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INFLUENCE OF COMPLEX FORMATION ON THE CHROMATOGRAPHIC BEHAVIOUR OF INORGANIC IONS ON SODIUM CARBOXYMETHYLCELLULOSE AND DOWEX 50-X4 (Na^+) THIN LAYERS

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SUMMARY

The chromatographic behaviour of 16 metal ions on thin layers of sodium carboxymethylcellulose and Dowex 50-X4 (Na^+) was investigated. The eluents used were acetate, gluconate, lactate and oxalate buffer solutions at constant ionic strength. The influence on the R_F values of some parameters (the affinity of the ions for the exchanger, the concentration and the type of buffer solution) was determined. Criteria are proposed for the analytical use of these parameters.

The stability constants of the complexes with the above ligands and the selectivity coefficients of the ions for the two exchangers were calculated. Finally, the validity of the method for the determination of the stability constants for mono- and bidentate ligands is discussed.

INTRODUCTION

In a previous paper[1], it was pointed out that for tri- and tetravalent ions, interesting separations on sodium carboxymethylcellulose (CMCNa) and Dowex 50-X4 (Na^+) thin layers can be obtained when eluting with buffer solutions at constant ionic strength. For this reason, we considered it useful to study the behaviour of mono- and divalent ions using acetate, lactate, gluconate (used previously) and oxalate ions as ligand agents.

Special care was devoted to the determination of the selectivity coefficients of the metal ions for the exchangers and the stability constants of the different complexes.

EXPERIMENTAL

The buffer solutions were prepared so that the ratio of the concentrations of the acid and its salt was 1:2. In the case of the oxalate buffer, $H_2C_2O_4$ and $Na_2C_2O_4$ were used. The ionic strength was kept constant ($\mu = 1$) by means of sodium perchlorate.

The CMCNa layers (300 μm) were prepared with 4.5 g of the exchanger in 50 ml of water, and the Dowex 50-X4 (Na^+) layers by mixing 3 g of the resin and 6 g of microcrystalline cellulose in 40 ml of water. The resin, obtained by neutralizing the acid form with NaOH, was rinsed with water and methanol and dried at room temperature.

The chromatographic measurements were carried out at 25°. The migration distance was 11 cm unless stated otherwise. The spots were detected with solutions of 8-hydroxyquinoline in ethanol (followed by exposure to ammonia vapour), with aqueous solutions of sodium rhodizonate and with ammonium sulphide.

RESULTS AND DISCUSSION

The R_F values of 16 metal ions on CMCNa layers, when eluting with solutions of increasing concentrations of acetate, gluconate and lactate, are reported in Table I.

TABLE I

R_F VALUES OF MONO- AND DIVALENT IONS ON CMCNa THIN LAYERS

Elution with buffer solutions: (*a*) acetate (pH = 5.05); (*b*) gluconate (pH = 4.15); (*c*) lactate (pH = 3.95). e.s. = Elongated spot.

Ion	*0.05 mole/l*			*0.10 mole/l*			*0.30 mole/l*			*0.50 mole/l*		
	a	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*
Tl(I)	0.59	0.61	0.60	0.60	0.61	0.61	0.60	0.63	0.61	0.60	0.65	0.62
Ag(I)	0.29	0.31	0.32	0.31	0.34	0.35	0.38	0.44	0.46	0.43	0.53	0.55
Hg(I)	e.s.	0.23	e.s.	e.s.	0.35	e.s.	e.s.	0.59	e.s.	0.74	0.72	0.95
Pb(II)	0.00	0.01	0.01	0.01	0.04	0.03	0.07	0.19	0.13	0.18	0.41	0.26
Hg(II)	0.03	e.s.	e.s.	e.s.	e.s.	e.s.	e.s.	e.s.	0.16	0.66	0.59	0.29
Cu(II)	0.02	0.11	0.22	0.04	0.22	0.39	0.16	0.55	0.72	0.31	0.72	0.83
Cd(II)	0.06	0.09	0.11	0.10	0.15	0.19	0.23	0.35	0.42	0.33	0.51	0.56
Zn(II)	0.12	0.24	0.35	0.14	0.37	0.58	0.25	0.65	0.86	0.35	0.80	0.97
Mn(II)	0.24	0.30	0.33	0.27	0.35	0.42	0.37	0.54	0.71	0.45	0.67	0.83
Co(II)	0.22	0.33	0.39	0.25	0.45	0.58	0.35	0.68	0.85	0.44	0.81	0.95
Ni(II)	0.20	0.33	0.45	0.23	0.47	0.68	0.34	0.72	0.91	0.43	0.85	0.97
Ba(II)	0.29	0.34	0.32	0.30	0.39	0.36	0.33	0.57	0.49	0.36	0.70	0.58
Sr(II)	0.38	0.43	0.41	0.40	0.48	0.45	0.45	0.65	0.59	0.49	0.77	0.68
Ca(II)	0.32	0.41	0.38	0.34	0.49	0.45	0.41	0.68	0.66	0.48	0.78	0.77
Mg(II)	0.46	0.50	0.51	0.49	0.53	0.57	0.58	0.63	0.77	0.65	0.71	0.86
Be(II)	0.13	0.14	0.17	0.19	0.20	0.25	0.42	0.39	0.47	0.58	0.52	0.59

