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Counterion Fractionation in the Osmosedimentation of Polyelectrolytes

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Abstract

Osmosedimentation of Na^+/K^+ poly(styrene sulfonate) aqueous solutions at 3000 rpm creates polyelectrolyte and counterion concentration gradients; Na^+ and K^+ gradients are not identical and Na^+/K^+ separation factors as high as 1.04 are obtained. Solutions of Na^+/K^+ Blue Dextran and poly(acrylate) were also examined, but in the last case there was no detectable separation of the two countercations. The results are interpreted by considering the differences in Na^+ and K^+ ion mobilities in water, as well as their relative binding abilities to the polyanions.

Key Words: Counterions; Polyelectrolyte osmosedimentation; Fractionation

INTRODUCTION

Sedimentation and centrifugation techniques are used in chemical separation in many ways. Practical use of these techniques ranges from decantation in the treatment of water and sewage to cell and biopolymer fractionation in molecular biology and biotechnology.

Thermodynamic analysis of sedimentation phenomena suggests that many additional separations might be performed by sedimentation, but these are prevented because of the slow sedimentation of small particles in viscous media (*1*, *2*).

As an example, consider the case of isotope enrichment by ultracentrifugation. This is done in the gas phase by using uranium hexafluoride (*3*), which is a rather untractable substance. In practice, this cannot be done

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by using solutions of UF_6 or UO_2^+ salts because sedimentation rates in these would be negligible, even at very high ultracentrifugation speeds.

Experimental work from this laboratory some years ago demonstrated that sedimentation rates can be greatly enhanced if dialysis cells instead of normal centrifuge tubes are used as solution containers (*4–7*). This enhancement is due to coupling of the osmotic and sedimentation mass currents (*8*, *9*), and the techniques based on this coupling were named osmosedimentation (under gravity) and osmocentrifugation (*10*).

These techniques allowed us to do a number of hitherto unpractical experiments: determination of polymer and particle $\overline{M}_w$s by sedimentation under gravity or in low-speed centrifuges, determination of the corresponding virial coefficients, polymer fractionation by weight, and generation of density gradients under low speeds (*11*).

In the present work we describe the behavior of Na^+/K^+ polyanion solutions in osmocentrifugation. This work is aimed at verifying the fractionation of low-MW species by osmosedimentation.

EXPERIMENTAL

Blue Dextran 2000 (BD) was obtained from Pharmacia as lot KH 38333; poly(acrylic acid) (PAA) was from Polysciences, lot 65134 (code 0627, $\overline{M}_w = 5 \times 10^4$), and poly(sodium styrene sulfonate) was from Aldrich, code 24, 305-1, lot 0201355.

The osmocentrifugation cells were built of acrylic or reinforced polyester sheets, following the usual design (*5*). The cells were 10 cm tall, each compartment had a 4.5 cm^3 volume, and the useful membrane area was 15 cm^2. The membranes used in these cells were cast according to previous work in this laboratory (*12*).

Prior to osmocentrifugation experiments, PAA was neutralized (within 0.3%) with an equimolar aqueous solution of NaOH/KOH. All polyelectrolyte solutions were dialyzed against equimolar aqueous solutions of NaCl and KCl. Electrolyte concentration varied during dialysis, so both initial and final concentrations are given in the tables in the Results Section.

Osmocentrifugation cells were filled with equal volumes of polyelectrolyte solution and NaCl/KCl solution of the same concentration used for dialysis. The cells were mounted in the swinging buckets of a Sorvall RC 3B centrifuge and spun under the conditions given in the Results Section.

RESULTS

Osmocentrifugation experiments were performed with the following polyelectrolytes as sodium and potassium salts: poly(styrene sulfonate)

(PSS), poly(acrylate) (PA), and Blue Dextran (BD). The last is a high-MW dextran to which an anionic, blue dye is covalently bound.

