

Specific Counterion Binding to Cationic Polyelectrolytes

CHARLES W. BURKHARDT, DENNIS P. PARAZAK, KEVIN J. MCCARTHY, and GEORGE J. JACKSON, *Petrolite Corp., 100 North Broadway, St. Louis, Missouri 63102*

INTRODUCTION

We have previously shown that the performance of a cationic polyelectrolyte used as a flotation aid in induced air flotation is an inverse function of the solvent quality of the water in which it is used. Its performance improves as the solvent becomes increasingly poor.¹

Following Flory² we define a θ solvent for a polymer as one in which the molecules are unperturbed and the second virial coefficient is zero. The solvent quality of water for a cationic polyelectrolyte can be altered by the addition of simple inorganic salts. Increased salt concentration provides increased charge shielding by the counterion until the molecules reach an unperturbed state. The solvent has become a θ solvent, and the salt concentration at this point may be conveniently called the θ salt concentration.

For many polyelectrolytes, when this θ salt concentration is exceeded, the polymer precipitates. Incipient phase separation, then, may be realistically used to approximate the θ salt concentration of an inorganic salt for a cationic polyelectrolyte.

In this note we show that the concentration of an inorganic salt needed to produce θ conditions for a cationic polyelectrolyte varies widely, and depends primarily upon the polarizability of the anion. This specificity, which has been known for some time³, results in a Hofmeister type of series which follows the sequence $\text{SCN}^- > \text{ClO}_4^- > \text{I}^- > \text{IO}_4^- > \text{MnO}_4^- > \text{Br}^- \text{NO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{HCO}_3^- > \text{HPO}_4^{2-} > \text{F}^-$. In this sequence SCN^- produces θ conditions at the lowest concentration, F^- the highest.

EXPERIMENTAL

The polymer used was poly(1,2 dimethyl-5-vinylpyridinium chloride). It was synthesized in our laboratories and quaternized to 20 mol% with methyl chloride. Polymer samples were exhaustively dialyzed and freeze dried before use. The degree of quaternization was determined from the chloride content of purified, dried samples. This polymer is a convenient choice since its combination of low charge density and hydrophobic segments cause it to precipitate at reasonably accessible salt levels.

The water used in all experiments was distilled deionized water. The inorganic salts were reagent grade and used as received. pH was maintained at $9 \pm .2$ units with dilute sodium or ammonium hydroxide. All experiments were run at room temperature, $23 \pm 2^\circ\text{C}$.

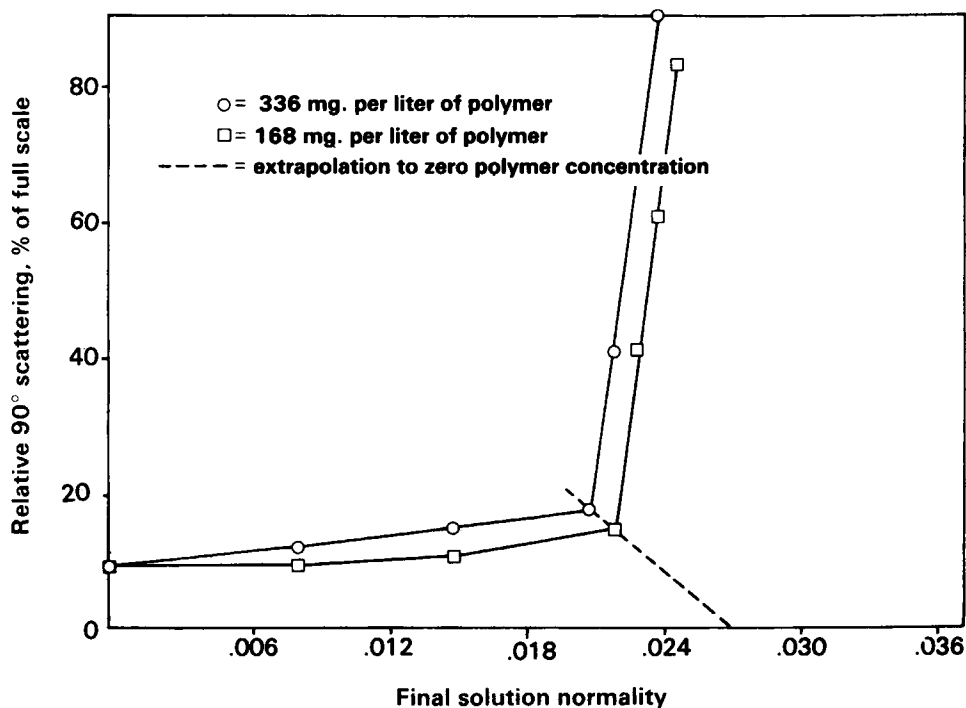


Fig. 1. Polymer solutions titrated with 0.1 M KNO_3 .

