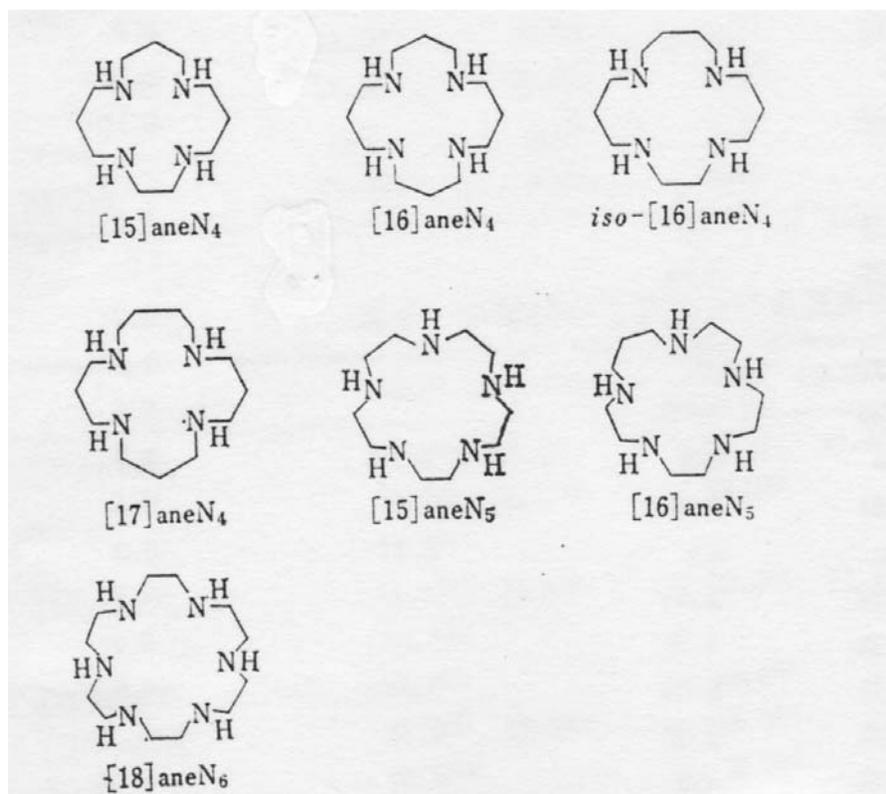
[18]aneN₆

Complexation with ATP Anion and HPO_4^{2-}

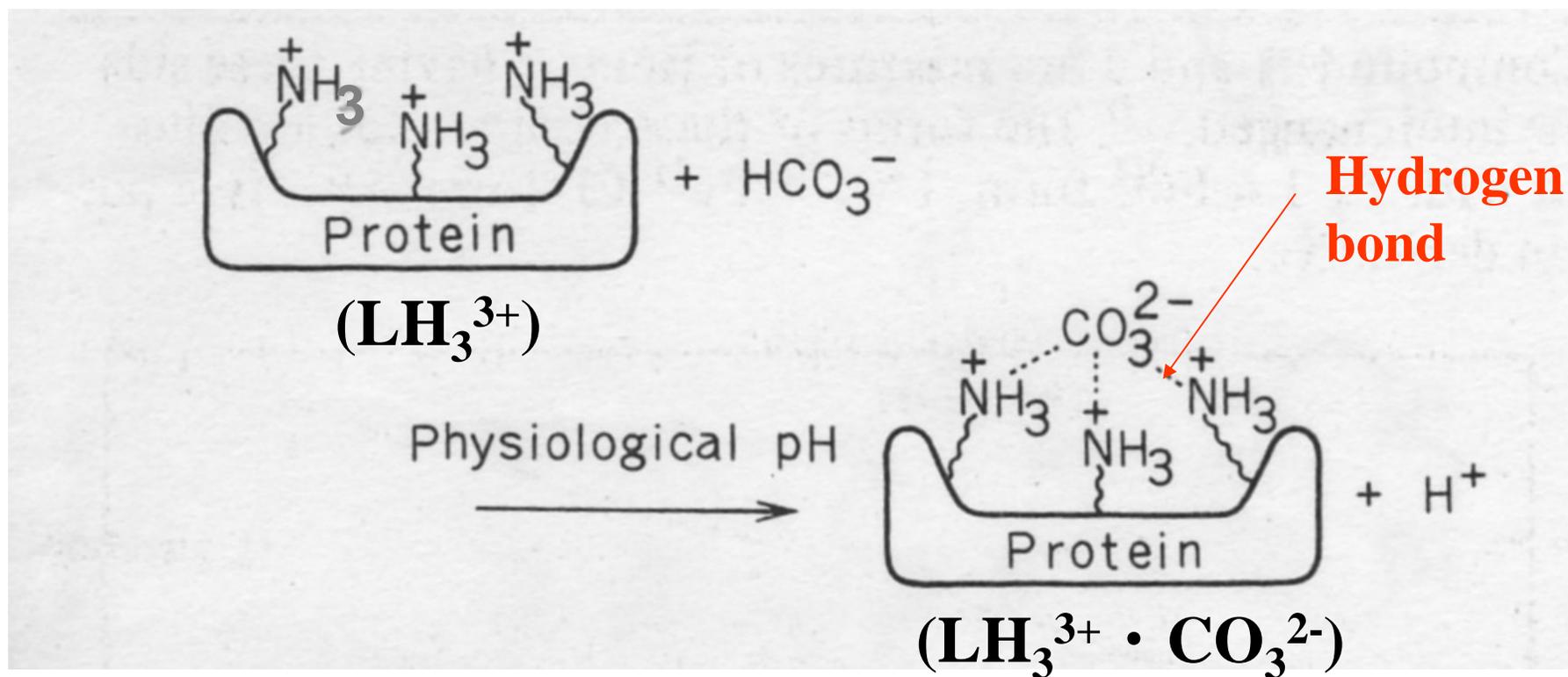**Structure of complex of ATP anion with triprotonated [18]aneN_6.**

This triprotonated macrocycle also comlexes with HPO_4^{2-}

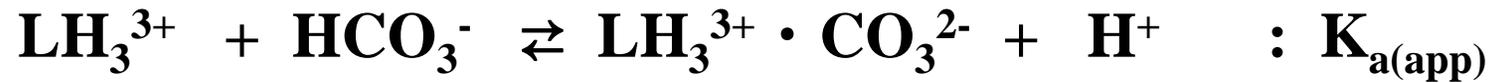**Kimura's groups.** *J. Am. Chem. Soc.*, Vol. 104, 3182(1982).