Osmocentrifugation runs were designed according to a three-variable, two-level factorial plan in which the variables are: initial polyelectrolyte concentration, initial total counterion concentration, and centrifugation time.

After each run the cell contents were drawn and divided into five fractions from top to bottom. Polyelectrolyte, sodium, and potassium ion concentrations were determined in each fraction from the cell solution compartment. The solvent compartment contents were also drawn and pooled prior to concentration determinations.

The difference between the concentrations of the lower and upper compartments was calculated ($\Delta C = C_l - C_u$) in each run, and it was divided by the average concentration (C_m) to give a measurement of the concentration gradient across the cell ($\Delta C/C_m$).

The results thus obtained with the three polyelectrolytes are listed in Tables 1, 2, and 3. Graphical presentations of these results are in Figs. 1, 2, and 3.

The effect of each variable over $\Delta C/C_m$ was determined (*13*) and is given in Table 4.

The results obtained are the following.

1) In Blue Dextran solutions, the polyelectrolyte concentration gradient increases with counterion concentration and centrifugation time. The same trends are observed in PSS and PA, except for CI concentration being a negligible factor in PA, under these conditions.
2) Counterion concentration gradients always increase with centrifugation time; they have negative effects on polyelectrolyte concentrations in PSS and PA and a negligible effect in BD. The counterion initial concentration has a negative effect on their concentration gradient in BD, but a positive effect in PSS.
3) Effects of the variables on sodium and potassium concentration gradients in a given system were always the same, within experimental error.
4) There are significant differences between sodium and potassium concentration gradients when these are obtained with BD and PSS. These differences are more significant with BD solutions at longer times and higher polyelectrolyte concentrations. When PSS is used, larger differences are observed among the gradients obtained at higher salt concentration and lower polyanion concentration. Sodium and potassium concentration gradients are identical, within experimental error, in polyacrylate solutions.

TABLE 1

Concentration Gradients in NaK Poly(Styrene Sulfonate) Osmosedimentation at 3000 rpm

Polyelectrolyte concentration ($g \cdot dm^{-3}$)	Total counterion concentration [($mol \cdot dm^{-3}$) × 10^3]		Centrifugation time (h)	$\Delta C/C_m$			
	Dialysis solution	Polyelectrolyte solution, after dialysis		Na,KPS[a]	Na	K	SF_{K}^{Na} [b]
9.0	1.1	2.8	20	0.33 ± 0.03	0.32 ± 0.01	0.39 ± 0.04	1.03
9.0	1.1	2.8	60	0.47 ± 0.01	0.34 ± 0.03	0.38 ± 0.01	~1
9.0	2.5	3.0	20	0.51 ± 0.05	0.42 ± 0.02	0.51 ± 0.03	1.04
9.0	2.5	3.0	60	0.80 ± 0.05	0.60 ± 0.05	0.69 ± 0.01	1.04
25.0	1.1	5.3	20	0.19 ± 0.01	0.18 ± 0.01	0.18 ± 0.01	~1
25.0	1.1	5.3	60	0.17 ± 0.02	0.24 ± 0.07	0.24 ± 0.07	~1
25.0	2.5	6.9	20	0.31 ± 0.01	0.26 ± 0.01	0.29 ± 0.02	~1
25.0	2.5	6.9	60	0.39 ± 0.02	0.34 ± 0.04	0.36 ± 0.04	~1

[a] Determined from absorbance readings at 280 nm.

[b] Separation factor.