Incipient phase separation was determined by monitoring the relative scattering at 90° from dilute polymer solutions as a function of added salt. The instrument was a Brice-type photometer⁴. Unpolarized radiation of 436 nm was used. First, 50 mL of solution containing 10 to 15 mg of polymer were placed in a semioctagonal cell in the instrument, and the phototube voltage adjusted to give about 2 to 2 1/2% of full scale reading. Aliquots of standard salt solution were added to the cell from a buret through small bore Teflon tubing. The solutions were stirred magnetically to ensure complete mixing and the stirrer turned off. Readings were taken when the output signal reached a steady state. This process was repeated with slightly more concentrated polymer solutions containing 20–30 mg of polymer in 50 mL. Relative scattering was plotted against the final normality of the salt in the solutions. Figure 1 is a plot of the data obtained with KNO_3 .

Since the onset of increased scattering is concentration dependent we extrapolated through the breaks in the curves to zero polymer concentration for θ_s .

RESULTS AND DISCUSSION

The results are listed in Table I. Theta salt concentrations, (θ_s), are given in ionic strength according to the equation:

$$I = \frac{1}{2} \sum_i C_i z_i^2$$

where C_i is in moles per liter.

TABLE I
Theta Salt Concentrations

Salt	Ionic strength for theta condition (in molarity)
NaF	0.43
K ₂ HPO ₄	0.42
NaHCO ₃	0.19
K ₂ SO ₄	0.14
NaCl	0.092
NH ₄ Cl	0.106
KBr	0.027
KNO ₃	0.027
KMnO ₄	0.0057
KIO ₄	0.0025
KI	0.0017
KClO ₄	0.0015
KSCN	0.0013

TABLE II
Ionic Radii Values

Ion	ri (Å)
F ⁻	1.36
HPO ₄ ²⁻	3.00
HCO ₃ ⁻	2.78
SO ₄ ²⁻	2.92
Cl ⁻	1.81
Br ⁻	1.96
NO ₃ ⁻	2.68
I ⁻	2.16
ClO ₄ ⁻	2.94
SCN ⁻	2.65

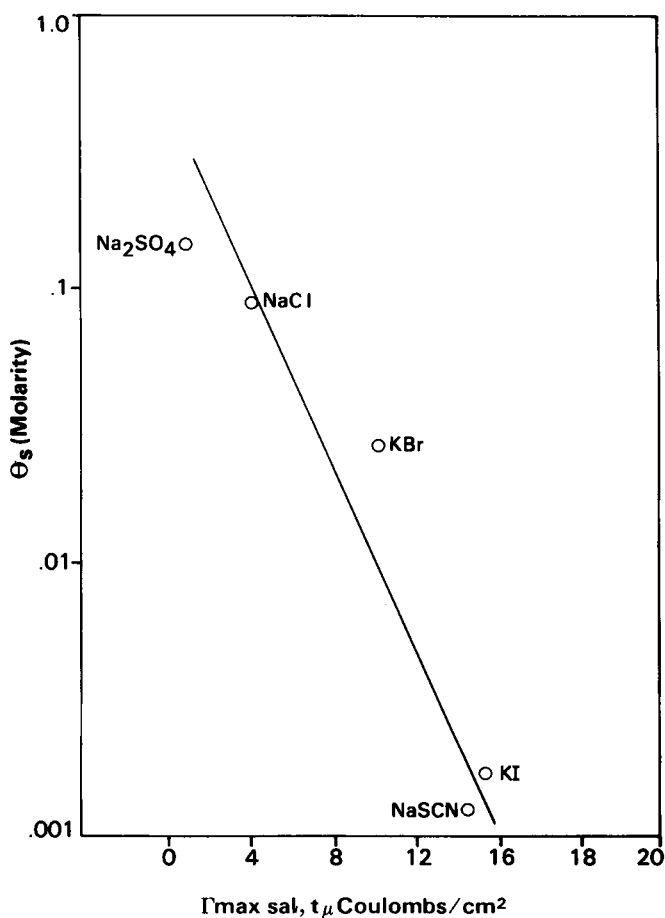


Fig. 2. $\log \theta_s$ as a function of surface excess, Γ , at the electrocapillary maximum.