Hydrogen bond

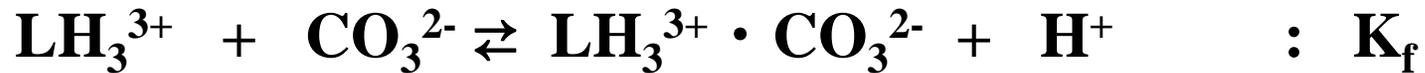# Complexation of Polyprotonated Macrocyles with Carbonate as Carbonate Receptor Model

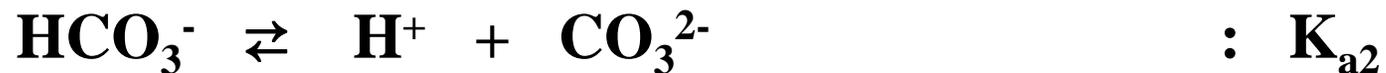**Kimura's group:** *J. Am. Chem. Soc.*, Vol. 104, 4984 (1982).

Hydrogen bond

(LH_3^{3+})

$(LH_3^{3+} \cdot CO_3^{2-})$

$$LH_3^{3+} + HCO_3^- \rightleftarrows LH_3^{3+} \cdot CO_3^{2-} + H^+ \qquad :$$

K

Enhancement of Acidity of Weak Acid

$$LH_3^{3+} + HCO_3^- \rightleftharpoons LH_3^{3+} \cdot CO_3^{2-} + H^+ \qquad : K_{a(app)}$$

$$K_{a(app)} = \frac{[LH_3^{3+}CO_3^{2-}][H^+]}{[LH_3^{3+}][HCO^-]}$$

$$LH_3^{3+} + CO_3^{2-} \rightleftharpoons LH_3^{3+} \cdot CO_3^{2-} + H^+ \qquad : K_f$$

$$K_f = \frac{[LH_3^{3+}CO_3^{2-}]}{[LH_3^{3+}][CO_3^{2-}]}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad\qquad : K_{a2}$$

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

From three equations mentioned above, we have the following relation:

$$K_{a(app)} = K_f \times K_{a2}$$

Meaning of Equation $K_{a(app)} = K_f \times K_{a2}$

Strong binding of carbonate with polyprotonated macrocyclic polyamines enhances acid dissociation constant of bicarbonate. Namely, this complexation promotes dissociation of weak acid.

Then, we are interested in weak anion exchangers based on apliphatic polyamines without aromatic crosslinkers, because it is expected that these kinds of anion exchangers exhibit non-Hofmeister anion selectivity.

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Anion Exchange Fiber FVA

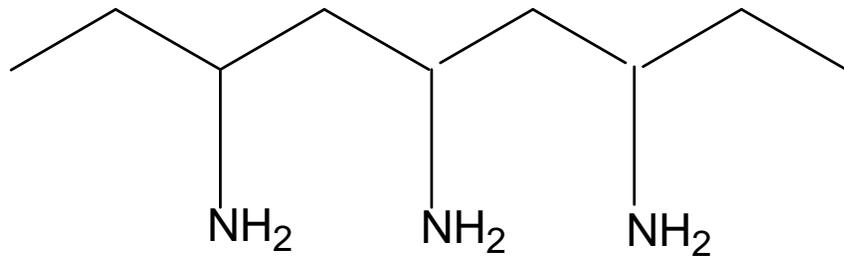## "Arsenate Removal from Water by a Weak-base Anion Exchange Fibrous Adsorbent FVA"

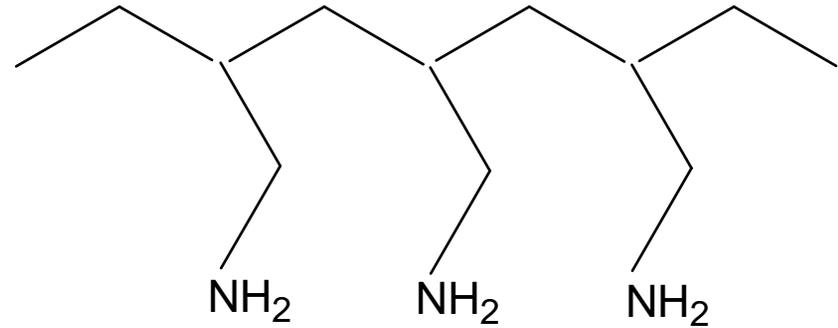**FVA: Polyolefin fiber having grafted polyvinylamine chains**
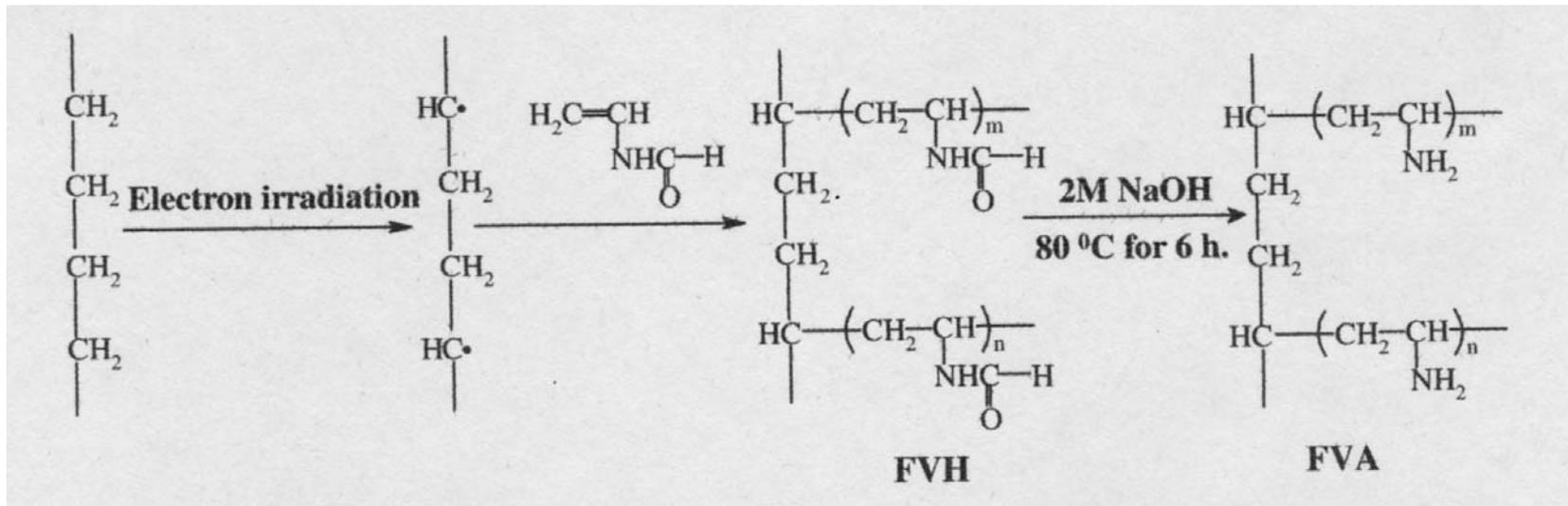
Preparation Route of Anion Exchange Fiber FVA

Our group: Water Res., Vol. 42, 689-696 (2008).

