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## THE BEHAVIOUR OF CATION-EXCHANGE THIN LAYERS WITH ALKALINE AND NEUTRAL SALT SOLUTIONS AS ELUENTS\*

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## SUMMARY

The behaviour of weak and strong ion exchangers in the sodium salt form is studied using neutral solutions of uni- and divalent ions and alkaline solutions of univalent ions as eluents. The influence of various parameters (rate of exchange reaction, diffusion rate, swelling capacity, etc.) on the chromatographic behaviour of the ions has been investigated. The conditions for the determination of ionic charge and the selectivity coefficients of the exchangers for some univalent and divalent ions are given.

## INTRODUCTION

The formation of two different eluent fronts on ion-exchange papers eluted with mineral and organic acids was investigated by OSSICINI AND LEDERER<sup>1</sup>. The presence of a double front on sodium carboxymethylcellulose thin layers (CMCNa) eluted with mineral acids has been confirmed by COZZI *et al.*<sup>2</sup>. The existence of a hydrogen ion concentration gradient on layers of alginic acid and carboxymethylcellulose (CMC) (eluting with solutions of mineral acids, buffer solutions and neutral saline solutions) and on layers of CMCNa (eluting with buffer solutions) was pointed out by COZZI *et al.*<sup>3</sup>. The hydrogen ion gradient is also formed with strong ion exchangers, such as the mixture (1:1) of Dowex 50-X4 and cellulose, eluting with buffer solutions. The hydrogen ion gradient is affected by acidic eluents and/or acidic forms of an ion exchanger. We therefore tested ion exchangers in sodium salt forms, eluted with neutral and alkaline salt solutions, to ascertain whether the gradient-forming process was restricted to the hydrogen ions or was a general rule.

## EXPERIMENTAL

*Conductivity measurements*

The following method was employed to measure the ion concentration along the layer. Bands ( $2 \times 10$  cm) of the eluted plate were homogeneously dispersed in

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20 ml of distilled water by means of a magnetic stirrer. A Metrom Herisau E382 conductimeter was employed to measure the conductivity of the suspensions.

In the case of  $\text{Ba}(\text{NO}_3)_2$  as eluent, the conductivity measurements were completed by revealing the migration distance of  $\text{Ba}(\text{II})$ . We sprayed the plates with a saturated solution of sodium rhodizonate. The migration distance of  $\text{Mg}(\text{II})$  was detected with a 1% solution of 8-hydroxyquinoline in alcohol-ammonia (50:1).

#### *pH measurements*

pH measurements along the layer were described in a previous paper<sup>3</sup>.

#### *Preparation of layers*

Dowex 50-X4 (200–400 mesh) was converted to the sodium form by treatment with 1 M NaCl. The resin was rinsed with water to eliminate  $\text{Cl}^-$ ; then it was treated with methanol and dried 24 h in the open air. Then 4.5 g of Dowex 50-X4 were added to 4.5 g of cellulose (N.123 commercially available from Carl Schleicher & Schüll) and reduced in a suspension with water (40 ml) to prepare 300- $\mu$  layers. Layers made of Dowex 50-X4 and cellulose (1:1) have previously been successfully employed<sup>4</sup>. Two types of CMCNa have been used, with an exchange capacity of 0.89 and 1.18 mequiv./g, respectively. 4.5 g of the exchanger were suspended in 40 ml and 50 ml of water, respectively, to prepare 300- $\mu$  thin layers. The data reported refer to the exchanger with an 0.89 mequiv./g exchange capacity, unless indications to the contrary are given. Such an exchanger was successfully used in previous work<sup>2,3</sup>.

The eluents were salt solutions of NaCl,  $\text{NaClO}_4$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Mg}(\text{NO}_3)_2$  and  $\text{MgCl}_2$ . The concentration of each is reported in Table I. The detecting agents described in a previous study<sup>5</sup> were used. The chromatographic measurements were carried out at 25° using the DBGM Cryobox Desaga chamber for thin-layer chromatography at constant temperature.

## RESULTS AND DISCUSSION

### *Elution on CMCNa and Dowex 50-X4 layers*

In the present study we examine the behaviour of CMCNa and Dowex 50-X4 layers with neutral and alkaline salt solutions of univalent ions and with neutral solutions of divalent ions.