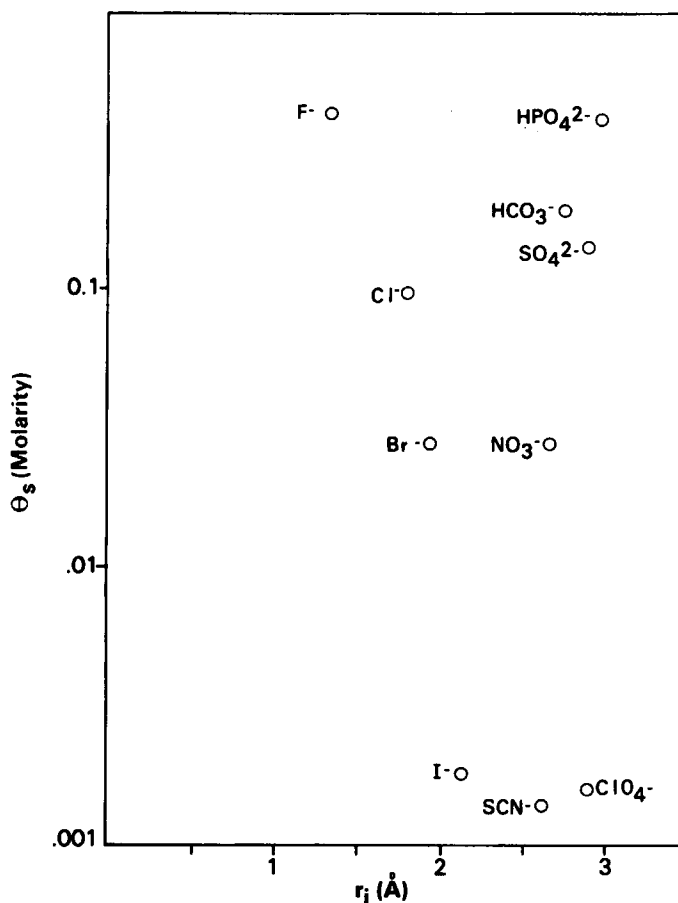


Fig. 3. Plot of $\log \theta_s$ as a function of ionic radii.

In the remainder of this note we will examine the validity of the titration procedure, and show that the specific behavior of an anion toward a cationic polymer is related to the anion's polarability.

It is reasonable to assume that an inorganic anion will adsorb onto a positive charge located on a polymer chain in much the same way it will adsorb onto a positive charge located at a polarized mercury solution interface. A simple way to verify this assumption and check the validity of our titration procedure is to plot $\log \theta_s$ as a function of Γ ; the salt adsorption density at the electrocapillary maximum. Such a plot is shown in Figure 2. The data was taken from Adamson.⁵

The correlation shown in Figure 2 is quite good and provides evidence that the titration procedure has validity.

To determine if anion size determines their specificity, we have plotted $\log \theta_s$ as a function of ionic radii. Table II lists the value of ionic radii.

This data is shown in Figure 3. There is little overall correlation between anion adsorption density and ionic size.

