

## Selectivity of Polyuronates for Lanthanide Ions

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Selectivities of polyguluronate, polymannuronate, and cross-linked polymethacrylate in reaction with pairs of lanthanide ions have been determined by equilibrium dialysis and neutron activation analysis of the dialysates. The polyuronates differ from resins containing carboxylate and sulfonate groups in having a higher affinity for the ions of intermediate size (Eu, Sm) than for either larger or smaller ions, whereas a gradual increase or decrease in affinity with ionic size is the case for the resins.

Much work has been carried out on the ion-exchange behaviour of lanthanides on cation-exchange resins.<sup>1-3</sup> The main conclusions are that the affinity for lanthanides increases with increasing ionic radius for sulfonic resins<sup>2</sup> and decreases with increasing ionic radius for carboxylic resins.<sup>3</sup> To our knowledge no experiments have been carried out on polyelectrolytes containing both carboxyl and hydroxyl groups in the same molecules. Investigations on the ion exchange properties of alginate have shown<sup>4,5</sup> that this substance is rather unique in having a very high selectivity in the reaction with alkaline-earth metal ions. It was therefore interesting to study its reaction with trivalent lanthanide ions having ionic radii in the same range as the alkaline-earth metals.

Alginate contains both D-mannuronic and L-guluronic acid residues in the same molecule. Fractions enriched in either L-guluronic or D-mannuronic acid residues differ markedly in ion-selectivities,<sup>4,5</sup> and in this work these fractions were studied separately.

Selectivities between pairs of lanthanides were determined by an equilibrium dialysis technique.<sup>4</sup> The analysis of the lanthanides was based upon the measurement of radioactive tracers of the lanthanides once equilibrium had been reached. Most of the lanthanides produce radioactive isotopes with a relatively high specific activity when irradiated with thermal neutrons in a nuclear reactor. In the present studies, pairs of lanthanides were chosen such that both could be measured simultaneously from the size of their peaks in a  $\gamma$ -spectrometer. The accuracy of the present method is dependent upon the

selected  $\gamma$ -peak from each lanthanide and how the peaks (in the chosen pair) are separated and measured. However, because only the ratio between a pair of lanthanides is needed for calculating a selectivity coefficient, a systematic error in the measurement of one or both the lanthanides is compensated for to a certain extent in its calculation.

### EXPERIMENTAL

**Materials.** Two alginate fragments with widely different chemical composition were prepared as previously described.<sup>6</sup> One sample had a number average degree of polymerization,  $\overline{DP}_n$ , of 47 and contained 91 % L-guluronic acid residues. The other had  $\overline{DP}_n = 26.2$  and contained 91 % D-mannuronic acid residues. The sodium salts of these fragments were used in the selectivity experiments, and they are for the sake of simplicity called "polyguluronate" and "polymannuronate", respectively.

Some selectivity experiments were carried out on the cross-linked polymethacrylic acid resin Amberlite IRC 50 in sodium form. The same resin was used by Arnold *et al.*<sup>3</sup> in their study.

**Methods.** For the experiments 2 ml of a 0.05 N solution of polyguluronate or polymannuronate were used. This corresponds to 0.1 m equiv. This solution was sealed in a dialysis bag and transferred to an Erlenmeyer flask which contained 20 ml of an equimolar solution of two lanthanides. The lanthanides together represented 0.2–0.3 m equiv.

The lanthanide tracers were made by irradiating milligram amounts of analytical grade lanthanide oxides with neutrons. After irradiation the samples were dissolved in a suitable acid (HCl or HNO<sub>3</sub>), evaporated to dryness and then dissolved in distilled water. Tracers of each of the two lanthanides which were to be used in a selectivity experiment were mixed together and adjusted so that both of the selected  $\gamma$ -energies could be simultaneously registered. This radioactive mixture was then added to the corresponding inactive lanthanide mixture before transference to an Erlenmeyer flask containing the dialysis bag. The bag was shaken for 24 h, and then washed twice with distilled water. After the first washing process the activity in the washing water had already fallen to

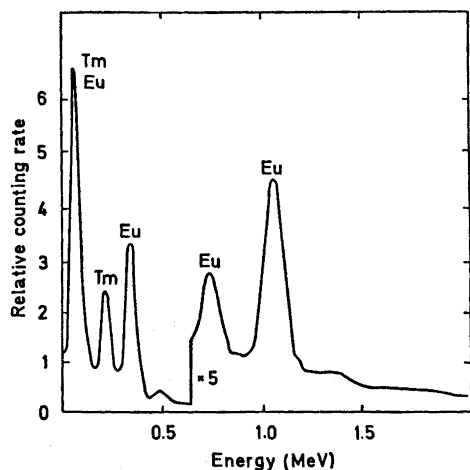


Fig. 1. Gamma-spectrum showing the distribution of Tm and Eu inside the dialysis bag after equilibrium against a 1:1 mixture of the two elements.