TABLE 2

Concentration Gradients in NaK Blue Dextran (BD) Osmosedimentation at 3000 rpm and 20°C

Polyelectrolyte concentration ($g \cdot dm^{-3}$)	Total counterion concentration [$(mol \cdot dm^{-3}) \times 10^3$]		Centrifugation time (h)	$\Delta C / C_m$			
	Dialysis solution	Polyelectrolyte solution, after dialysis		BD	Na	K	SF_K^{Na}
8.0	2.5	3.1	20	2.25 ± 0.05	0.66 ± 0.01	0.70 ± 0.01	1.02
8.0	2.5	3.1	45	2.49 ± 0.03	0.68 ± 0.02	0.74 ± 0.01	1.02
8.0	3.3	3.9	20	2.34 ± 0.06	0.46 ± 0.01	0.52 ± 0.01	1.03
8.0	3.3	3.9	45	2.62 ± 0.01	0.60 ± 0.05	0.66 ± 0.05	~1
12.0	2.5	3.6	20	2.00 ± 0.05	0.64 ± 0.01	0.70 ± 0.03	1.02
12.0	2.5	3.6	45	2.17 ± 0.05	0.63 ± 0.02	0.71 ± 0.01	1.03
12.0	3.3	4.1	20	2.17 ± 0.03	0.55 ± 0.01	0.60 ± 0.02	1.02
12.0	3.3	4.1	45	2.35 ± 0.06	0.59 ± 0.01	0.67 ± 0.01	1.03

TABLE 3
Concentration Gradients in NaK Poly(Acrylate) Osmosedimentation at 3000 rpm and 20°C

Polyelectrolyte concentration ($g \cdot dm^{-3}$)	Total counterion concentration [($mol \cdot dm^{-3}$) × 10^3]		Centrifugation time (h)	$\Delta C / C_m$		
	Dialysis solution	Polyelectrolyte solution, after dialysis		PAA[a]	Na	K
5.1	3.2	5.1	20	0.46 ± 0.05	0.35 ± 0.07	0.40 ± 0.06
5.1	3.2	5.1	90	0.74 ± 0.01	0.55 ± 0.07	0.57 ± 0.06
5.1	5.6	8.5	20	0.35 ± 0.05	0.32 ± 0.05	0.33 ± 0.05
5.1	5.6	8.5	90	0.69 ± 0.03	0.54 ± 0.06	0.54 ± 0.06
10.0	3.2	9.0	20	0.43 ± 0.03	0.38 ± 0.08	0.40 ± 0.08
10.0	3.2	9.0	90	0.53 ± 0.05	0.40 ± 0.07	0.42 ± 0.07
10.0	5.6	11.0	20	0.46 ± 0.03	0.22 ± 0.05	0.23 ± 0.05
10.0	5.6	11.0	90	0.61 ± 0.03	0.48 ± 0.04	0.48 ± 0.01

[a] Poly(acrylic acid).

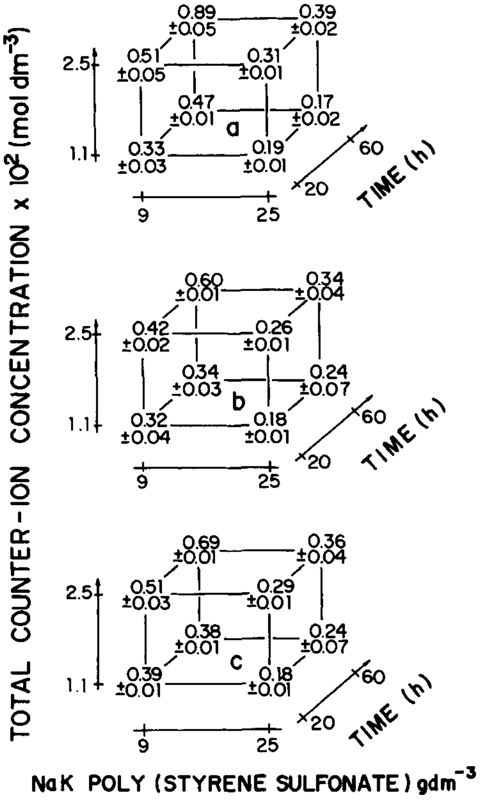

FIG. 1. Concentration gradients in NaK poly(styrene sulfonate) aqueous solutions as a function of polyanion and total counterion concentration, and centrifugation time. a) $\Delta C_{\mathrm{PSS}}/C_{m,\mathrm{PSS}}$; b) $\Delta C_{\mathrm{Na}}/C_{m,\mathrm{Na}}$; c) $\Delta C_{\mathrm{K}}/C_{m,\mathrm{K}}$. $\Delta C/C_m$s are the numbers at the cubes' vertices.