*Elution using neutral salt solutions of univalent cations.* In Fig. 1, specific conductivity (*c*) values along the layer are reported for CMCNa (curves b, d, e, g, i) and Dowex 50-X4 (curves a, c, f, h, j), the eluents being water (curves a, b), 0.1 M  $\text{NaClO}_4$  (curves c, d), 0.5 M  $\text{NaClO}_4$  (curves e, f), 1 M  $\text{NaClO}_4$  (curves g, h) and 2 M  $\text{NaClO}_4$  (curves i, j). Similar behaviour for both the layers is observed with an increasing salt concentration. An increase in the quantity of salt is observed in fact in the solvent front. For  $\text{NaClO}_4$  concentrations < 1 M and for eluent concentrations > 1 M, the salt concentration decreases along the layer. Such a phenomenon is more pronounced on CMCNa.

The observed behaviour can be explained by recalling that when a resin is placed in contact with a salt solution, (e.g.  $\text{NaClO}_4$ ),

$$(a_{\text{Na}^+} \cdot a_{\text{ClO}_4^-})_{\text{resin}} = (a_{\text{Na}^+} \cdot a_{\text{ClO}_4^-})_{\text{solution}}$$

This relation, considered in a qualitative way, indicates that the adsorption of the salt by the ion exchanger depends on the salt in the solution and increases with increasing concentration of the latter.

When the exchanger adsorbs the solvent in preference to the salt, the patterns reported by curves c, d, e, f and h are obtained. On the contrary, in the case that, other than the solvent, the exchanger adsorbs a considerable amount of the dissolved salt, curves g, i and j are obtained. The different patterns of curves g and h are explained by the different exchange capacities of the two resins (3.56 mequiv./g for Dowex 50-X<sub>4</sub>, 0.89 mequiv./g for CMCNa) and by a greater water adsorption in the case of CMCNa. As regards the behaviour of the layers eluted with water, we wish to emphasise that CMCNa was carefully washed with water before preparing the layers.

*Elution using neutral solutions of divalent ions.* In the case of elution with neutral solutions of divalent ions the formation of two fronts on the layer has also been observed. The first one depends on the migration distance of the divalent ions. The distance between the two fronts decreases with increasing salt concentration (Table V).

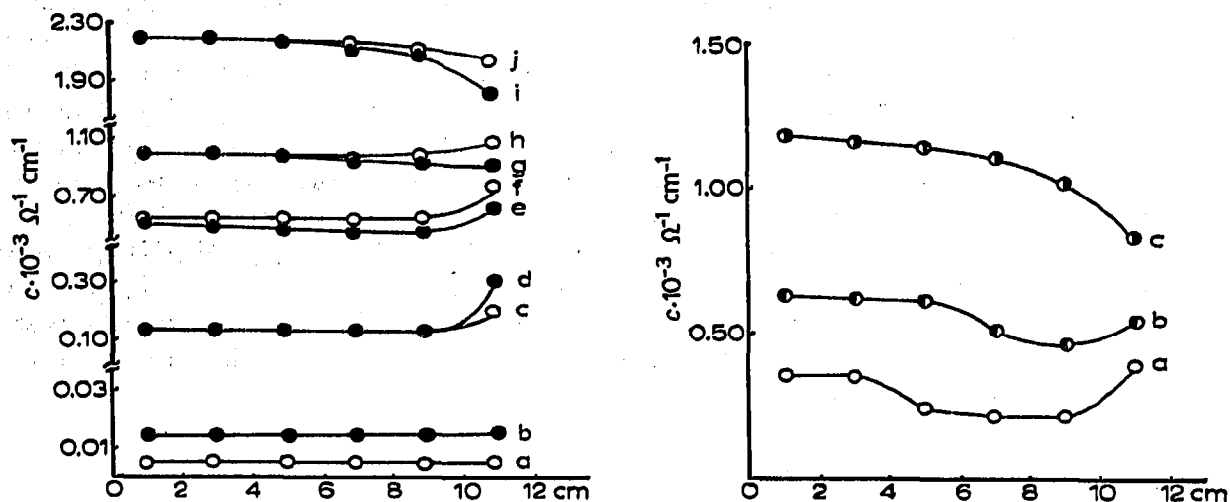


Fig. 1. Specific conductance of CMCNa (●—●) and Dowex 50-X<sub>4</sub> (○—○) suspensions referred to the center of the strips. Eluents: a, b = H<sub>2</sub>O; c, d = 0.1 M NaClO<sub>4</sub>; e, f = 0.5 M NaClO<sub>4</sub>; g, h = 1 M NaClO<sub>4</sub>; i, j = 2 M NaClO<sub>4</sub>.

