

COUNTERIONS CONTRIBUTIONS IN POLYELECTROLYTE ADSORPTION

I. POCHARD, P. COUCHOT, C. GEFFROY, A. FOISSY and J. PERSELLO

Université de Franche-Comté¹

INTRODUCTION

Polyelectrolytes are often used in industrial processes involving suspensions. Their dispersive properties in colloidal suspensions make them interesting in many fields of science and engineering including paper and paint industries, boring fluids or water treatment.

The adsorption of polyion onto colloidal particles can be greatly influenced by the presence of cations in the solution. Actually, complexation can occur between cations and polymer changing conformational and electrostatic properties of the polyion.

The aim of this study is to characterize the interactions between sodium polyacrylate and two different cations, calcium II and baryum II to determine how they contribute to the adsorption process.

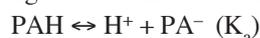
Experimental techniques employed for this study are potentiometric titrations of polyacrylic acid in order to determine acid/base properties of sodium polyacrylate under various salts conditions, ion selective electrode analyses of free Ca^{2+} and Ba^{2+} throughout the interaction of these cations with sodium polyacrylate. Finally, calorimetry is involved to measure binding energies of divalent ions onto sodium polyacrylate.

RESULTS AND DISCUSSION

Acid/base behavior of sodium polyacrylate

The protonation constant [1]

We calculated the protonation constant of sodium polyacrylate from the results obtained with the potentiometric curve. It agrees with the following reaction:



(1) Laboratoire d'Electrochimie et des systèmes microdispersés,
16, route de Gray,
25030 Besançon - France

where PA^- stands for acidic groups along the chain. Therefore:

$$K_a = \frac{[\text{PA}^-][\text{H}^+]}{[\text{PAH}]} \quad \text{and} \quad \text{p}K_a = \text{Log} \frac{[\text{PAH}]}{[\text{PA}^-]} + \text{pH}$$

If α is the degree of dissociation of the polymer, the latter equation becomes:

$$\text{p}K_a = \text{Log} \frac{1 - \alpha}{\alpha} + \text{pH}$$

Hence, as opposed to monoacid behavior, the protonation constant of a polymer changes with its degree of dissociation. This equilibrium constant includes in fact an electrostatic and chemical contribution:

$$\text{p}K_a = 0.4343 \frac{\Delta G_{\text{el}}}{kT} + \text{p}K_{\text{int}}$$

$\text{p}K_{\text{int}}$ is the intrinsic protonation constant. It can be evaluated by several calculation models, but we estimate with reasonable accuracy that it is equal to $\text{p}K_a$ at $\alpha = 0$ [23]. Thus, for our system, $\text{p}K_{\text{int}}$ is about 4,6 which agrees with values in the literature [2] and [3].

Influence of the supporting electrolyte

We observe a difference in polyacid behavior in the presence of monovalent or divalent cations. Thus, monovalent cations interact only in an electrostatic way with polyelectrolytes whereas divalent ones are complexed by them. In the first case, the decrease in $\text{p}K_a$ values is only due to the screening effect and in the second case, ionized groups of the polyion are complexed by cations. Furthermore, Figure 3 shows that complexation of Ca^{2+} (or Ba^{2+}) is not hindered by the presence of a 1:1 electrolyte. Finally, a difference in the influence of calcium II and baryum II is not apparent even though baryum seems to be more strongly complexed than calcium.

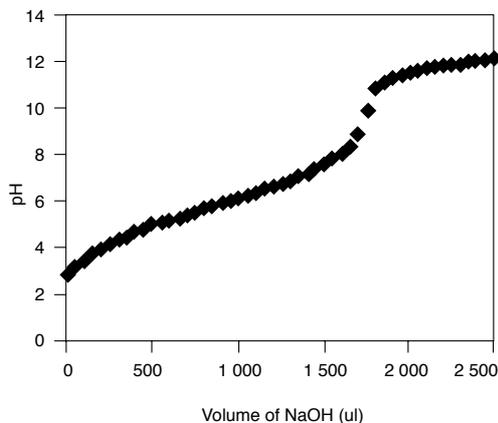


Figure 1
Potentiometric curve of polyacrylic acid.

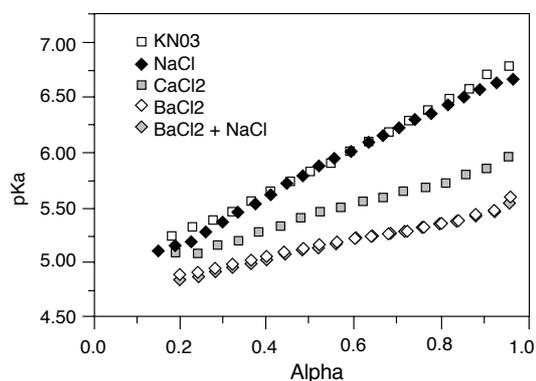


Figure 2
Protonation constant versus degree of dissociation for polyacrylic acid.

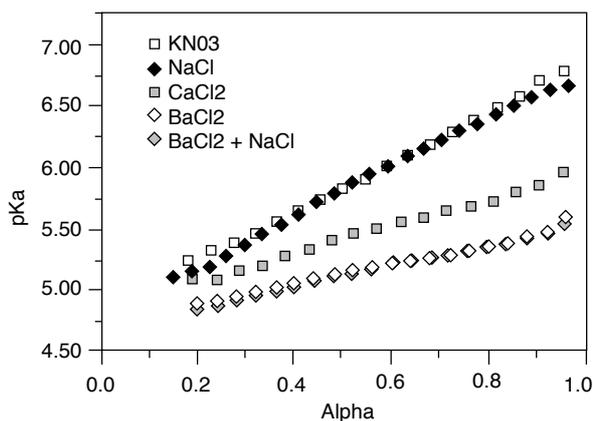


Figure 3
Influence of the support electrolyte on protonation constant of polyacrylic acid.