DISCUSSION

Centrifugation of aqueous solutions of NaCl and KCl at 3000 rpm in the same centrifuge and rotor used in this work should generate very small concentration gradients. At equilibrium, the upper limits for concentration gradients can be calculated, assuming ideal behavior for a 1–1 electrolyte:

$$\frac{d(\ln C_{\mathrm{NaCl}})}{d(r^2)} = 4.2 \times 10^{-5}\ \mathrm{cm}^{-2}$$

and

$$\frac{d(\ln C_{\mathrm{KCl}})}{d(r^2)} = 4.5 \times 10^{-5}\ \mathrm{cm}^{-2}$$

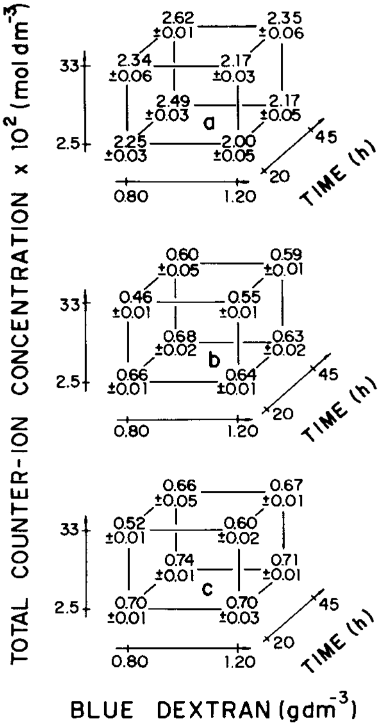

FIG. 2. Concentration gradients in NaK Blue Dextran solutions. a) $\Delta C_{\mathrm{BD}}/C_{m,\mathrm{BD}}$; b) $\Delta C_{\mathrm{Na}}/C_{m,\mathrm{Na}}$; c) $\Delta C_{\mathrm{K}}/C_{m,\mathrm{K}}$.

The corresponding $\Delta C/C_m$, under the experimental conditions used in this work, are 7.1×10^{-4} and 8.0×10^{-4}. Theoretical gradients for the salts are very small, about three orders of magnitude smaller than the Na^+ and K^+ ion concentration gradients obtained in this work. This shows the extent to which a polyelectrolyte can drag counterions as it undergoes sedimentation.

Centrifugation time always had a positive effect on concentration gradients. This is easy to understand, considering that the centrifugation times used are less than those required to reach equilibrium.

Increasing the polyelectrolyte initial concentration (Cp) C_p decreases the polyelectrolyte concentration gradients. This is probably due to two causes: 1) in these highly nonideal solutions, apparent MWs are a function of polyelectrolyte concentration; 2) by increasing C_p, the solution viscosity is also increased. This has an adverse effect on the overall mass transfer rate within the osmosedimentation cell.

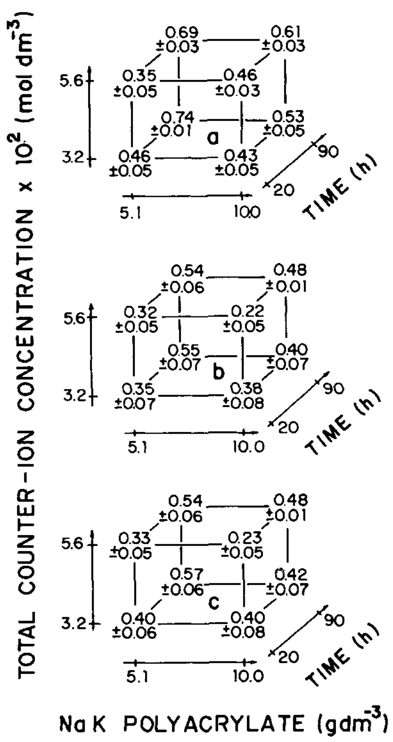

FIG. 3. Concentration gradients in NaK poly(acrylate) solutions. a) $\Delta C_{PAA}/C_{m,PAA}$; b) $\Delta C_{Na}/C_{m,Na}$; c) $\Delta C_{K}/C_{m,K}$.