With the exception of Tl(I), owing to its poor tendency to form complexes with the three ligands, and of Ba(II) with acetate, the other ions are strongly influenced both by the concentration and the type of ligand. On the basis of these two factors, some interesting separations can be obtained. From an analytical point of view, the separation of Ag(I), Tl(I), Hg(I) and Pb(II), when eluting with 0.03 *M* gluconate, is particularly interesting (see Fig. 1). It should be noted that at such a concentration of the ligand, no elongated spots, which are generally obtained for mercury, are observed. The starting solutions of Hg(I) and Hg(II) were obtained by dissolving the two nitrates in dilute nitric acid.

Other good separations are those of Cu(II) from Cd(II) when eluting with lactate concentrations above 0.3 *M*, of Mn(II) from Co(II) and Ni(II) with 0.1 *M* lactate concentration, and of Zn(II) from Cd(II) with gluconate or lactate over a wide range of concentrations of the two ligands.

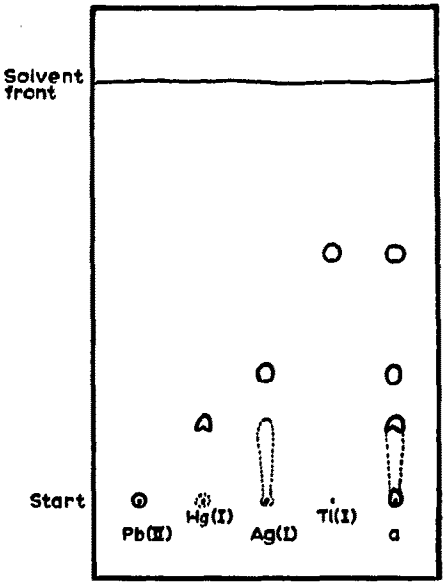

Fig. 1. Thin-layer chromatogram of some ions on CMCNa. (a) Pb(II), Hg(I), Ag(I) and Tl(I). Sodium gluconate concentration 0.03 *M*.

TABLE II

R_F VALUES OF MONO- AND DIVALENT IONS ON DOWEX 50-X4 (Na$^+$) THIN LAYERS

Elution with buffer solutions: (*a*) acetate (pH=5.05); (*b*) gluconate (pH=4.15); (*c*) lactate (pH=3.95).