Polyvinylamine and Polyallylamine

Polyvinylamine

Polyallylamine

S. Kobayashi *et al.*, *Macromolecules*, Vol. 22, 2363-2366(1989).
Average pK_a of polyvinylamine: 8.5 - 8.6,

Average pK_a of polyallylamine: 9.7

Polyallyamine **is more highly protonated** than polyvinylamine, because of longer distance between adjacent amino groups.

Protonated sites of polyvinylamine **are more flexible** than those of polyvinylamine because of methylene spacer.

2. Batch-mode study: Anion selectivity sequence

# Properties of Crosslinked Polyallylamine Resin (PAA) Measured in This Work

Particle size in dry state	**0.13-0.18 mm**
Volume in dry state	**1.30 mL/g**
Volume in wet state	**4.50 mL/g**
Volume in dry state (free base form)	**1.06 mL/g**
Volume in wet state (free base form)	**3.06 mL/g**
Water content	**69 %**
Chloride content	**10.2 mmol/g**
Nitrogen content (Free base form)	**14.6 mmol/g**

Provided by Nitto Boseki Co. Ltd., Tokyo, Japan. Resin for research works. Chloride form unless otherwise specified. Gel type resin. Crosslinker and degree of crosslinking were not disclosed in detail.

Batch-mode Adsorption of Phosphate
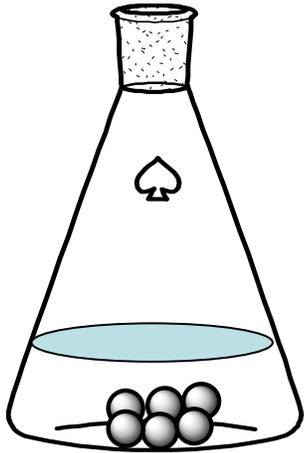
1) 50 mL of 0.01 M phosphate solution with different pH in the absence or presence of foreign anions

2) 0.050 g of PAA resin **in free amine form**

3) Shaken for 24 h at 30 ^{o}C

4) Measurements of pH and phosphate concentration in supernatant

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Uptake of Phosphate in the Absence and Presence of Foreign Anions
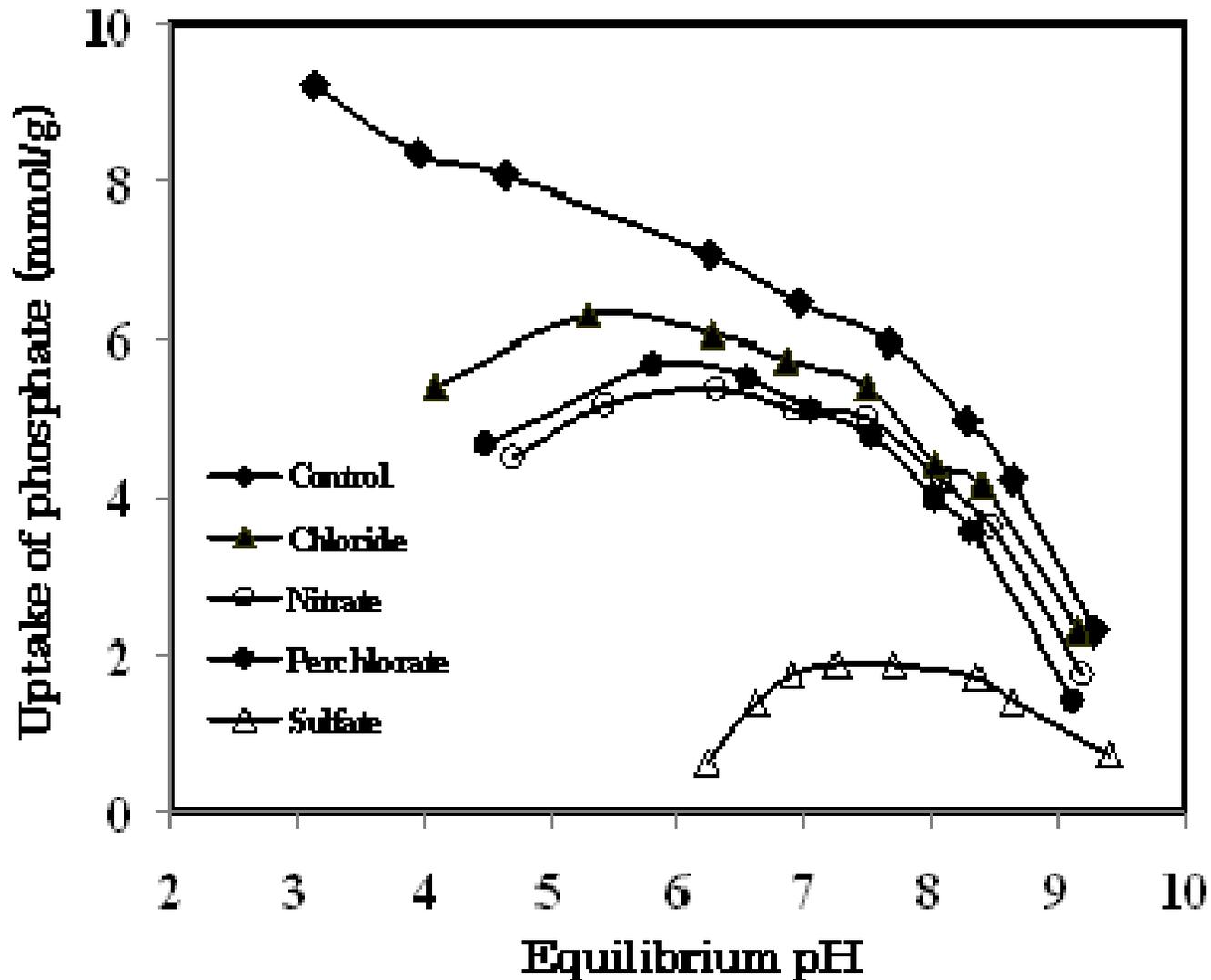
Competing anion to phosphate molar ratio is 5.