Fig. 2. Specific conductance of CMCNa suspensions referred to the center of the strips. Eluents: a = 0.1 M Mg(NO<sub>3</sub>)<sub>2</sub>; b = 0.25 M Mg(NO<sub>3</sub>)<sub>2</sub>; c = 0.5 M Mg(NO<sub>3</sub>)<sub>2</sub>.

The specific conductivity patterns along CMCNa layers are shown in Fig. 2. They refer to 0.1, 0.25 and 0.5 M Mg(NO<sub>3</sub>)<sub>2</sub> as eluents (curves a, b, c), respectively. For curves a and b, a first portion has been observed where the conductivity varies slightly. This portion represents the Mg(II) migration distance (first front). The following portion where remarkable conductivity changes are registered is due to the Na<sup>+</sup> released by ionic exchange. It should be noted that the second portion is similar to that reported for diluted univalent salts as eluents (Fig. 1).

In the case of curve c, the first front is very near that of the solvent; the minimum observed in curves a and b is missing. The continuous decreasing of specific conductance for curve c may be referred to the adsorption of Mg(II) from the layer, such adsorption increasing with the salt concentration in the eluent.

*Elution using alkaline solutions of univalent ions.* Alkaline solutions consisting of  $\text{NaClO}_4$  and  $\text{NaOH}$  and neutral salt solutions gave a similar  $\text{NaClO}_4$  concentration gradient along the layer. It is interesting to observe the pH gradient along the layer as a function of the pH of the eluent. For weakly alkaline eluents (pH 7–10), a pH constant value of about 7 is registered. When the eluent alkalinity increases (pH 10–12), the formation of a pH gradient along the layer is observed (as was seen with ion exchangers in acid form with mineral acids as eluents).

*Parameters influencing the chromatographic behaviour of the ions*

*Elution using neutral salt solutions of divalent ions*

$R_F$  values of some ions on CMCNa layers with  $\text{NaClO}_4$  and  $\text{NaCl}$  solutions at different concentrations are reported in Table I. In general, upon increasing the concentration of  $\text{NaClO}_4$  in the eluent, a discrete increase in  $R_F$  values is observed up to a concentration of 0.7–1 M. For higher concentrations the increase tends, in each case, to decrease in accordance with the greater adsorption of the salt with respect to the solvent by the exchanger. For concentrations of salt in eluent less than 1 M, the  $R_M / -\log a_{\text{NaClO}_4}$  diagram (Fig. 3) also seems to indicate that the ion-exchange process is not the only parameter that conditions the retention mechanism of the ions. In any case, with Tl(I) being the only exception, an analogous curvilinear pattern was observed.