Ion	*0.05 mole/l*			*0.10 mole/l*			*0.30 mole/l*			*0.50 mole/l*		
	a	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*
Tl(I)	0.12	0.12	0.12	0.12	0.13	0.12	0.12	0.14	0.13	0.12	0.16	0.13
Ag(I)	0.15	0.15	0.16	0.16	0.17	0.17	0.19	0.22	0.23	0.22	0.26	0.28
Hg(I)	e.s.	e.s.	e.s.	e.s.	e.s.	e.s.	e.s.	e.s.	e.s.	e.s.	e.s.	0.75
Pb(II)	0.18	0.18	0.14	0.33	0.33	0.25	0.71	0.70	0.60	0.82	0.83	0.75
Hg(II)	e.s.	e.s.	e.s.	e.s.	e.s.	0.59	e.s.	e.s.	0.81	e.s.	e.s.	0.87
Cu(II)	0.36	0.61	0.72	0.54	0.84	0.86	0.82	0.97	0.97	0.96	0.97	0.97
Cd(II)	0.22	0.22	0.22	0.31	0.32	0.32	0.65	0.65	0.65	0.79	0.79	0.79
Zn(II)	0.22	0.38	0.55	0.27	0.57	0.70	0.50	0.86	0.91	0.66	0.97	0.97
Mn(II)	0.20	0.22	0.24	0.22	0.26	0.30	0.32	0.43	0.53	0.40	0.56	0.67
Co(II)	0.22	0.29	0.34	0.26	0.40	0.50	0.40	0.71	0.87	0.51	0.85	0.97
Ni(II)	0.22	0.36	0.41	0.26	0.53	0.64	0.40	0.84	0.96	0.51	0.97	0.97
Ba(II)	0.04	0.05	0.04	0.04	0.06	0.04	0.05	0.12	0.05	0.06	0.18	0.06
Sr(II)	0.10	0.12	0.10	0.11	0.15	0.11	0.13	0.26	0.15	0.15	0.35	0.19
Ca(II)	0.13	0.18	0.16	0.14	0.23	0.20	0.19	0.41	0.34	0.23	0.54	0.45
Mg(II)	0.27	0.27	0.29	0.29	0.30	0.34	0.37	0.38	0.50	0.44	0.45	0.63
Be(II)	0.32	0.27	0.29	0.48	0.39	0.42	0.83	0.64	0.69	0.96	0.75	0.81

Apart from the type and concentration of the ligand, the affinity of the ions for the exchanger also plays an important role in their chromatographic behaviour. Such an influence can be seen from the R_F values reported in Table II, which refer to the metal ions on Dowex 50-X4 (Na^+) thin layers when eluting with the same solutions as those used on CMCNa layers.

It can be seen, in fact, by comparing the R_F values on the two layers, that, as the concentration and the type of ligand change, different behaviours are observed owing to the variation of the affinity of the ions for the exchanger. Among the monovalent ions, such behaviour is evident for Ag(I) and, among the divalent ions, for Pb(II), Cu(II), Cd(II), Zn(II), Ba(II), Sr(II), Ca(II) and Mg(II). As regards Cd(II), however, it should be noted that on Dowex the R_F values are virtually the same when eluting with the three different ligands, unlike the effect observed on CMCNa. The differences observed on this last exchanger can be attributed to the different pH values of the buffer solutions. A change in the pH value should have an influence on the affinity of the ion for the exchanger and, therefore, on the reversibility of the exchange reaction between Cd(II) in the resin and Na(I) in the solution.

The dependence of the reversibility of the exchange reaction on the affinity of the ion for the exchanger has already been pointed out[2] for CMCNa with Cd(II), Cu(II), Pb(II), Be(II) and Zn(II). According to such an assumption, a decrease in the affinity of the ion for the CMCNa, leading to an increase in reversibility and to higher R_F values, should be observed as the pH decreases. Such an assumption is confirmed, because the R_F values of cadmium increase as the pH of the solution decreases. It must be noted, furthermore, that such behaviour is particularly clear at high ligand concentrations, in relation to the same pH value on the layer and in the solution[3].

The different R_F sequence for Pb(II) and Be(II) on the two layers when eluting with the same ligands seems to be consistent with the different pH values of the buffer solutions. The behaviour of Cu(II) on CMCNa agrees with that which can be predicted on the basis of the pH of the eluents. In fact, the R_F sequence is similar on both layers apart from a greater difference, on CMCNa layers, between the R_F values relative to the three ligands. Such behaviour is justified, as the sequence of stability constants of the three ligands with Cu(II) (lactate > gluconate > acetate) is opposite to that of the corresponding pH values of the solutions.

All the data considered up to now refer to the behaviour of the ions with monodentate ligands, which differ from each other due to the presence of one or more OH groups. Our study has been extended so as to include a bidentate ligand, such as oxalate, in order to obtain a complete picture of the influence of complex formation on the ion-exchange process and, especially, to characterize possible differences due to the different kinds of complexes. The use of such ligands generally involves the need for buffer solutions with a lower concentration than that of acetate, gluconate and lactate solutions. The concentration range of sodium oxalate is, in fact, included between 10^{-3} and $9 \cdot 10^{-2}$ *M*.

Some of the best separations that can be obtained with oxalate on CMCNa are reported in Table III. Table III also includes, apart from the mono- and divalent ions, some trivalent ions whose behaviour has already been studied[1].

TABLE III

SEPARATIONS OBTAINED ON CMCNa THIN LAYERS

Elution with oxalate buffer solutions. Migration distance: 12 cm.