In the Absence of Competing Anions

With an increase in pH, phosphate uptake markedly decreased. This pH profile can be explained by combined effects of the decrease in mole fraction of protonated sites in the resin and an increase in mole fraction of divalent phosphate species in solution with an increasing in pH.

pKa = 9.7
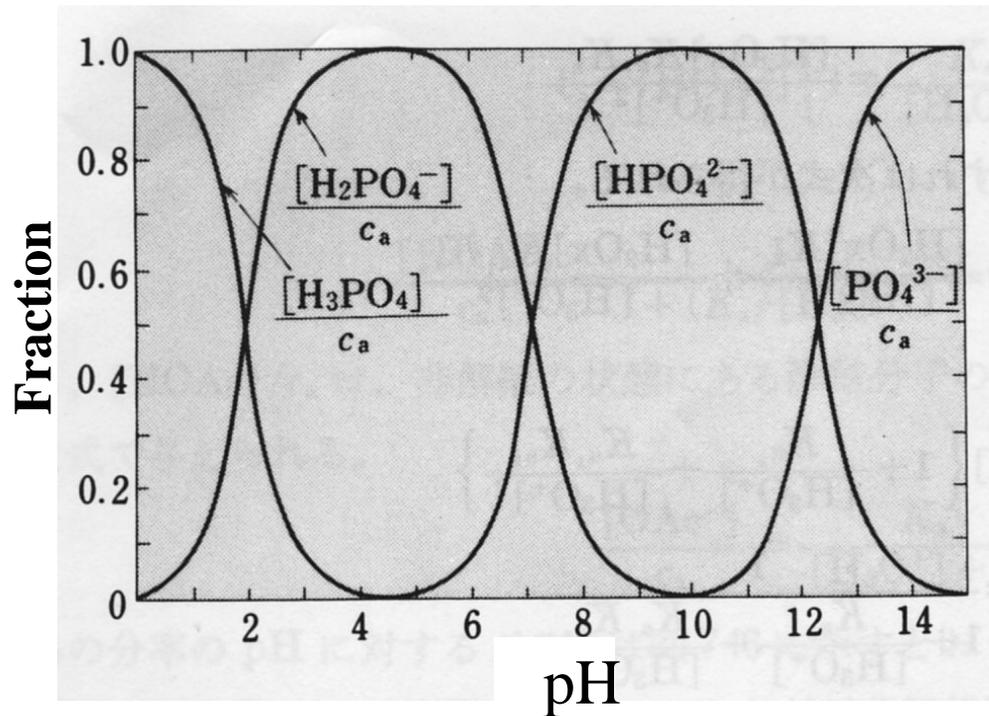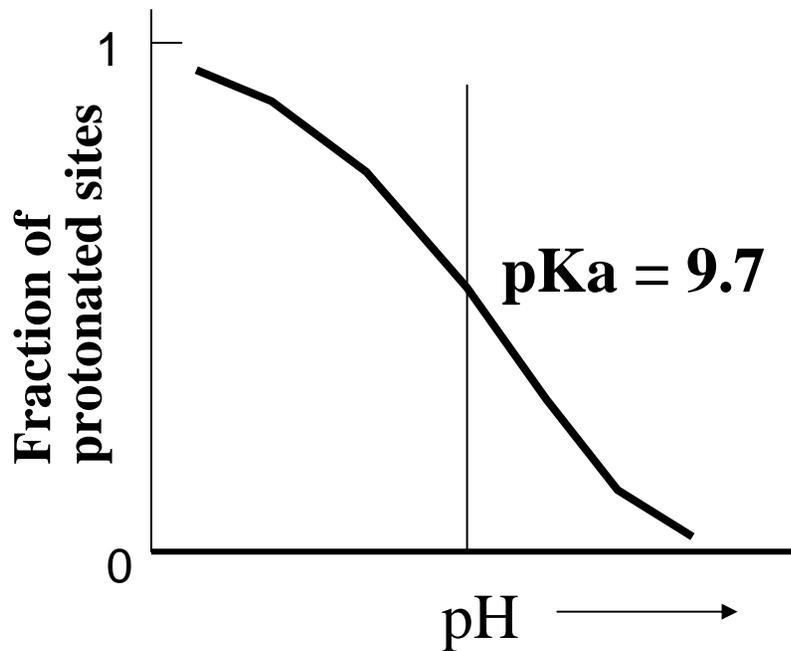
Effect of Cl^-, NO_3^-, ClO_4^-

Basicity of Cl^-, NO_3^-, and ClO_4^- is so weak that hydrogen bond formation is difficult to occur. Basicity of $H_2PO_4^-$ ($pK_b = 11.9$) is also low and phosphate uptake was interfered with these univalent anions to some extent below pH 6.

Above pH 7, dominant phosphate species is divalent anion HPO_4^{2-}. Then, interference of univalent anions decreased because of electroselectivity and hydrogen bond formation of HPO_4^{2-} ($pK_b = 6.8$) with protonated sites.

Effect of Sulphate

Although interference of sulphate is marked below pH 6, interference is reduced above pH 6.

High interference below pH 6 can be explained by electroselectivity.

Above pH 7, dominant phosphate species is HPO_4^{2-} (pK_b=6.8). HPO_4^{2-} will be able to form the following complex through hydrogen bond.

$$HPO_4^{2-} \; + \; 2RNH^{3+} \; \rightleftarrows \; (2RNH_3^+ \cdot HPO_4^{2-})$$

Because pK_b of SO_4^{2-} is 12.1, SO_4^{2-} is difficult to form hydrogen bond. Then, PAA resin prefers HPO_4^{2-} to SO_4^{2-}.

