

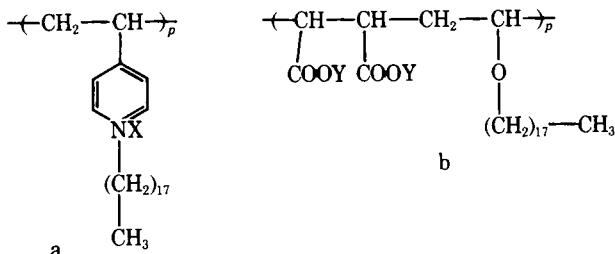
## Liquid-Liquid Ion Exchange Chromatography with Amphiphilic Polyelectrolytes

### INTRODUCTION

Although liquid ion exchangers are relatively new as compared with ion exchange resins, they have found increasing applications in the separation of metallic species in inorganic or analytical biochemistry and in the domain of large-scale applications for the recovery of rare earth and uranium.<sup>1,2</sup>

All known examples of liquid extractants with ion exchange properties involve a molecular ionogenic compound with a large solubility in water-immiscible organic liquids. There are several advantages of liquid ion exchangers in comparison with the resins. For instance, they have greater specificity toward ions, and since diffusion in the organic solution of a liquid exchanger proceeds faster than in the swollen ion exchange resins, separation efficiency is enhanced. However, up to now, most processes of ion exchange between liquid phases were limited to a small number of available molecular compounds including mainly aliphatic amines for anionic exchangers and alkyl esters of phosphoric or phosphonic acids for cationic exchangers.

In a recent work we have examined the behavior of long-chain amphiphilic polyelectrolytes which in the salt form are soluble in a number of water-immiscible organic solvents and fulfill the requirements for a liquid ion exchanger with selective properties. These compounds are anionic or cationic polyelectrolytes of the following chemical structure:



Polymer a is obtained by quaternizing poly(4-vinylpyridine) with *N*-octadecyl bromide. Polymer b is a 1-1 copolymer of maleic acid and octadecyl vinyl ether.

The use of polyelectrolytes is interesting from the following points of view:

1. A wide number of suitable polyelectrolytes might be synthesized easily at low cost. The exchange capacity of the polymers is large since an ionogenic group is attached to each hydrophobic residue.

2. Despite their high exchange capacity, the solubility of the polymers in water is very small and surface activity leading to the formation of emulsions is less pronounced than for low molecular weight surfactants. Actually, emulsion formation is very often encountered with small amphiphilic molecules, and this difficulty makes molecules like quaternary ammonium salts or sulfonic and carboxylic acids undesirable.

In the present paper, we shall outline some of the equilibrium and kinetic properties of the poly(4-vinyl-*N*-octadecylpyridinium) ion dissolved in *N*-octanol.\*

### EXPERIMENTAL

#### Materials

Poly(4-vinyl-*N*-octadecylpyridinium) salt was obtained by quaternization of poly(4-vinylpyridine) with *N*-octadecyl bromide in tetramethyl sulfone using the procedure of Fuoss et al.<sup>3</sup> The carefully purified polymer sample, after dilution in acidified methanol, was titrated potentiomet-

\* Investigations on liquid ion exchange and structural properties of the anionic polyelectrolytes were carried out and are reported elsewhere (R. Varoqui and E. Pefferkorn, in press in *J. Phys. Chem.*).

rically with  $5 \times 10^{-3}N$  silver nitrate and yielded a degree of quaternized pyridinium nitrogen of  $95 \pm 2\%$ . The average molecular weight was  $9.5 \times 10^4$ .

### Partition Coefficient Measurements

Partition coefficient data of ions were obtained by shaking a solution of 1 wt-% polymer in *N*-octanol in contact with an aqueous solution containing a mixture of two electrolytes of  $10^{-1}N$  total concentration. The composition of both phases was analyzed by means of radioactive isotope ions.

### Ion Exchange Chromatography

Chromatographic separation techniques which employ liquid ion exchangers such as Amberlite LA-1, di(2-ethylhexyl) phosphate, tricaprylmethylammonium chloride, or other materials as stationary phase have been described in the literature.<sup>4-6</sup> Our stationary phase in chromatographic columns was prepared by soaking porous glass beads (Spherosil XOC005, 100-200 mesh, specific surface  $10 \text{ m}^2/\text{g}$ , Rhône-Progil) in the polymer solution. Columns of  $22 \text{ cm} \times 0.754 \text{ cm}^2$  dimensions were used. In order to obtain a good packing, the excess organic solution on the surface of the beads was removed by controlled heating. The total exchange capacity was determined after saturation of the column with  $\text{Cl}^{36}$  and using  $0.03M$  *HBr* as eluant. Columns of total exchange capacity ranging from 1 to 4 mE (corresponding to 20 to 80 wt-% polyelectrolyte concentrations) were tested.