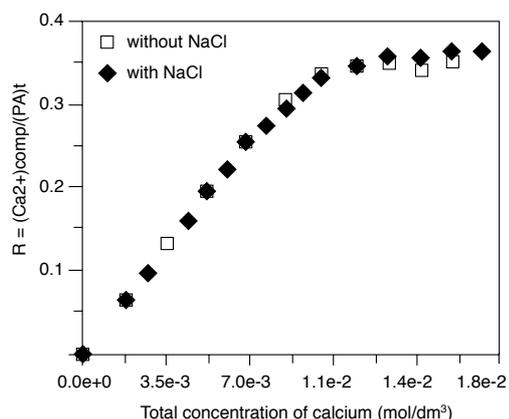


Figure 4
Complexation curve of sodium polyacrylate by calcium chloride.

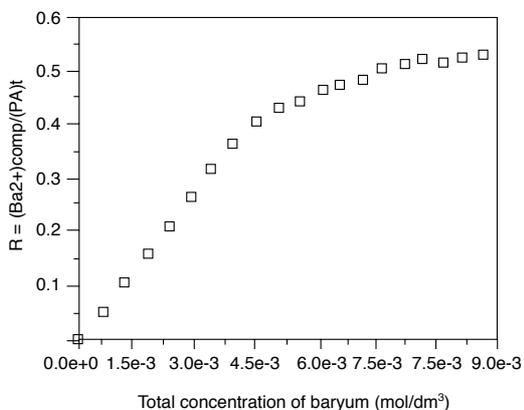


Figure 5
Complexation curve of sodium polyacrylate by baryum chloride.

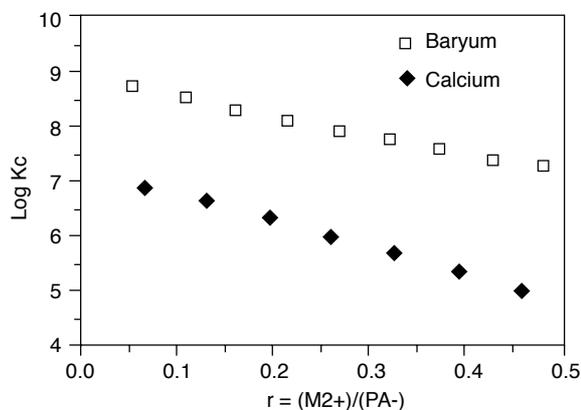


Figure 6
Complexation constant of calcium and baryum II on sodium polyacrylate versus ratio between cation concentration and monomer one.

Complexation of divalent ions by PANa

Figure 4 shows that monovalent ions have a negligible effect on the M^{2+} /PANa complexation. Figures 4 and 5 reveal that the complexation of calcium and baryum ions with sodium polyacrylate is bidentate, the number of complexed cations per total $[PA^-]$ being slightly lower than 0.5 at the end of neutralisation (especially for Ca^{2+}). This allows concluding that few functional groups on the polymer chain are not accessible for the divalent cations. Moreover, these results permit the calculation of the complexation constant of Ca^{2+} and Ba^{2+} on PANa in almost the same way as for the protonation constant:

$$M^{2+} + 2 PANa \leftrightarrow PA_2M + 2 Na^+ \quad (K_c)$$

$$K_c = \frac{[PA_2M]}{[M^{2+}][PA^-]^2} \quad \text{and} \quad \text{Log } K_c = \log \frac{[PA_2M]}{[PA^-]^2 [M^{2+}]}$$

$[M^{2+}]$ is measured with ISE; $[PA^-]$ is calculated from the initial concentration of polyacrylate in the solution taking into account the fraction of free Na^+ on PANa; $[PA_2M]$ is the difference between $[M^{2+}]$ added and $[M^{2+}]$ complexed. Results are shown in Figure 5.

The complexation constant values vary during the complexation reaction showing a decrease in the affinity of cations for the polymer as the polyion's charge decreases. Figure 6 reveals that baryum ions have more affinity for sodium polyacrylate than calcium.

Microcalorimetric measurements [4]

Microcalorimetric analyses exhibit a positive variation in enthalpy when the complexation reaction occurs for

the Ba^{2+} /PANa system and the Ca^{2+} /PANa one. These complexations are thus endothermic. Consequently, to obtain negative free energy, complexations have to be accompanied by desolvation of both counterions and polymer.

The variation of enthalpy when complexing baryum is slightly lower than for calcium/PANa interactions. This result corroborates those found in complexation analyses with ionic selective electrode technique. Hence, complexation of baryum on sodium polyacrylate is more favorable than complexation of calcium.

ACKNOWLEDGMENTS

The authors would like to thank l'Institut français du pétrole and in particular the applied chemistry, biotechnologies and materials divisions which have supported this work.

REFERENCES

- 1 Miyajima, Yoshida and Högfeldt (1993), *J. of Colloid and Interface Science*, **156**, 383.
- 2 Dupont (1993), *Thesis*, Besançon, France.
- 3 Fenyó, Laine and Muller (1979), *J. of Polymer Science*, **17**, 193.
- 4 Partyka, Lindheimer, Zaini, Keh and Brun, *Langmuir* (1986), **2**, 101.

Final manuscript received in January 1997