TABLE I

 $R_F$  VALUES OF METAL IONS ON CMCNa THIN LAYERS

Ion <sup>a</sup>	Eluent: $\text{NaClO}_4$ (M)						Eluent: $\text{NaCl}$ (M)				Amount ( $\mu\text{g}$ )
	0.1	0.3	0.5	0.7	1	2	0.3	0.5	1	2	
Ag(I)	0.07	0.14	0.19	0.23	0.26	0.30	0.00	0.00	0.00	0.00	1.2
Tl(I)	0.19	0.35	0.45	0.50	0.58	0.69	0.36	0.37	0.00	0.00	2.5
Cu(II)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.03	1.0
Co(II)	0.02	0.07	0.12	0.15	0.20	0.23	0.08	0.17	0.30	0.43	0.6
Ni(II)	0.01	0.05	0.09	0.12	0.17	0.18	0.07	0.15	0.27	0.37	0.8
Zn(II)	0.01	0.04	0.07	0.09	0.11	0.11	0.08	0.13	0.21	0.33	0.6
Cd(II)	0.00	0.03	0.03	0.03	0.03	0.03	0.11	0.26	0.46	0.72	0.5
Hg(II)	0.00	0.00	0.00	0.00	0.00	0.00	0.95	0.96	0.96	0.96	4.0
Pb(II)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.14	1.0
Mn(II)	0.01	0.07	0.13	0.18	0.24	0.28	0.12	0.23	0.36	0.51	1.0
Be(II)	0.02	0.04	0.05	0.06	0.06	0.06	0.05	0.06	0.07	0.07	0.3
Mg(II)	0.03	0.16	0.27	0.33	0.44	0.55	0.18	0.30	0.48	0.61	0.5
Ca(II)	0.02	0.11	0.17	0.22	0.29	0.35	0.11	0.18	0.31	0.38	1.0
Sr(II)	0.03	0.15	0.24	0.31	0.38	0.44	0.15	0.24	0.38	0.45	1.5
Ba(II)	0.01	0.08	0.15	0.21	0.28	0.37	0.08	0.15	0.28	0.37	1.2
In(III)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.06	2.0
Bi(III)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.08	1.0

<sup>a</sup> Al(III), Ga(III), Sc(III), Fe(III), Th(IV) and U(VI) remain at the start with both the eluents.

From a careful review of the data reported in Table I, we might expect very interesting results using CMCNa layers for analytical purposes in the inorganic field. Firstly, a small quantity of substance sufficient for detection, which is also favoured by the compactness of the spots, should be observed. Thus only very small differences

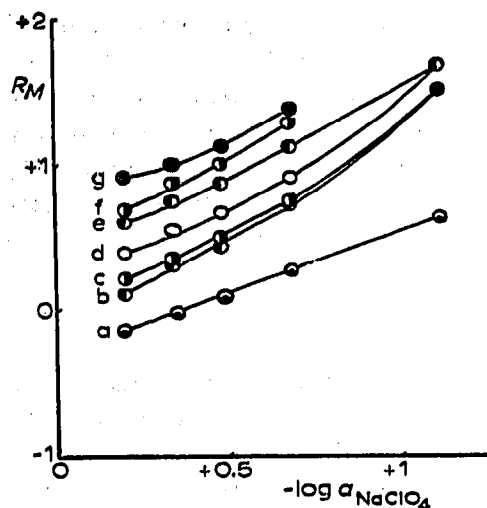


Fig. 3. Relationship of  $R_M$  values to  $-\log a_{\text{NaClO}_4}$  for: a = Tl; b = Mg; c = Sr; d = Ca; e = Co; f = Ni; g = Zn; on CMCNa thin layers.

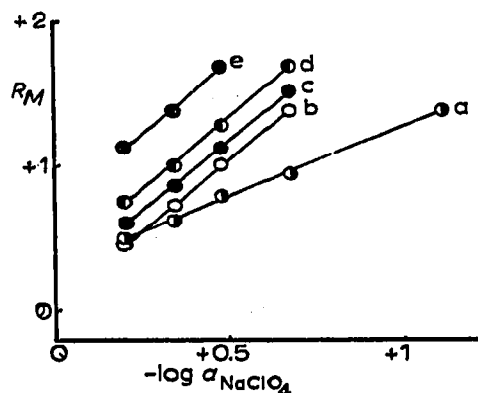


Fig. 4. Relationship of  $R_M$  values to  $-\log a_{\text{NaClO}_4}$  for: a = Ag, Tl; b = Mg; c = Mn, Zn, Co, Ni, Cu; d = Ca, Cd; e = Ba on Dowex 50-X4 thin layers.

between the  $R_F$  values ( $\geq 0.05$ ) are necessary to separate two elements clearly. For example, perhaps it is possible to separate the elements of a given analytical subgroup, such as Cu(II), Bi(III), Pb(II), Cd(II) and Hg(II), with 2 M NaCl as eluent, notwithstanding the small differences in the  $R_F$  values of Cu(II), Pb(II) and Bi(III).

The behaviour of Dowex 50-X4 differs from that of CMCNa using  $\text{NaClO}_4$  solutions as eluents, both with regard to the retention mechanism for the ions at low eluent concentrations and to the possibility of application in the analytical field. The ion-exchange process seems to be the main parameter in the ion retention mechanism, as can be seen from the  $R_F$  values presented in Table II, and, above all, from the pattern of the relationship  $R_M/-\log a_{\text{NaClO}_4}$  (Fig. 4). It seems to be true at least for salt concentrations in the eluent lower or equal to 1 M.