Sammary of Anion Selectivity Sequence of PAA Resin

pH: between 7 and 9

Hydrogenphosphate (HPO_4^{2-}) > Sulphate (SO_4^{2-}) >> ClO_4^- ≈ NO_3^- ≥ Cl^-

pH: less than 6

Sulphate (SO_4^{2-}) > dihydrogenphosphate ($H_2PO_4^-$) > ClO_4^- ≈ NO_3^- ≥ Cl^-

3. Column-mode study: Phosphate uptake under high flow rates of feeds

Column

Feed: Concentration of phosphate = C_o

Inner diameter of column: 1.3 cm

PAA resin in free base form (0.27g)

Filter
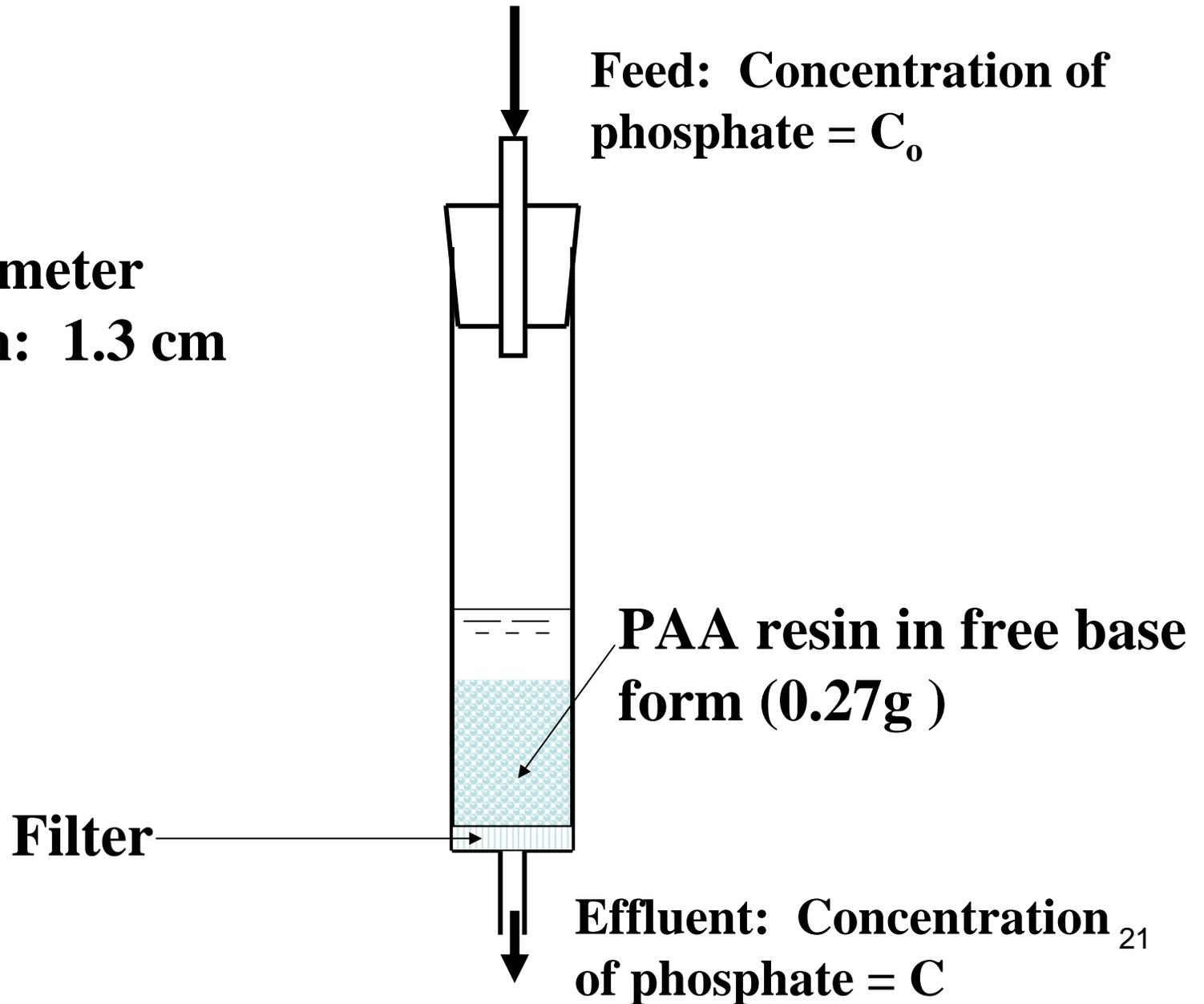
Effluent: Concentration of phosphate = C

Column Operations

2 M HCl 60 mL at 7 mL/h (3.5 h^{-1} in SV), Resin bed volume 1.4 mL

↓

Water 100 mL at 20 mL/h (10 h^{-1} in SV), **Resin bed volume 2.0 mL**

Used as the reference volume

↓

Adsorption: Supply of phosphate feeds under various conditions

↓

Water 60 mL at 20 mL/h (10 h^{-1} in SV)

↓

Elution and regeneration: 2 M HCl 60 mL at 7 mL/h (3.5 h^{-1} in SV)
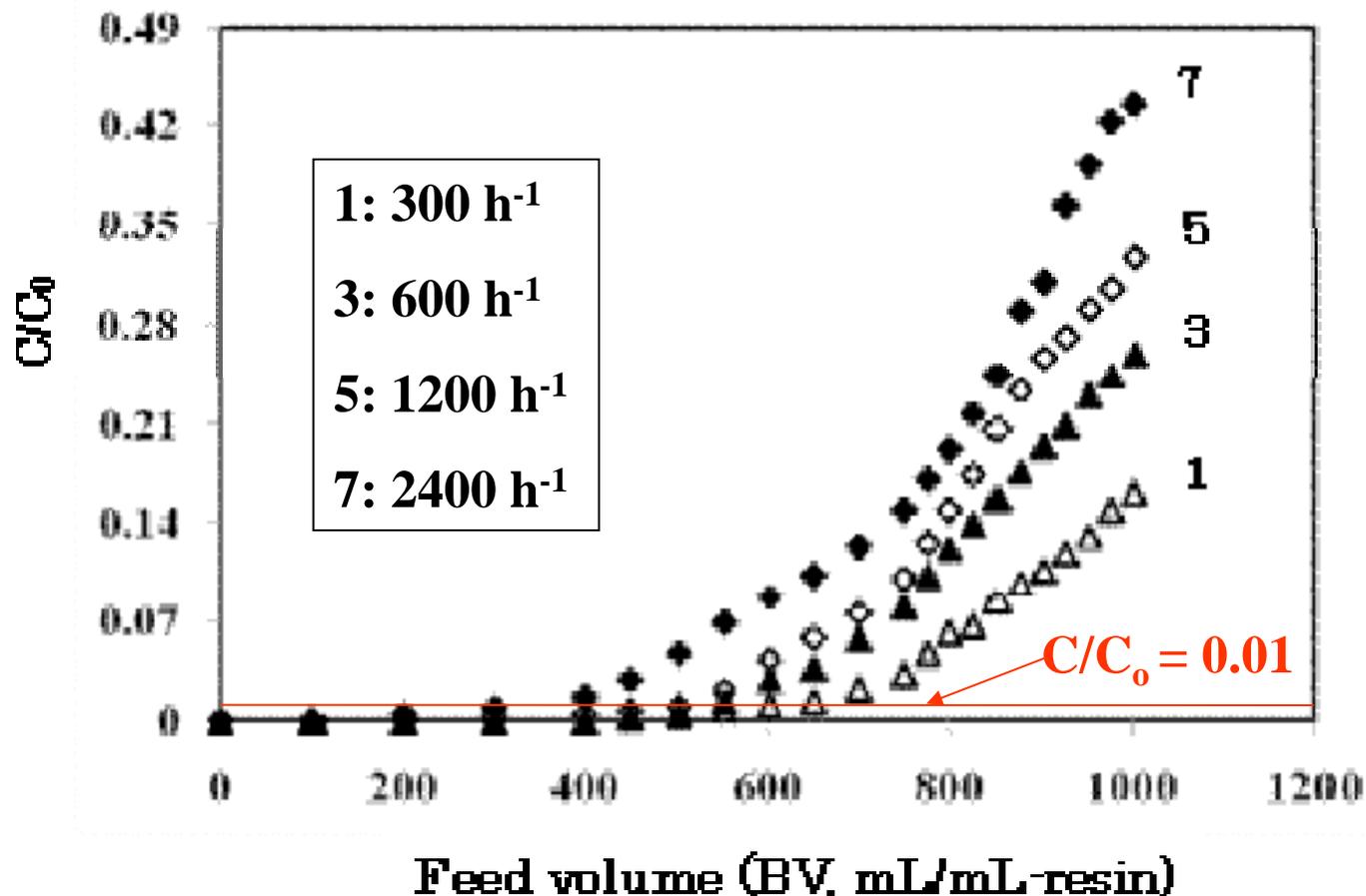
Definition of Breakthrough Parameters

