

CHROM. 6073

### Ion-exchange thin-layer chromatography of polyvalent ions on sodium carboxymethylcellulose and Dowex 50 X4(Na<sup>+</sup>)

In a previous paper<sup>1</sup> the chromatographic behaviour of mono-, di-, and polyvalent ions on sodium carboxymethylcellulose (CMCNa) and Dowex 50 X4(Na<sup>+</sup>) thin layers, when eluted with neutral salt solutions, was closely examined. It was observed that polyvalent ions, unlike most other ions, remain at their point of origin. In order to increase their mobility, buffer solutions (lactate, acetate and gluconate) at constant ionic strength were used. In this way it was possible to demonstrate the influence of complex formation on the chromatographic characteristics of these ions.

#### Experimental

The buffer solutions were prepared so that the ratio of the acid and its salt was 1:2; the ionic strength was kept constant ( $\mu=1$ ) with sodium perchlorate. The CMCNa layers (exchange capacity 1.18 mequiv./g) were prepared as described previously<sup>1</sup>; those of Dowex 50 X4(Na<sup>+</sup>) were obtained by mixing 3 g of the resin and 6 g of microcrystalline cellulose in 40 ml of water. The spots were detected with a 1% solution of 8-hydroxyquinoline in 95% ethanol (saturated with ammonia), followed by exposure to ultraviolet (UV) light.

TABLE I

$R_F$  VALUES OF POLYVALENT IONS ON CMCNa THIN LAYERS: ELUTION WITH LACTATE BUFFER SOLUTIONS. MIGRATION DISTANCE 11 CM

Ion <sup>a</sup>	Sodium lactate concentration (moles/l)						
	0.04	0.06	0.08	0.10	0.15	0.20	0.30
UO <sub>2</sub> (II)	0.01	0.03	0.07	0.09	0.19	0.25	0.41
Th(IV)	0.02	0.08	0.19	0.26	0.54	0.62	0.85
Bi(III)	0.01	0.02	0.03	0.05	0.12	0.17	0.32
In(III)	0.00	0.03	0.06	0.10	0.21	0.30	0.55
Cr(III)	0.08	0.09	0.10	0.12	0.15	0.17	0.21
La(III)	0.11	0.17	0.24	0.30	0.48	0.54	0.72
Ce(III)	0.11	0.18	0.25	0.32	0.51	0.58	0.75
Pr(III)	0.12	0.19	0.26	0.34	0.53	0.60	0.80
Nd(III)	0.12	0.20	0.27	0.34	0.54	0.62	0.82
Sm(III)	0.13	0.21	0.29	0.37	0.57	0.68	0.84
Eu(III)	0.27	0.35	0.41	0.49	0.66	0.77	—
Gd(III)	0.17	0.26	0.34	0.44	0.62	0.76	—
Tb(III)	0.21	0.31	0.41	0.51	0.71	0.82	—
Dy(III)	0.25	0.38	0.47	0.61	0.79	0.88	—
Sc(III)	0.25	0.37	0.46	0.61	0.79	0.89	—
Y(III)	0.30	0.43	0.55	0.68	0.85	—	—
Ho(III)	0.30	0.45	0.56	0.69	0.85	—	—
Er(III)	0.36	0.53	0.65	0.76	—	—	—
Tm(III)	0.47	0.64	0.75	0.84	—	—	—
Yb(III)	0.48	0.69	0.78	0.86	—	—	—
Lu(III)	0.57	0.75	0.82	—	—	—	—
Al(III)	0.77	0.91	0.96	—	—	—	—
Ga(III)	0.93	0.96	—	—	—	—	—

<sup>a</sup> = Zr(IV) and Fe(III) give elongated spots.

### Results and discussion

As regards the compactness of the spots and the analytical possibilities, the best results were obtained on CMCNa using the lactate buffer for elution and are reported in Table I.

Good agreement between the chromatographic behaviour of lanthanides and their tendency to form complexes with lactate ions is observed. In fact, the  $R_F$  values of these ions (for a given ligand concentration) increase according to the increasing values of their global formation constants<sup>2</sup>, with the exception of europium which gives rise to a sickle-form spot.

With regard to possible separations among the lanthanides, it would appear that most of those where the heavier rare earths are concerned are feasible as the chromatogram in Fig. 1 shows. Such separations may be compared with those obtained with different layers and eluents and are, in some cases, better than those proposed by other authors<sup>3-5</sup>. The use of thin layers often has the advantage of requiring a shorter elution time (25-30 min compared to as much as 28 h) than that necessary in the case of ion-exchange papers<sup>6</sup> or papers impregnated with ion exchangers<sup>7-9</sup>.

On changing from lactate to gluconate the analytical possibilities are reduced since a levelling of the  $R_F$  values is observed. With these two ligands no essential differences are observed in the case of Cr(III), Al(III), Ga(III), and UO<sub>2</sub>(II), but an increase in mobility is noted for In(III) and Th(IV) on changing from lactate to