Other parameters begin to affect the relationship  $R_M/-\log [\text{NaClO}_4]$  markedly when the  $\text{NaClO}_4$  concentration is higher than 1 M, as the curvilinear portions in Fig. 5 show. The confirmation of the prevalence of the ion-exchange process is given by the straight-line slopes in Fig. 4 for  $\text{NaClO}_4 \leq 1$  M. The values of these slopes have been reported for every ion in Table III; the values agree perfectly with those one might have expected on the basis of the ion charge<sup>6</sup>.

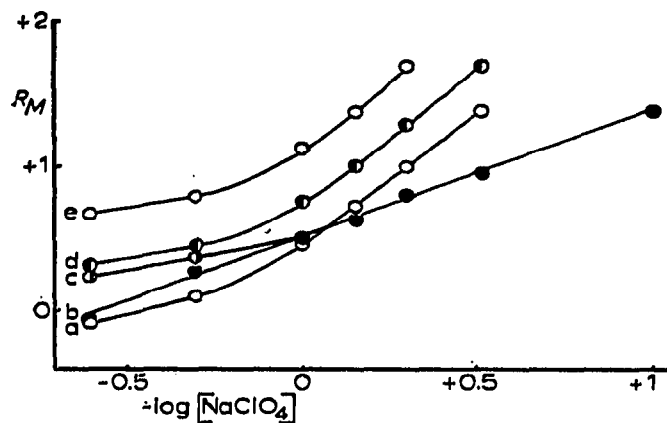
On the contrary, the slope values we deduce from the  $R_M/-\log [\text{NaClO}_4]$  graph are 5–11% lower than the preceding ones. On CMCNa layers a different behaviour was observed. All the ions exhibited a graph with a slope clearly lower than that which could be foreseen, the only exceptions being Tl(I) and Ag(I) for which we found slope values of 0.78 and 0.88, respectively.

*Ion retention.* The different behaviour of the ions on the two exchangers cannot be ascribed to the smaller exchange power of CMCNa with respect to Dowex 50-X4 (ref. 7). In fact, in spite of the greater exchange power of the mixed layers (consisting of CMCNa + Dowex 50-X4, 1:1) with respect to those consisting of only CMCNa, a few ions such as Ag(I), Tl(I), Mg(II) and Ca(II) behave in agreement with the law

TABLE II

 $R_F$  VALUES OF METAL IONS ON DOWEX 50-X<sub>4</sub> THIN LAYERS

Ion	Eluent: NaClO <sub>4</sub> (M)						
	0.1	0.3	0.5	0.7	1	2	4
Ag(I)	0.04	0.10	0.14	0.19	0.24	0.30	0.37
Tl(I)	0.04	0.10	0.14	0.19	0.24	0.35	0.54
Hg(I)	0.00	0.00	0.00	0.00	0.04	0.07	0.11
Cu(II)	0.00	0.03	0.07	0.12	0.20	0.32	0.38
Co(II)	0.00	0.03	0.07	0.12	0.20	0.32	0.45
Ni(II)	0.00	0.03	0.07	0.12	0.20	0.32	0.45
Zn(II)	0.00	0.03	0.07	0.12	0.20	0.32	0.46
Cd(II)	0.00	0.02	0.05	0.09	0.15	0.26	0.33
Hg(II)	0.00	0.00	0.02	0.05	0.08	0.14	0.18
Pb(II)	0.00	0.00	0.00	0.00	0.00	0.09	0.15
Mn(II)	0.00	0.03	0.07	0.12	0.20	0.32	0.44
Be(II)	0.00	0.05	0.11	0.19	0.30	0.48	0.56
Mg(II)	0.00	0.04	0.09	0.16	0.26	0.44	0.55
Ca(II)	0.00	0.02	0.05	0.09	0.15	0.26	0.33
Sr(II)	0.00	0.02	0.05	0.09	0.14	0.23	0.31
Ba(II)	0.00	0.00	0.02	0.04	0.07	0.14	0.18
Al(III)	0.00	0.00	0.00	0.00	0.05	0.16	0.34
Ga(III)	0.00	0.00	0.00	0.00	0.05	0.15	e.s. <sup>a</sup>
In(III)	0.00	0.00	0.00	0.00	0.02	0.10	e.s.
Th(IV)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
U(VI)	0.00	0.03	0.06	0.08	0.10	0.13	0.13