Breakthrough point of phosphate:
   Feed volume in bed volumes (BV)
   up to $C/C_o = 0.01$.

Breakthrough capacity:
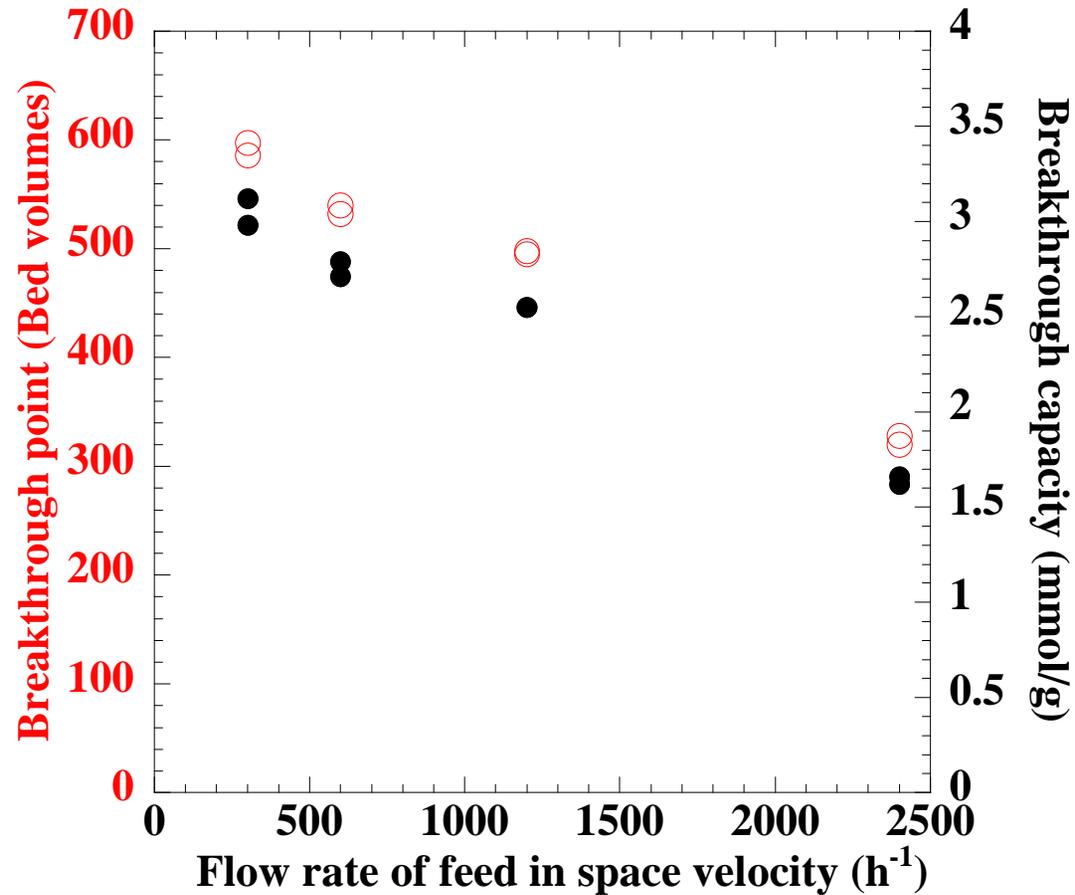   Phosphate uptake up to breakthrough point in mmol/g.

Effect of Flow Rate of Feed

Inside the figure:

