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## A TWO PHASE MODEL FOR THE BINDING OF CATIONS TO LONG-CHAIN POLYPHOSPHATE ANIONS

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Abstract Binding of uni- and divalent cations to long-chain polyphosphate anions was investigated in the presence of excess uni-univalent salt. It was concluded that the binding occurs mainly in a "territorial binding" mode, i.e., most of the bound cations move freely within a specified volume around the polymer. Intrinsic complex formation (site binding) should be expressed as an equilibrium in the polymer phase.

### INTRODUCTION

Binding of univalent or divalent cations to negatively charged linear polymers in solutions containing excess uni-univalent salt is of interest from both practical and theoretical viewpoints<sup>1,2</sup>. In particular, quantitative interpretation of metal ion binding to polyelectrolytes with phosphate groups is needed to understand metal-induced phenomena in biological systems. Among synthetic and naturally occurring polyelectrolytes, long-chain polyphosphate anions, PP, have unique characteristics. PP is composed of the phosphate group itself; since the PP molecule does not have an organic backbone, this polymer may be regarded as one of the most hydrophilic polyelectrolytes, facilitating the theoretical treatment of the counterion-polyelectrolyte binding<sup>3</sup>. In this investigation, a potentiometric study was carried out for the systems of  $\text{HCl/PP/BCl}$ ,  $\text{AgNO}_3/\text{PP/BNO}_3$ , and  $\text{Cu(NO}_3)_2/\text{PP/BNO}_3$  ( $\text{B} = \text{Li, Na, K, (CH}_3)_4\text{N}$ ) at 25°C. Also a  $^{31}\text{P}$  NMR study was carried out on the  $\text{Zn}^{2+}/\text{PP}$  binding system in the presence of  $(\text{CH}_3)_4\text{NCl}$ .

### A POTENTIOMETRIC STUDY

The concentrations of free A,  $[A]$ , ( $A = H^+, Ag^+, Cu^{2+}$ ) in mixed solutions of A, PP, and excess B were determined by use of ion-selective electrodes. The binding isotherms (plots of  $\theta$ , i.e., the average number of A ions bound per one phosphate unit, vs  $\log [A]$ ) were obtained at different concentrations of B,  $[B]$ . From the plots,  $\log [A]$  values corresponding to a fixed  $\theta$  value were determined for different  $\log [B]$  values. A good linear relationship was obtained between  $\log [A]$  and  $\log [B]$  for the various  $\theta$  values. This empirical relationship can be expressed as follows:

$$\log [A] = s(\theta) \log [B] + \log k(\theta) \quad (1)$$

where  $s(\theta)$  and  $\log k(\theta)$  represent the slopes and the intercepts of the straight lines, respectively. Even though the variation in  $k(\theta)$  was large,  $s(\theta)$  values were almost constant and the limiting values for  $s(\theta)$  at  $\theta=0$  were 1 for the H/Li and Ag/Li systems and 2 for the Cu/Li system. This indicates that the binding of cations to PP anions can be treated as the cation exchange reaction of an A ion and B ion between the polymer phase and the bulk solution phase<sup>4</sup>, i.e., the binding of one  $A^{Z+}$  ion releases Z univalent counterions from the polymer phase (Fig. 1). If  $s(\theta)$  is equal to Z, then  $k(\theta)$  equals:

$$k(\theta) = \frac{1}{K_{ex}^A} \cdot \frac{[\bar{A}]}{[\bar{B}]^Z} \quad (2)$$

where the bar above A or B represents the exchanger phase and  $K_{ex}^A$  is a selectivity coefficient, defined as  $K_{ex}^A = \frac{[\bar{A}][B]^Z}{[A][\bar{B}]^Z}$ .  $[\bar{A}]$  and  $[\bar{B}]$  can be expressed as in eqns(3) and (4) by the use of  $\theta$ , the total capacity of PP exchanger,  $n_{PO_3}$ , and the polymer phase volume,  $V_P$ :

$$[\bar{A}] = \theta n_{PO_3} V_P^{-1} \quad (3)$$

$$[\bar{B}] = (1 - Z\theta) n_{PO_3} V_P^{-1} \quad (4)$$

Combining eqns(2), (3), and (4),  $k(\theta)$  can be expressed as

$$k(\theta) = \frac{1}{K_{\text{ex B}}^A} \cdot \frac{\theta}{(1 - Z\theta)^Z} \cdot \left( \frac{V_P}{n_{\text{PO}_3}} \right)^{Z-1} \quad (5)$$