### RESULTS AND DISCUSSION

The data reported in Figure 1 are relative to the distribution of mono- and divalent anions against chloride using sodium as coion in the aqueous solution. The equivalent ionic fraction  $\beta$

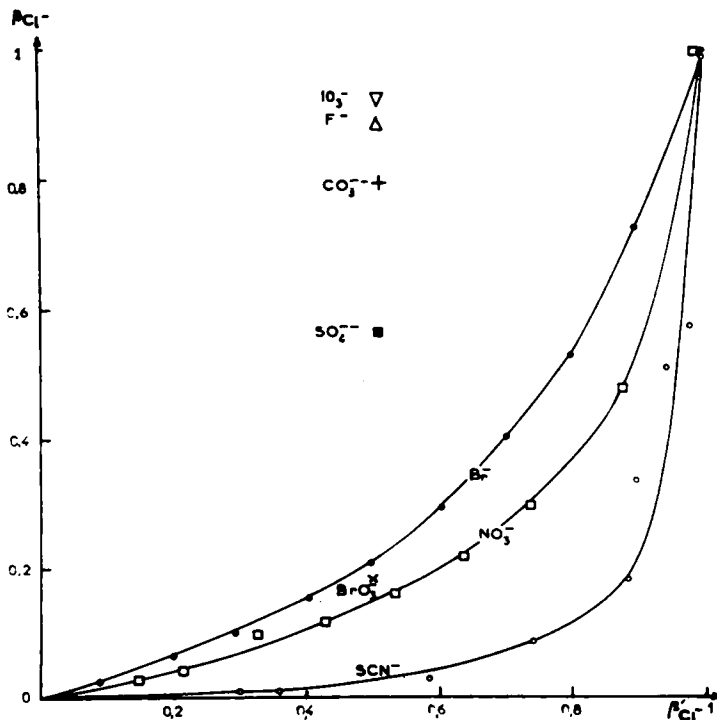
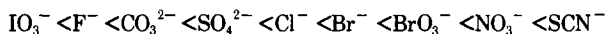


Fig. 1. Ion exchange isotherm for  $\text{Br}^-/\text{Cl}^-$  ( $\bullet$ ),  $\text{NO}_3^-/\text{Cl}^-$  ( $\square$ ), and  $\text{SCN}^-/\text{Cl}^-$  ( $\circ$ ) exchange at  $10^{-1}$  normality of the external solution,  $\text{IO}_3^-/\text{Cl}^-$  ( $\nabla$ ),  $\text{F}^-/\text{Cl}^-$  ( $\Delta$ ),  $\text{SO}_4^{2-}/\text{Cl}^-$  ( $\blacksquare$ ),  $\text{CO}_3^{2-}/\text{Cl}^-$  ( $+$ ),  $\text{BrO}_3^-$  ( $\times$ ) at  $\beta_{\text{Cl}^-} = 0.5$ .

of chloride in the octanol phase is represented against the equivalent ionic fraction  $\beta'$  of chlorides in the water phase. Full isotherms are given for the NaCl-NaBr, NaCl-NaSCN, and NaCl-NaNO<sub>3</sub> mixtures. Results at  $\beta'_{\text{Cl}} = 0.5$  are given for NaCl-NaIO<sub>3</sub>, NaCl-Na<sub>2</sub>SO<sub>4</sub>, and NaCl-Na<sub>2</sub>CO<sub>3</sub> mixtures. Since free-electrolyte invasion in the organic phase is exceedingly small ( $\approx 10^{-6}M$  for  $10^{-2}M$  salt in the aqueous phase), the equilibrium distribution is relative to counterions adsorbed on the polymeric sites in the low dielectric-constant octanol medium and those dissociated in the water phase.

The selectivity sequence is the following:



This order is the same as the one found in investigations on water-swollen polyelectrolyte resins<sup>7</sup>; however, in the present case much greater selectivities are observed.

Figure 2 gives the elution graph for a mixture of chlorides and bromides in a liquid-liquid partition elution chromatography experiment. The example of alkali chlorides, though trivial, is given here for the purpose of illustration of some characteristics of those columns. For the separation of the halides, the column was first saturated with 0.1N Na<sub>2</sub>SO<sub>4</sub>; then a 0.07-ml mixture of NaBr + NaCl, both halides at 0.25N, was adsorbed at the top of the column and subsequently eluted with 0.1N Na<sub>2</sub>SO<sub>4</sub>. The volume of solution fed during the charge period corresponds to  $\approx 2.2\%$  of the total column exchange capacity. The column characteristics for that experiment were the following: column exchange capacity, 1.6 mE; fractional void volume, 0.65; elution rate, 1.66 ml/min.