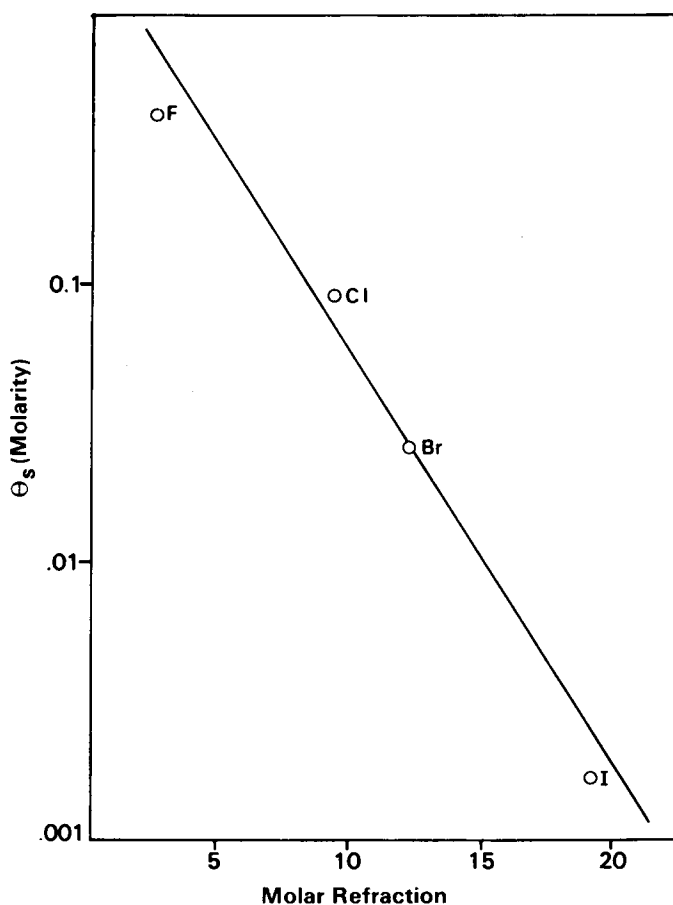


Fig. 4. Plot of $\log \theta_s$ as a function of molar refraction for the Halides.

Effective charge shielding requires close approach for the anions. Since ionic size is only partially responsible for this closeness of approach, it must be provided by ionic polarizability. Figure 4 is a plot of $\log \theta_s$ as a function of molar polarization of the halides. This relationship is essentially the same as one shown by Gregor et al.,³ in their plot of the binding of the halides to anion exchange resin as a function of halide ion molar refraction.

We have found two other correlations which indicate that polarization is the primary factor that determines the extent of anionic binding to cationic polyelectrolytes. These are shown in Figures 5 and 6.

Figure 5 is a plot of $\log \theta_s$ as a function of the strength of the oxyacids. The effectiveness of a particular anion as a precipitant for a cationic polyelectrolyte is very dependent on the relative strength of the protonic acid in water. As seen in Figure 5, there is good correlation between the ionic strength of a theta salt solution and the dissociation constant of the protonic acid in water. The stronger the protonic acid, the more effective, or specific, is the counterion.

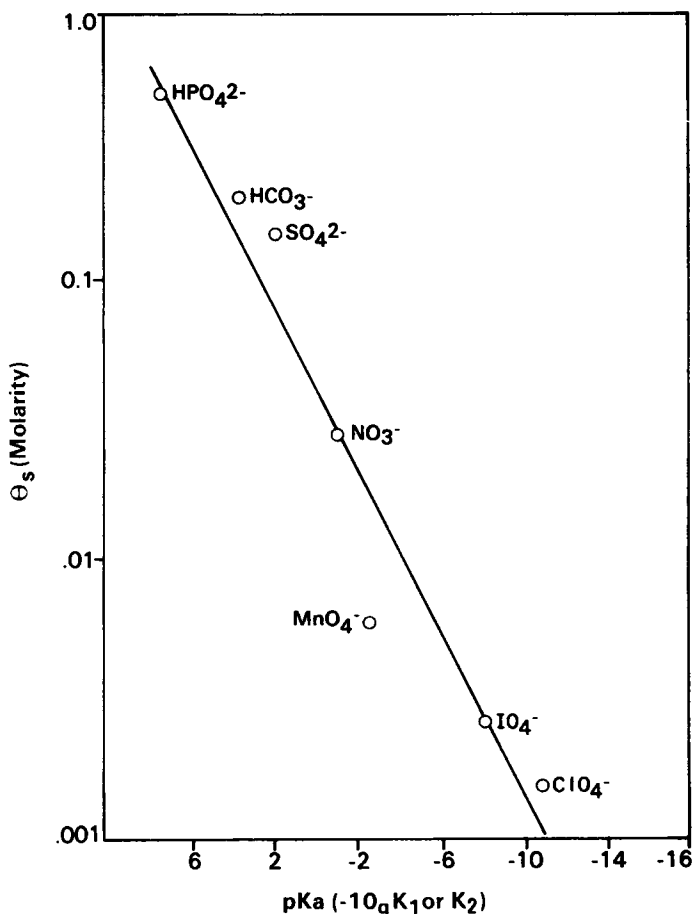


Fig. 5. Plot of $\log \theta_s$ as a function of pKa for the oxyacids.