<sup>a</sup> e.s. = elongated spot.Fig. 5. Relationship of  $R_M$  values to  $-\log[\text{NaClO}_4]$  for: a = Mg; b = Tl; c = Ag; d = Ca, Cd; e = Ba on Dowex 50-X<sub>4</sub> thin layers.

of mass action, the others being not appreciably affected by an increase in salt concentration in the eluent (Table IV). The  $R_F$  values obtained on layers of CMCNa having different exchange capacities for several ions (again shown in Table IV) also seem to exclude such an hypothesis. There are essentially two other parameters that are able, in an ionic exchange process, to control the retention mechanism of the layer:

- (a) exchange rate at the surface
- (b) diffusion rate within the resin.

TABLE III

SLOPES OF THE RELATIONSHIP  $R_M / -\log a_{\text{NaClO}_4}$  (A) AND  $R_M / -\log [\text{NaClO}_4]$  (B) FOR IONS OF VARIOUS IONIC CHARGE ON DOWEX 50-X<sub>4</sub> THIN LAYERS

Ion	Slope	
	(A)	(B)
Ag(I)	0.97	0.88
Tl(I)	0.97	0.88
Mg(II)	1.94	1.78
Ca(II)	1.96	1.82
Sr(II)	1.84	1.64
Ba(II)	2.00	1.90
Co(II)	1.90	1.74
Ni(II)	1.90	1.74
Mn(II)	1.90	1.74
Zn(II)	1.90	1.74
Cd(II)	1.96	1.82
Cu(II)	1.90	1.74
Be(II)	1.90	1.76

TABLE IV

$R_F$  VALUES OF METAL IONS ON THIN LAYERS CONSISTING OF DOWEX 50-X<sub>4</sub> + CMCNa (1:1) AND CMCNa WITH EXCHANGE CAPACITY OF 0.89 AND 1.18 mequiv./g, RESPECTIVELY

Eluents: (A) NaClO<sub>4</sub>, 0.3 M, (B) NaClO<sub>4</sub>, 0.5 M, (C) NaClO<sub>4</sub>, 1 M.

Ion	Dowex 50-X <sub>4</sub> + CMCNa			CMCNa (0.89 mequiv./g)			CMCNa (1.18 mequiv./g)		
	(A)	(B)	(C)	(A)	(B)	(C)	(A)	(B)	(C)
Ag(I)	0.07	0.10	0.17	0.14	0.19	0.26	0.12	0.18	0.25
Tl(I)	0.10	0.14	0.24	0.35	0.45	0.58	0.33	0.44	0.56
Cu(II)	0.00	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.00
Co(II)	0.02	0.06	0.12	0.07	0.12	0.20	0.05	0.11	0.18
Ni(II)	0.01	0.05	0.11	0.05	0.09	0.17	0.04	0.08	0.14
Cd(II)	0.00	0.01	0.03	0.03	0.03	0.03	0.00	0.02	0.02
Zn(II)	0.02	0.05	0.08	0.04	0.07	0.11	0.03	0.07	0.10
Be(II)	0.02	0.04	0.06	0.04	0.05	0.06	0.02	0.03	0.05
Mg(II)	0.04	0.09	0.26	0.16	0.27	0.44	0.14	0.26	0.43
Ca(II)	0.02	0.05	0.14	0.11	0.17	0.29	0.08	0.17	0.28
Sr(II)	0.02	0.05	0.12	0.15	0.24	0.38	0.14	0.24	0.38
Ba(II)	0.00	0.02	0.06	0.08	0.15	0.28	0.07	0.14	0.26

The behaviour of the ions on mixed layers of Dowex 50-X<sub>4</sub> + CMCNa, as already commented on previously, seems to exclude a determining influence of this parameter in that the diffusion rate should influence the behaviour of divalent ions in practically the same way.