The positive effect of total counterion concentration over polyelectrolyte concentration is also easily understood: at a higher counterion concentration (and an overall higher concentration of low-MW salts), polyelectrolyte chains are less expanded and interchain repulsion decreases. Both factors contribute to higher apparent $\overline{M}_w$s at higher salt concentrations.

The differences between Na^+ and K^+ concentration gradients can also be qualitatively understood by the following reasoning.

1) Differences in mobility and in weight between K^+ and Na^+ (*14*) should contribute to the creation of larger concentration gradients of the former because it can move after the sedimenting polyelectrolyte faster than Na^+.
2) The concentration gradients should also be affected by the strength of polyelectrolyte–counterion binding. In this case, PAA should drag Na^+ more effectively than K^+ (*15*); PSS would operate in the opposite way.

TABLE 4

Effects of the Major Variables on the Concentration Gradients Obtained in the Osmosedimentation Experiments

		Effects of the variables		
System	Concentration gradient of	Polyelectrolyte concentration	Total counterion concentration[a]	Centrifugation time
NaK BD	BD	−0.25 ± 0.04	0.14 ± 0.04	0.22 ± 0.04
	NA	0.01 ± 0.01	−0.10 ± 0.01	0.05 ± 0.01
	K	0.02 ± 0.01	−0.10 ± 0.01	0.06 ± 0.01
NaK PSS	PSS	−0.29 ± 0.02	0.23 ± 0.02	0.16 ± 0.02
	Na	−0.16 ± 0.03	0.11 ± 0.03	0.06 ± 0.03
	K	−0.20 ± 0.03	0.13 ± 0.03	0.06 ± 0.03
NaK PAA	PAA	−0.05 ± 0.02	0.01 ± 0.02	0.22 ± 0.02
	Na	−0.07 ± 0.03	−0.03 ± 0.03	0.18 ± 0.03
	K	−0.08 ± 0.03	−0.05 ± 0.03	0.17 ± 0.03

[a] In the dialysis solution.

> We did not find data on DB interactions with these ions, but we can expect a PSS-like behavior because the negative groups in DB are sulfonates. The expected behavior was thus found for PSS and DB. In the case of PAA, there seems to be a balance between the two factors: greater weight of K^+, greater affinity of Na^+.

A more detailed and quantitative discussion of these phenomena is rather difficult at the moment. First, because it would require a complete model for polyelectrolyte sedimentation, which is not available (*16*, *17*); second, because models for mass transfer in the osmosedimentation cell are only available for cell geometries much simpler (*9*) than the one used in this work.

The present results show that Na^+ and K^+ ions can be separated in the osmocentrifugation cell. The separation factors (SF) are low; the highest SF found was 1.04. However, this shows that low-MW species can be fractionated in a sedimentation experiment in a low-speed centrifuge. This opens the possibility for a new technique for low-atomic-number-isotope fractionation.

Further work on this subject will have to explore many alternatives: use of nonaqueous (or partly-aqueous solvents) should generate larger gradients and, perhaps, larger separation factors; a closer approach to osmosedimentation equilibrium is desirable according to the present data; a number of other operational variables (centrifugation speed and temperature) or polyelectrolyte characteristics (degree of substitution, MW, degree of neutralization, and α for the case of acrylics) could be optimized for better separation. This would allow us to make full use of the main advantages of osmosedimentation experiments: use of both low-speed centrifuges and liquid media.

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