When  $Z=1$ , i.e., A is a univalent cation, the volume term,  $V_P/n_{\text{PO}_3}$ , vanishes and the selectivity coefficient can be evaluated by use<sup>3</sup> of the corresponding  $k(\theta)$  value as,

$$K_{\text{ex B}}^A = \theta(1 - \theta)^{-1} k(\theta)^{-1} \quad (6)$$

Plots of  $K_{\text{ex B}}^A$  and  $k(\theta)$  vs  $\theta$  for Ag/Li system are shown in Fig. 2. The constancy of the  $K_{\text{ex B}}^A$  values in this  $\theta$  range in spite of the substantial variation in  $k(\theta)$  value also supports the model proposed here.

#### A $^{31}\text{P}$ NMR STUDY

The two phase model indicates the difficulty of a straightforward characterization of the intrinsic complex formation on PP anions in the thermodynamic study. Combination of thermodynamic data with spectroscopic information may give additional insight in this problem. Since it has been shown that the  $^{31}\text{P}$  NMR chemical shift ( $\delta$ ) of the middle phosphate group on the PP molecule is sensitive to the nature of countercations<sup>5</sup>, a  $^{31}\text{P}$  NMR study has been combined with a thermodynamic binding study in the system of Zn/PP. The binding isotherms were determined by means of a dye spectrophotometric technique<sup>6</sup>, which determines the free Zn concentration directly in the polyelectrolyte solution. The value of  $\delta$  was determined as a function of  $\theta$  in a solution containing  $(\text{CH}_3)_4\text{NCl}$  and  $(\text{CH}_3)_4^+\text{-PP}^-$  (0.02 monomole/L) (Fig. 3). The plots obtained at different ionic strengths are reduced to the same curve in Fig. 3, indicating that the shift depends only on the value of  $\theta$ , not on the ratio of the total amount of Zn to PP present<sup>5</sup>. The plots show a downfield shift at low  $\theta$  values followed by an upfield shift at higher  $\theta$  value ( $\theta \geq 0.25$ ).

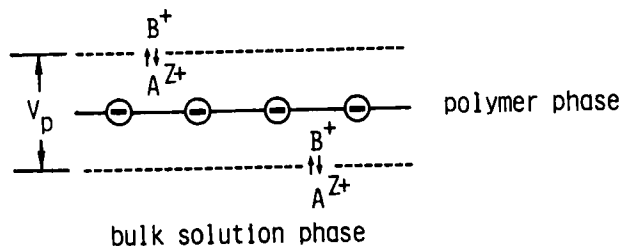


FIGURE 1 Cation exchange reaction between the PP polymer phase and the bulk solution phase.

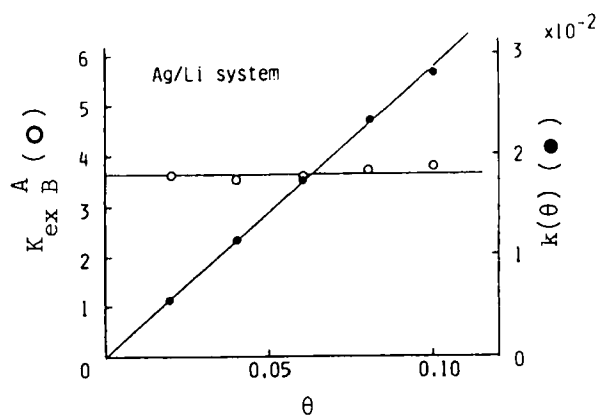


FIGURE 2 Selectivity coefficient of the Ag/Li exchange on the PP polymer.

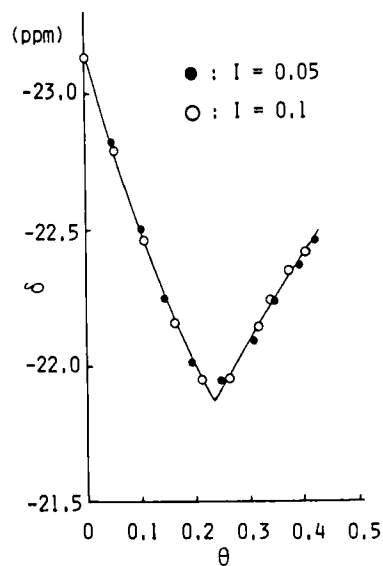


FIGURE 3  
Plots of  $\delta$  vs  $\theta$ .

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