The observed differences in the chromatographic behaviour of the same ions on layers of CMCNa and Dowex 50-X<sub>4</sub> could thus be attributed to the different ionic reaction rate at the resin/solution interface. In fact, the rate of the exchange reaction in both directions is very different in carboxylic resins<sup>8</sup>, depending on the affinity of the ion for the exchanger, whereas in the case of sulphonic resins the two rates are practically equal.

*Elution using neutral solutions of divalent ions*

In Table V  $R_F$  values are reported for several ions eluted with solutions of  $Mg(NO_3)_2$ ,  $MgCl_2$  and  $Ba(NO_3)_2$ , of varying concentrations. In each case a regular increase of  $R_F$  values with increasing salt concentration in the eluent can be observed, in contrast to what is observed eluting with univalent salt solutions under the same conditions of concentrations and ionic strength. The difference in behaviour can be explained by the greater affinity of  $Mg(II)$  and  $Ba(II)$  with respect to  $Na(I)$  for the exchanger. This causes a levelling of the affinities of the ions involved in the exchange and, therefore, an increase in the rate of the ionic exchange reaction.

TABLE V

$R_F$  VALUES OF METAL IONS ON CMCNa THIN LAYERS OBTAINED USING NEUTRAL SOLUTIONS OF DIVALENT IONS AS ELUENT

Ion	$Mg(NO_3)_2$ (M)			$MgCl_2$ (M)		$Ba(NO_3)_2$ (M)	
	0.1	0.5	I	0.5	I	0.1	0.5
Ag(I)	0.24	0.36	0.48	0.00	0.00	0.29	0.44
Tl(I)	0.48	0.72	0.76	n.d. <sup>a</sup>	n.d.	0.48	0.72
Be(II)	n.d.	n.d.	n.d.	n.d.	n.d.	0.10	0.28
Zn(II)	n.d.	n.d.	n.d.	n.d.	n.d.	0.18	0.46
Cd(II)	0.06	0.16	0.28	0.72	0.82	0.10	0.19
Cu(II)	0.02	0.06	0.07	0.06	0.08	0.03	0.07
Co(II)	0.21	0.52	0.66	0.61	0.69	0.28	0.60
Ni(II)	0.18	0.48	0.61	0.58	0.65	0.25	0.57
Hg(II)	0.00	0.01	0.01	0.98	0.98	0.00	0.01
Hg(I)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn(II)	0.26	0.54	0.62	0.66	0.74	0.32	0.71
Pb(II)	0.00	0.02	0.04	0.07	0.25	0.00	0.02
Sr(II)	0.37	0.67	0.78	0.67	0.78	n.d.	n.d.
Ba(II)	0.31	0.60	0.66	0.60	0.66	n.d.	n.d.
Al(III)	n.d.	n.d.	n.d.	n.d.	n.d.	0.00	0.02
Fe(III)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Bi(III)	0.00	0.00	0.00	0.02	0.04	0.00	0.08
U(VI)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1st front	0.42	0.78	0.92	0.87	0.93	0.33	0.71

<sup>a</sup> n.d. = not determined.

Such hypotheses are confirmed by the data in Table VI relative to the slopes of the lines obtained by graphing the  $R_M$  values of several ions, on layers of carboxymethylcellulose in the magnesium salt form (CMCMg), as a function of  $-\log[Mg(NO_3)_2]$ . In fact, ions having an affinity similar to magnesium, with respect to the exchanger, behave in accordance with the law of mass action. They are Ag(I), Tl(I), Sr(II), Ba(II) and, to a lesser degree, Mn(II). The remaining ions are not influenced in an analogous manner upon increasing the concentration of the salt in the eluent.

It might also be interesting to compare the data obtained by us with those observed by KNIGHT<sup>9</sup> on cellulose-base ion-exchange papers. The sequence of affinities found on ion-exchange papers is respected at least for those ions common to both contributions studied on thin layers.