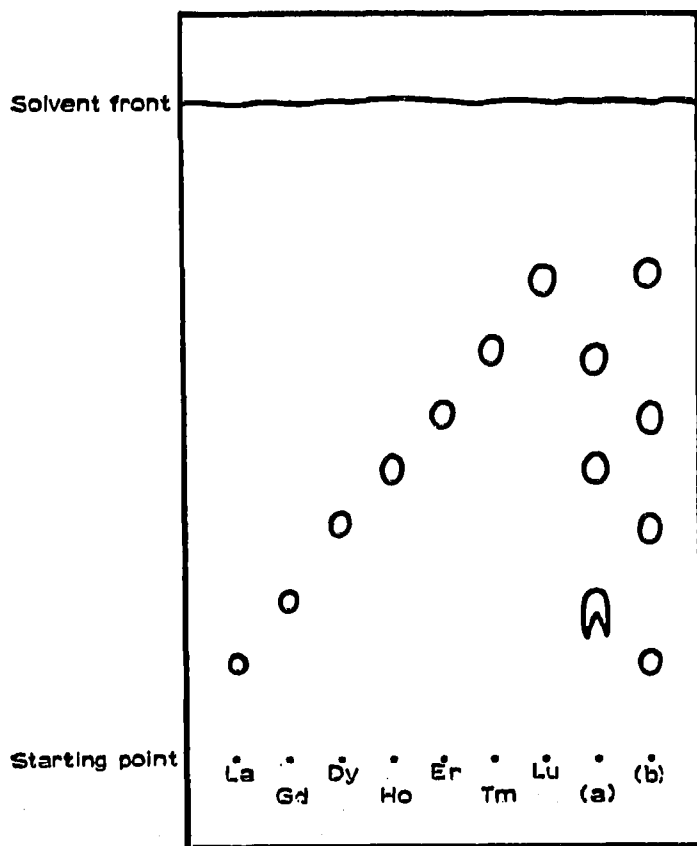


Fig. 1. Thin-layer chromatogram of some lanthanides on CMCNa. (a) Gd, Ho and Tm mixture; (b) La, Dy, Er and Lu mixture. Sodium lactate concentration: 0.06 M. Migration distance 15 cm.

TABLE II

SEPARATIONS OBTAINED ON CMCNa THIN LAYERS: ELUTION WITH GLUCONATE BUFFER SOLUTIONS

Separation	Sodium gluconate concentration ( <i>M</i> )	<i>R<sub>F</sub></i>
Sc/La/Y	0.2	0.45/0.56/0.71
Cr, In/Bi/Y <sup>a</sup> /Al, Ga	0.2	0.13/0.44/0.72/0.98
UO <sub>2</sub> /Th	0.4	0.37/0.63

<sup>a</sup> Yttrium may be replaced by any lanthanide included between Sm and Lu (*R<sub>F</sub>* range = 0.72–0.76).

gluconate. The chromatographic behaviour of Bi(III) is opposite to that of In(III) and Th(IV). These characteristics permit the separations reported in Table II, some of which are of great analytical interest.

When the acetate buffer is employed as eluent, unlike the case of the above-mentioned ligands, only mediocre results are obtained since the spots of most ions are not well-defined. However, as shown in the chromatogram in Fig. 2, it is possible to obtain an interesting separation between UO<sub>2</sub>(II), Zr(IV) and Th(IV).

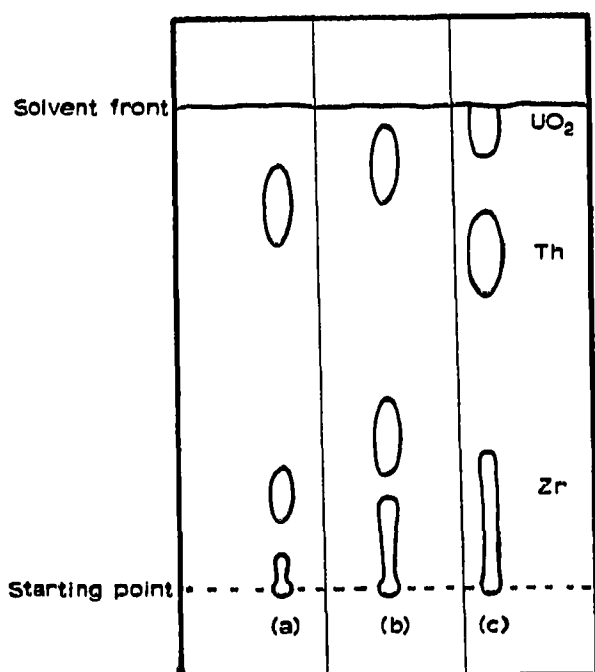


Fig. 2. Thin-layer chromatogram of Zr, Th and UO<sub>2</sub> mixture on CMCNa. Sodium acetate concentration: (a) 0.4 *M*; (b) 0.5 *M*; (c) 1 *M*.

On Dowex 50 X4 (Na<sup>+</sup>) the *R<sub>F</sub>* values, for a given ligand concentration, are higher than those on CMCNa thin layers; this difference is particularly clear when eluting with acetate buffer. Many separations, some of which are reported in Table III, are possible on this exchanger. The separation of UO<sub>2</sub>(II) from In(III) and of these two from all the other ions investigated is of special interest. Among the latter are

TABLE III

SEPARATIONS OBTAINED ON DOWEX 50 X<sub>4</sub> (Na<sup>+</sup>) THIN LAYERS: ELUTION WITH ACETATE AND LACTATE BUFFER SOLUTIONS

<i>Separation</i>	<i>Conditions</i>	<i>R<sub>F</sub></i>
La/Y/Sc	0.2 M sodium acetate	0.10/0.34/0.65
La/Cr/Bi	0.3 M sodium acetate	0.19/0.48/0.93
UO <sub>2</sub> /In/others	0.1 M sodium acetate	0.92/0.79/less than 0.56
La/Ce/Gd/Yb, Lu	0.04 M sodium lactate	0.05/0.14/0.33/0.64
Cr/Y/Bi, In	0.10 M sodium lactate	0.09/0.24/0.85

included monovalent (Ag, Tl and Hg) and divalent ions which will concern a further note.

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