This phenomenon can be explained by the principle of charge dispersal which relates the effects of electronic charge distribution to the acidic strength of a molecule. A strong acid readily loses a proton to form a very stable electronic structure and the negative charge or electron density can be dispersed over the entire molecule from the electronegative site. The anion is very stable and its tendency to accept a proton is low. The stabilization of the anion by electron density diffusion is influenced by ionic size, available surface for charge distribution, and the extent of π bonding or resonance. Extended π bonding promotes charge dispersal. The more delocalized is the negative charge, the more acidic the molecule. This is particularly true of the oxyanions tested, but is not applicable to the binary acids.

Since the strong protonic acids exhibit the greatest counterion specificity, it is apparent that the electron density distribution over the entire ion is the important parameter in determining the anion's effectiveness as a polyelectrolyte precipitant. It is quite easy to visualize. A large anion with a high degree of charge delocalization will provide more effective shielding than an anionic counterion where the electronic charge is highly localized.

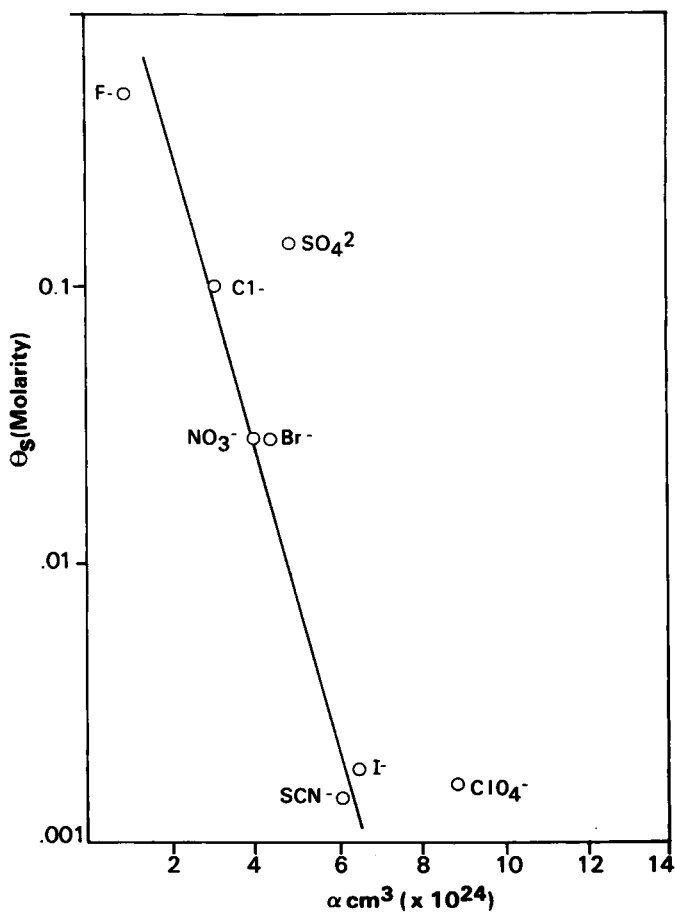


Fig. 6. Plot of $\log \theta_s$ as a function of ionic polarizability

Figure 6 is a plot of $\log \theta_s$ as a function of ionic polarizability. The data for the oxyanions and halogens is from Shanker and Agarwal.⁶ The correlations shown in both figures are quite good. The exceptions are the ionic polarizability of ClO_4^- and SO_4^{2-} . The value for ClO_4^- is assigned,⁷ and may well be somewhat high. We cannot explain the discrepancy in the case of SO_4^{2-} except to note that the percent double bond character which can be assumed between the S-O bond in SO_4^{2-} is not the same as that, for example, between the Cl-O bond in ClO_4^- .

We have shown that for some cationic polyelectrolytes the extent of specific counterion binding may be conveniently estimated by a simple titrimetric procedure, that the pronounced specificity shown by inorganic anions is primarily a function of ionic polarizability, and that concepts concerning specific ion binding to cationic polyelectrolytes may well be evaluated at a polarized mercury/water interface.

On the more practical side, it is possible, with the proper selection of counterions, to study the behavior of cationic polyelectrolytes under near

theta conditions at remarkably low salt levels, so as not to additionally perturb the system under study.

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