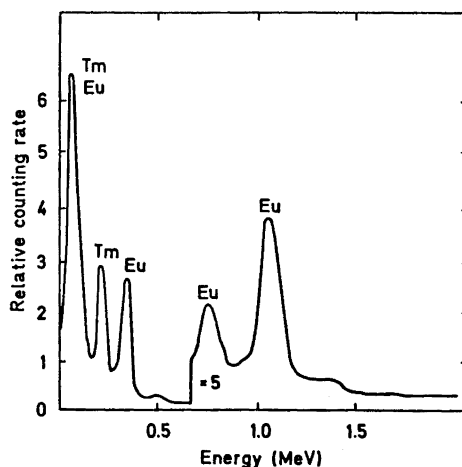


Fig. 2. Gamma-spectrum of the dialysate from the same experiment as in Fig. 1.

about 1 % of the activity in the dialysate. The  $\gamma$ -spectrum obtained from the lanthanide mixture in the dialysate was therefore not corrected for the amount washed away during the washing procedures which followed. The activity in the dialysis bag and in the dialysate were measured using a 400 channel  $\gamma$ -spectrometer and the concentration ratio for each pair was found from the ratio between the height of the  $\gamma$ -peaks. Figs. 1 and 2 show the spectra of europium and thulium, from the dialysis bag and the dialysate, respectively.

In the experiments in which the concentrations of europium and thulium were varied reciprocally, the same radioactive tracer mixture of europium and thulium was added. As the concentration of one of the lanthanides rises or falls, the specific activity of this lanthanide will follow an opposite pattern and give the same spectrum, assuming that the selectivity coefficient does not change. Much better accuracy is obtained in this way than if the specific activities had been kept the same.

### RESULTS

It has been shown<sup>4</sup> that in the exchange between calcium and magnesium ions the selectivity of polyguluronate varies considerably with the ionic composition of the polymer phase. This variation made it necessary to compare the selectivity of different pairs of metal ions at a particular ionic composition of the polyguluronate. To test for such behaviour in exchange-reactions with a pair of lanthanide ions, an ion-exchange experiment with polyguluronate (see Experimental) was carried out with europium and thulium ions, the ratio between these ions being varied within wide limits.

The selectivity coefficients were calculated from the formula

$$k_B^A = \frac{X_A}{X_B} \times R_A^B \quad (1)$$

where  $X_A$  and  $X_B$  are mol fractions of the two lanthanides, A and B, in the polymer phase and  $R_A^B$  is the ratio between the concentrations of the lanthanides, B and A, in the solution outside the dialysis bag at equilibrium. The results given in Table 1 show no significant dependence of the selectivity coefficients upon the ionic composition of the polymer phase.

According to this experiment the experimental condition for comparing selectivities within pairs of lanthanides seems not to be very critical. In all experiments below, equivalent amounts of the two lanthanides were present in the solution outside the dialysis bag at the start of the experiment; the

*Table 1.* Selectivity coefficients ( $k_{Tm}^{Eu}$ ) for polyguluronate in exchange between europium and thulium at different ionic compositions ( $X_{Eu}$ ) of the polymer phase, and ambient solution ( $R_{Tm}^{Eu}$ ).

$R_{Tm}^{Eu}$	$X_{Eu}$	$k_{Tm}^{Eu}$
8.7	0.935	1.73
2.62	0.818	1.70
0.87	0.617	1.85
0.29	0.340	1.77
0.087	0.125	1.61

amount of each metal ion being kept equal to the amount of charged groups on the polymers. The mol fractions of the two ions in the polymers at equilibrium varied in this way in most cases within the limits 0.35 and 0.65.

The selectivity coefficients for a series of pairs of lanthanides with the polyguluronate and polymannuronate fragments are shown in Table 2. They show that, for polyguluronate, the selectivity between pairs of ions from lanthanum to samarium is such that the polyguluronate accumulates the ion with the highest atomic number. The opposite is the case for pairs of ions of higher atomic number than samarium. The same general behaviour is shown by polymannuronate, albeit less markedly. Table 2 also gives some selectivity

Table 2. Selectivity coefficients,  $k_B^A$ , for polyguluronate, polymannuronate, and polymethacrylate (Amberlite IRC 50).

Ion A	Ion B	Polyguluronate	Polymannuronate	Poly-methacrylate
La	Ce	0.80		0.56 <sup>a</sup>
La	Nd	0.75	0.79	
La	Sm	0.57		
La	Eu	0.60	0.45	0.44 <sup>a</sup>
La	Tm	1.53		
Ce	Eu	1.82		
Nd	Eu	0.81		
Sm	Eu	1.08		
Eu	Tb	1.34	1.40	
Eu	Tm	1.95		0.81 <sup>b</sup>
Eu	Lu	3.01	1.77	
Tb	Ho	1.34		
Tb	Tm	1.43	1.24	
Tm	Lu	1.41		0.9 <sup>b</sup>
Yb	Lu	1.03		

<sup>a</sup> Data taken from Ref. 3.

<sup>b</sup> Own experiments.

coefficients for cross-linked polymethacrylate (Amberlite), partly taken from the literature and partly from our own experiments. Contrary to the results for the polyuronides, the affinity increases with increasing atomic number also for elements with a higher atomic number than samarium.