1: 300 h^{-1}

3: 600 h^{-1}

5: 1200 h^{-1}

7: 2400 h^{-1}

$C/C_o = 0.01$

Y-axis: C/C_0

X-axis: Feed volume (BV, mL/mL-resin)
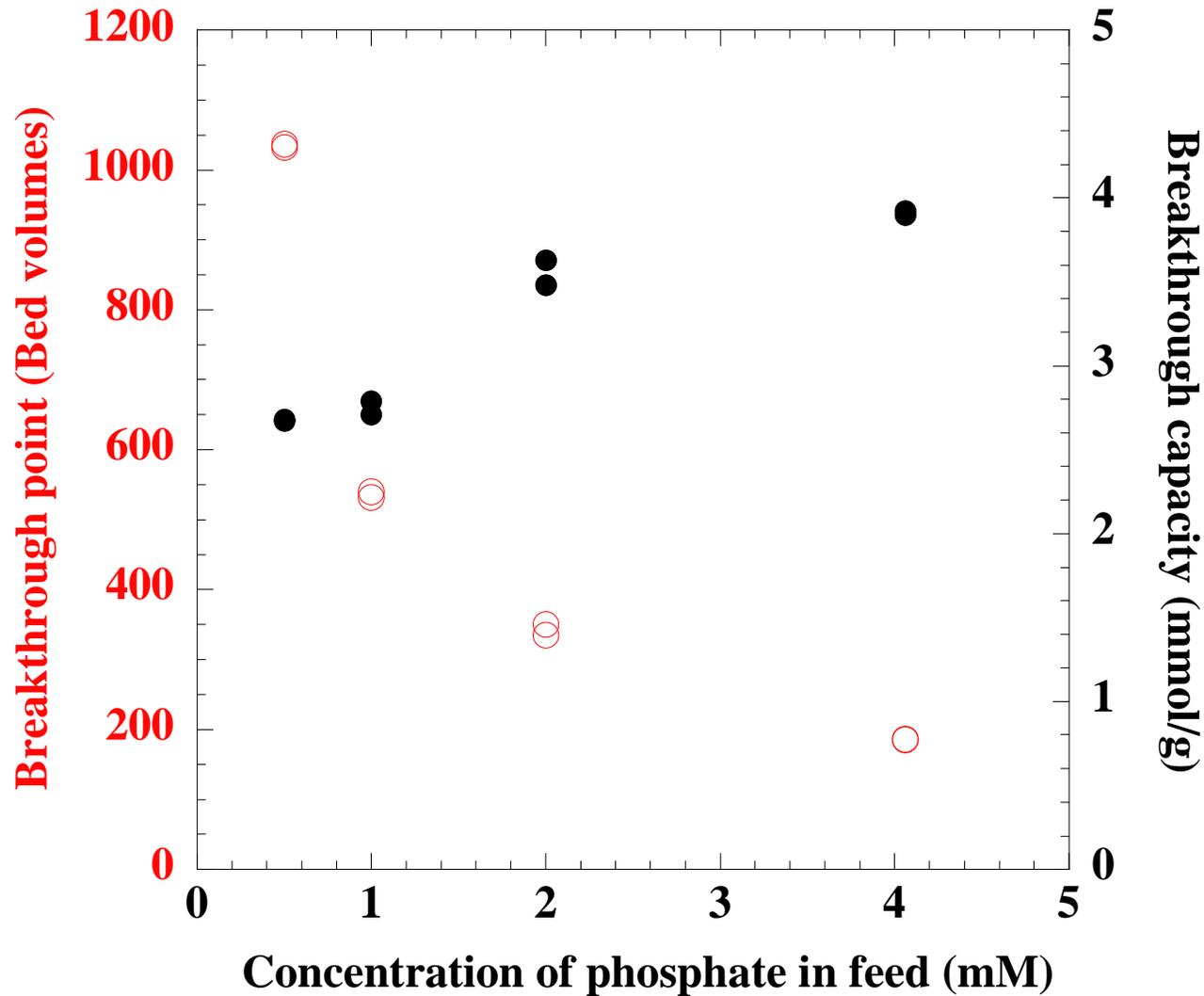
Feed: 1.0 mM phosphate, pH ca. 7.0.

1, 3, 5, 7: run No. Refer to Table 1
(Proceedings of IEX2008, p.492)
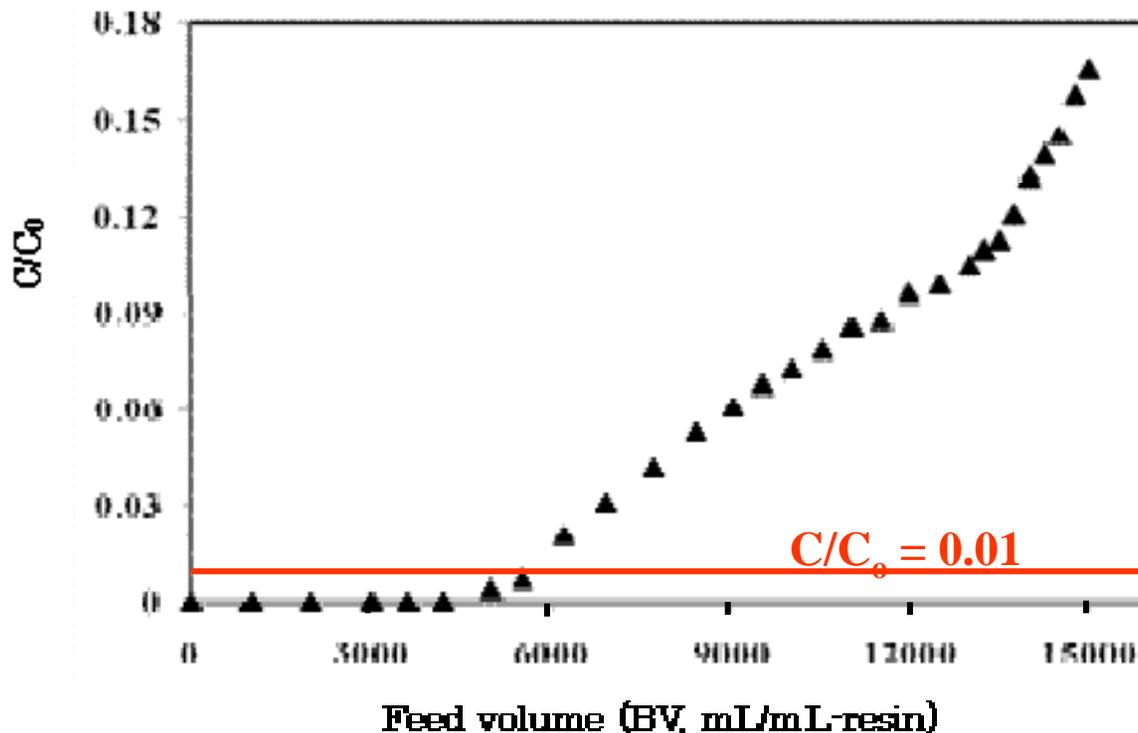
Effect of Feed Flow Rates on Breakthrough Parameters