The circles represent analyzed fractions of the eluate, the continuous line drawn is the ideal elution graph according to the classical plate theory<sup>8</sup> with a number of theoretical plates equal to 56 for bromide and 39 for chloride. Perfect separation of chloride and bromide is obtained under these conditions. From the peak volume of the elution curve, the selectivity coefficient  $K_{\text{Cl}}^{\text{Br}}$  was calculated and found equal to 4.40. The equilibrium experiments gave a slightly smaller value of 3.70. It should be noted that in the equilibrium processes, the volume of the oil layer with respect to the interfacial area was always very large so that distribution data refer in that case to counterions in the bulk of both phases. On the other hand, in the ion exchange column,

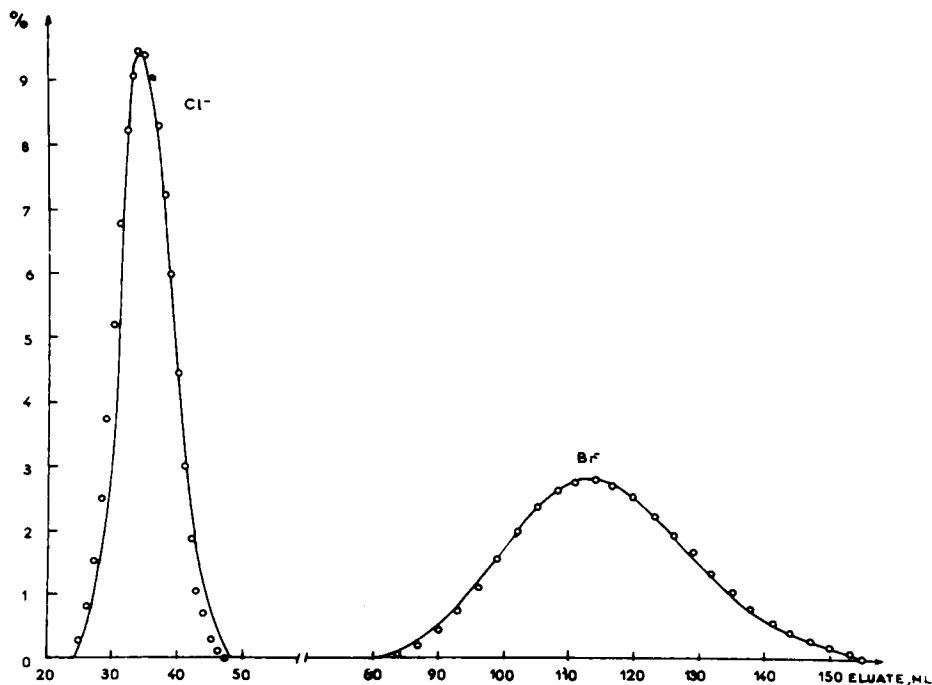


Fig. 2. Elution graph of halide mixture. Fraction of chloride and bromide in the eluate volume.

the surface-to-volume ratio is considerably increased so that surface exchange reactions controlled by the polymer adsorbed at the oil-water interface may occur with slightly different selective properties.

### CONCLUSIONS

The results of this study have shown that amphiphilic polyelectrolytes may be used as ionic carriers in achieving ion separations by liquid-liquid partition chromatography. Ordinary quaternary ammonium compounds can serve as liquid exchangers, but because of their solubility in water and tendency to form emulsions, their usefulness is very limited. The cationic polymers have the definite advantage of being completely insoluble in water and no change in properties—corresponding to the loss of some liquid exchanger—was detected in our column experiments after a great number of elution runs. Although the exchange capacity in the chromatographic experiments cannot exceed a value of approximately 0.5 mE per milliliter, fast reactions and high selectivities are gained with respect to the usual exchanger, and it may be expected that this particular class of long-chain polyelectrolytes can find applications for separations and purifications purposes in specific areas.

### References

1. W. Rieman III and H. F. Walton, *Ion Exchange in Analytical Chemistry*, Pergamon Press, Oxford, 1970, p. 226.
2. R. Kunin, in *Ion Exchange and Solvent Extraction*, J. A. Marinsky, and Y. Marcus, Eds., Marcel Dekker, New York, 1973, p. 155.
3. R. M. Fuoss, M. Watanabe, and B. O. Coleman, *J. Polym. Sci.*, **48**, 5 (1960).
4. R. J. Sochacka and S. Siekierski, *J. Chromatogr.*, **16**, 376 (1964).
5. J. F. Weiss and A. D. Kelmers, *Biochemistry*, **6**, 2507 (1967).
6. H. Freiser, *Anal. Chem.*, **40**, 522 R (1968).
7. R. M. Diamond and A. C. Whitney, *Ion Exchange*, Vol. 1, J. A. Marinsky, Ed., Marcel Dekker, New York, 1966, p. 277.
8. S. W. Mayer and E. R. Tompkins, *J. Am. Chem. Soc.*, **69**, 2866 (1947).

E. PEFFERKORN  
R. VAROQUI  
H. BENOIT

C.N.R.S.  
Centre de Recherches sur les Macromolécules  
6, Rue Boussingault  
67083 Strasbourg-Cedex, France

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