Selectivities of different substances may best be compared when all the selectivity coefficients are calculated with the same ion as the reference ion. All the data in Table 2 may be expressed as selectivity coefficients with lutetium as the reference ion, if the selectivity coefficients can be treated as true equilibrium constants, *i.e.* if in general,

$$k_A^C = k_A^B \times k_B^C \quad (2)$$

where A, B, and C represent different lanthanides.

From Table 2 it is seen that the selectivity coefficients  $k_{Lu}^{Eu}$  and  $k_{Lu}^{La}$  may be calculated as the product of a series of different selectivity coefficients. The result given in Table 3 shows that the scattering between the selectivity

Table 3. Comparison of selectivity coefficients,  $k_{Lu}^{Eu}$  and  $k_{Lu}^{La}$ , calculated from different combinations of selectivity coefficients.

$k_{Lu}^{Eu} = k_{Lu}^{Eu}$	= 3.01
$k_{Lu}^{Eu} = k_{Tm}^{Lu} \times k_{Tm}^{Eu}$	= 2.75
$k_{Lu}^{Eu} = k_{Lu}^{Tm} \times k_{Tm}^{Tb} \times k_{Tb}^{Eu}$	= 2.71
Average	<u>2.82</u>
$k_{Lu}^{La} = k_{Lu}^{Tm} \times k_{Tm}^{La}$	= 2.16
$k_{Lu}^{La} = k_{Lu}^{Eu} \times k_{Eu}^{La}$	= 1.69
$k_{Lu}^{La} = k_{Lu}^{Eu} \times k_{Eu}^{Sm} \times k_{Sm}^{La}$	= 1.74
$k_{Lu}^{La} = k_{Lu}^{Eu} \times k_{Eu}^{Nd} \times k_{Nd}^{La}$	= 1.72
$k_{Lu}^{La} = k_{Lu}^{Eu} \times k_{Eu}^{Ce} \times k_{Ce}^{La}$	= 1.85
Average	<u>1.83</u>

Table 4. Selectivity coefficients,  $k_{Lu}^{Me}$ , in the reaction between lutetium and the other lanthanides, Me.

	Yb	Tm	Ho	Tb	Eu	Sm	Nd	Ce	La
Polyguluronate	1.03	1.41	1.51	2.02	2.82	3.04	2.28	2.31	1.83
Polymannuronate		1.02		1.27	1.77		1.0		0.80
Polymethacrylate		0.90			0.73			0.57	0.32

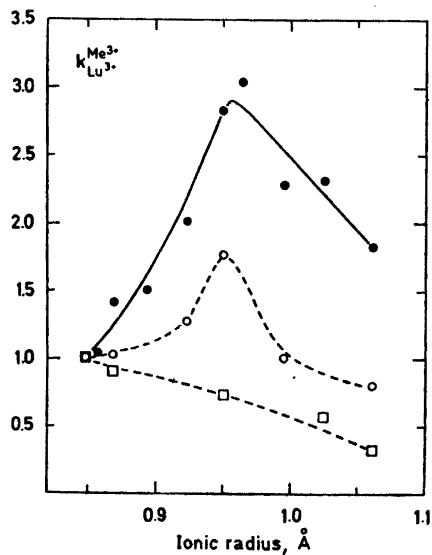


Fig. 3. Selectivity coefficients with lutetium as the reference ion as a function of the crystallographic ionic radius of the lanthanides. ●: Polyguluronate. ○: Polymannuronate. □: Cross-linked polymethacrylate [Amberlite IRC 50].

coefficients obtained in this way is tolerable. This should justify the calculation of the selectivity coefficients given in Table 4.

In Fig. 3 the selectivity coefficients with lutetium as the reference ion are given as a function of the crystallographic ion radius of the trivalent lanthanides.<sup>7</sup>

#### DISCUSSION

When the selectivities of polymannuronate and polyguluronate for the lanthanide ions are compared with those previously obtained<sup>5</sup> for the alkaline-earth ions, two main differences are apparent. First, the presently obtained selectivities of polyguluronate are generally lower than those for the alkaline-earth ions of the same size. Second, in exchange between the alkaline-earth ions polymannuronate and polyguluronate differ qualitatively in that polymannuronate distinguishes only between the large barium ion and the smaller ions, whereas polyguluronate distinguishes mainly between the ions of intermediate size (Mg, Ca, Sr). From Fig. 3 it is seen that both polymannuronate and polyguluronate have the highest affinity for the lanthanide ions with an ionic radius of about 0.95 Å. It is possible, therefore, that the higher valency of the lanthanide ions and the requirement of one extra carboxyl group for neutralisation make the position of the lanthanide ions relative to the binding site different from that of the alkaline earth metal ions.

For the alkaline-earth ions a specific binding to two or more points at the uronate molecule has been suggested.<sup>5</sup> The very critical dependence of the binding upon the ionic radius for the polyuronates compared to polymethacrylate shown in Fig. 3 makes, also in the present case, a non-specific electrostatic binding unlikely as the only binding mechanism.

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