TABLE VI

 $R_F$  VALUES OF METAL IONS ON CMCMg THIN LAYERS

Ion	Eluent: $Mg(NO_3)_2$ (M)				Slope of the relationship $R_M / -\log[Mg(NO_3)_2]$
	0.1	0.3	0.5	1	
Ag(I)	0.20	0.31	0.36	0.42	0.5
Tl(I)	0.44	0.58	0.63	0.72	0.5
Sr(II)	0.24	0.47	0.57	0.72	0.9
Ba(II)	0.22	0.44	0.54	0.70	0.9
Mn(II)	0.19	0.38	0.49	0.63	0.8
Co(II)	0.20	0.36	0.45	0.57	0.7
Ni(II)	0.18	0.32	0.41	0.52	0.7
Zn(II)	0.15	0.22	0.26	0.32	0.5
Cd(II)	0.06	0.10	0.13	0.17	0.5

TABLE VII

 $R_F$  VALUES OF SOME METAL IONS ON CMCNa THIN LAYERSThe data reported refer to solutions with an  $Na^+$  concentration of 0.5 M and different pH values.

Ion	pH of the eluent		
	9.5	11.5	12.0
Cu(II)	0.00	0.00	0.02
Co(II)	0.12	0.04	0.01
Ni(II)	0.09	0.03	0.00
Zn(II)	0.07	0.05	0.40
Cd(II)	0.03	0.03	0.01
Mg(II)	0.27	0.27	0.02
Pb(II)	0.00	0.00	0.02

*Elution using alkaline solutions of univalent ions*

Using a solution of pH 7 to 10 for elution, the  $R_F$  values (Table VII) are equal to those obtained with neutral eluents, in accordance with the fact that the pH on the layer does not change appreciably when working in the above-mentioned interval. For eluent pH values greater than 10, and in particular at the values 11.5 and 12.5 a sharp decrease in  $R_F$  values is observed for those ions having a tendency to give insoluble hydroxides. The behaviour of Zn(II) should be noted (related to its amphotericism). This could be used for analytical purposes.

*Selectivity coefficients*

From the data that we have reported up to this point it results that the selectivity coefficients can be calculated using  $R_F$  values on layers of Dowex 50-X4, up to a one molar concentration of the salt in the eluent. In the case of CMCNa, on the other hand, the selectivity coefficients can be determined only in the case of exchange between ions having similar affinities for the exchangers. This is the case with Tl(I) and some basic amino acids<sup>10</sup>.

In Table VIII are reported values of the selectivity coefficients calculated with equation:

$$\log K_s = R_M - n \log [Na^+]_R + \log \frac{A_1}{A_2} + n \log a_{Na^+}$$

TABLE VIII

SELECTIVITY COEFFICIENTS ( $K_s$ ) OF SOME METAL IONS FOR DOWEX 50-X4  
(1) Calculated from  $R_F$  values. (2) Data found in the literature (ref. 11).

Ion	$K_s$	
	(1)	(2)
Ag(I)	4.1	3.0
Tl(I)	4.1	4.2
Be(II)	1.2	1.4
Mg(II)	1.4	1.2
Ca(II)	2.6	1.7
Sr(II)	2.9	1.9
Ba(II)	6.1	3.0
Cu(II)	1.8	1.3
Co(II)	1.8	1.3
Ni(II)	1.8	1.4
Zn(II)	1.8	1.3
Mn(II)	1.8	1.4
Cd(II)	2.5	1.3

in which  $K_s$  is the selectivity coefficient,  $[Na^+_R]$  is the concentration of sodium in the resin in mequiv./g, and  $A_1/A_s$  is the ratio between the weights of the mobile phase and the stationary phase (3.70).

In the same table are reported, for confrontation, the selectivity coefficients obtained directly by determining the quantity of ions adsorbed by the resin at equilibrium in a solution of known concentration of the ion<sup>11</sup>. The difference between the values of the coefficients for a given ion is evidently due to the diversity in the techniques employed. The good agreement in the sequence of the affinities should, however, be noted.

### Conclusions

From the data obtained one can draw the following conclusions:

(1) Contrary to that which is observed for ionic exchangers in the acid form, in the case of exchangers in the sodium form (eluted with neutral solutions of univalent ions) a concentration gradient within a given interval of concentrations of the salt in the eluent is not observed.

(2) It is possible in such a concentration interval to determine the charge of an ion in solution. This possibility is limited to those ions for which the exchange reaction rates in the two directions are not very different.

(3) The retention of the ions on such layers does not seem to be influenced by the diffusion rate of the ions through the resin but rather by the exchange reaction rate at the surface.

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