Feed: 1.0 mM phosphate, pH ca. 7.0

Effect of Phosphate Concentration in Feed on Breakthrough Parameters

Feed: 0.5 – 4 mM phosphate, pH ca. 7.0. Flow rate of feed: 600 h^{-1}
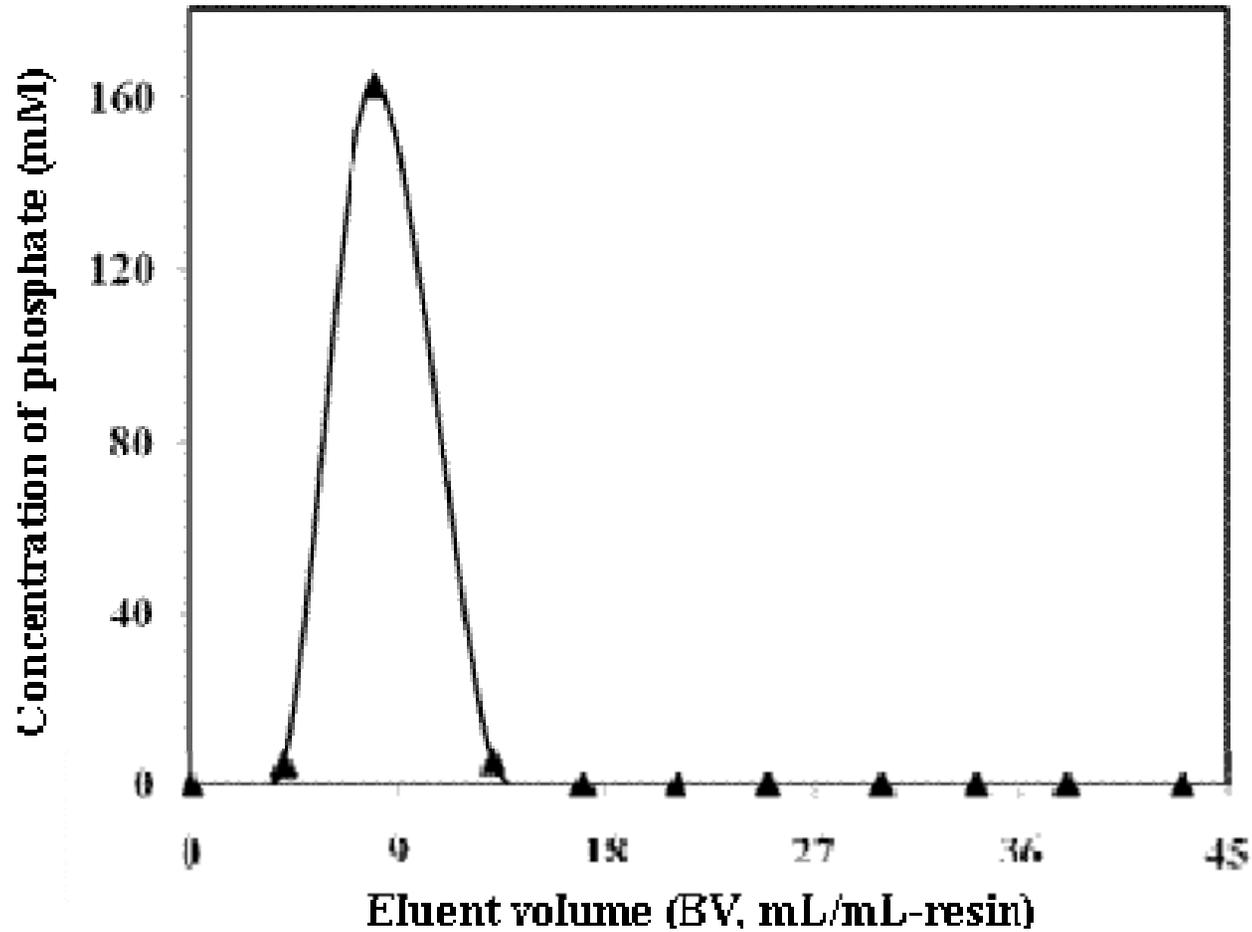
Rapid Removal of Phosphate from Dilute Solution of Phosphate

Breakthrough points for 1st and 2nd runs:
  5700, 5650 BV

Breakthrough capacities for 1st and 2nd runs:
  1.03, 0.97 mmol/g

$C/C_o = 0.01$

Feed. 0.035 mM phosphate (1.1 ppm of P) pH 7.
Feed flow rate: 3500 h^{-1}

Elution with HCl

Eluent: 2 M HCl, flow rate: 3.5 h^{-1} run No. 16.

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Elution and Recovery

Elution reaction

$$(RNH_3^+ \cdot H_2PO_4^-) \; + \; HCl \; \rightleftarrows \; (RNH_3^+ \cdot Cl^-) + H_3PO_4$$

$$(2RNH_3^+ \cdot HPO_4^{2-}) \; + \; 2HCl \rightleftarrows 2(RNH_3^+ \cdot Cl^-) \; + \; H_3PO_4$$
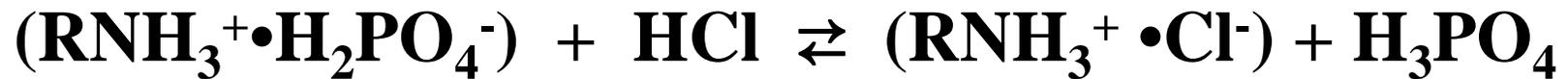
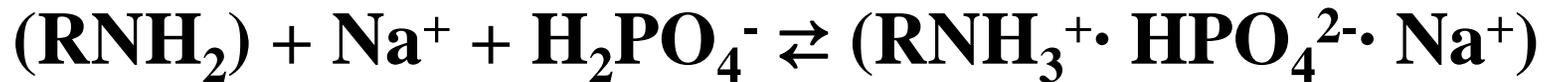**Percentage recoveries for 16 runs**
$102.9 \; \pm \; 3.5$

Summary

Crosslinked polyallylamine resin (PAA) exhibits a non-Hofmesiter anion selectivity sequence and high equilibrium capacities of 2.3 – 9.2 mmol of phosphate/g depending on pH.

Because of its non-Hofmeister behaviour, interference of chloride, nitrate, and perchlorate is minor. Even sulfate does not so strongly interfere with uptake of phosphate compared with strong base resins.

PAA exhibits breakthrough capacity as high as 1 mmol of P/g in uptake of phosphate from low concentration level of phosphate (1 ppm as P) at the high flow rate of 3500 h^{-1}.

Thank you for your attention.

Uptake of phosphate by PAA in free amine form from phosphate solutions

$$(RNH_2) + H_3PO_4 \;\rightleftarrows\; (RNH_3^+\cdot H_2PO_4^-)$$
$$(RNH_2) + Na^+ + H_2PO_4^- \rightleftarrows (RNH_3^+\cdot HPO_4^{2-}\cdot Na^+)$$

Uptake of phosphate by PAA in hydrochloride form from phosphate solutions

$$(RNH_3^+\cdot Cl^-) + H_2PO_4^- \rightleftarrows (RNH_3^+ \cdot H_2PO_4^-) + Cl^-$$
$$2(RNH_3^+ \cdot Cl^-) + HPO_4^{2-} \rightleftarrows (2RNH_3^+ \cdot HPO_4^{2-}) + 2Cl^-$$