Separation	*Sodium oxalate concentration (M)*	R_F
Be(II)/Mg(II)	10^{-3}	0.12/0.48
Pb(II)/Tl(I)	10^{-3}	0.01/0.59
Cr(III)/Al(III)/Fe(III)	$2.5\cdot10^{-3}$	0.00/0.40/0.97
Cr(III)/Mn(II)/Ni(II)/Fe(III)	$2.5\cdot10^{-3}$	0.00/0.35/0.59/0.97
Cd(II)/Cu(II)	$5\cdot10^{-3}$	0.09/0.78
Cd(II)/Zn(II)	$7\ 5\cdot10^{-3}$	0.12/0.77
Cd(II)/In(III)/Al(III), Ga(III)	$7.5\cdot10^{-3}$	0.12/0.48/0.96
Hg(I)/Hg(II)	$9\cdot10^{-2}$	0.00/0.19

Selectivity coefficients

In a previous paper[2], a difference has been pointed out between the values of the selectivity coefficients calculated on the basis of thin-layer chromatography and those obtained by determining the amount of ions adsorbed by the exchanger in a solution of known concentration of the ion. The good agreement between the sequences of the affinities, apart from the absolute value of the coefficients, has also been noted. As we used microcrystalline cellulose instead of cellulose, we tried to ascertain if the different nature of cellulose might have an influence on the selectivity

TABLE IV

SELECTIVITY COEFFICIENTS (K_s) OF MONO- AND DIVALENT IONS FOR CMCNa AND DOWEX 50-X4 (Na^+) AT THE GLUCONATE BUFFER pH (4.15)

Ion	I_0		K_s	
	CMCNa	*Dowex 50-X4 (Na^+)*	*CMCNa*	*Dowex 50-X4 (Na^+)*
Tl(I)	2.55	27.1	1.34	14.1
Ag(I)	9.95	22.8	5.22	11.9
Hg(I)	61.5	—	32.3	—
Pb(II)	—	144.2	—	39.0
Cu(II)	—	20.8	—	5.65
Cd(II)	127.0	24.8	34.5	6.72
Zn(II)	33.4	16.85	9.05	4.57
Mn(II)	12.1	17.45	3.27	4.73
Co(II)	16.2	16.85	4.4	4.57
Ni(II)	18.5	16.85	5.0	4.57
Ba(II)	9.85	102	2.67	27.6
Sr(II)	6.68	35.3	1.81	9.55
Ca(II)	8.75	25.8	2.37	7.0
Mg(II)	4.78	11.1	1.29	3.0
Be(II)	45.0	19.4	12.2	5.25

coefficients. In Table IV are reported values of the selectivity coefficients on CMCNa (not previously reported) and Dowex 50-X4 (Na^+) calculated by using the equation

$$K_s = \frac{a^x_{Na^+}}{[Na^+]^x_R} \cdot l_0$$

where x is the charge on the ion involved in the exchange reaction and $[Na^+]_R$ is 1.18 for CMCNa and 1.19 for Dowex 50-X4 (Na^+) plus microcrystalline cellulose. The l_0 values for the different ions have been determined by extrapolating the R_F values to zero ligand concentration and replacing such values in the relationship

$$\alpha = \frac{A_l}{A_s}\left(\frac{1}{R_F} - 1\right)$$

where A_l/A_s is the ratio of the weights of the mobile phase and the stationary phase. This ratio, under our experimental conditions, is 3.72–4.09 for CMCNa layers and 3.53–3.97 for Dowex 50-X4 (Na^+) layers. In both cases, a decreasing trend, similar to that observed by Grimaldi *et al.*[4] on ion-exchange papers, was not observed. For this reason, we considered an average value of A_l/A_s of 3.92 for the CMCNa and 3.70 for the Dowex layers. If one compares the values of the selectivity coefficients for the Dowex plus microcrystalline cellulose layers with those obtained on layers of the same exchanger plus cellulose, a sharp increase in the selectivity coefficients and a different sequence of the affinities for some ions is observed on changing from layers containing cellulose to those containing microcrystalline cellulose.

It should be noted, furthermore, that for a given ion, the selectivity coefficient is in some instances higher on CMCNa than on Dowex thin layers; for Pb(II) and Cu(II) it is so high that it has not been possible to determine it with sufficient accuracy. For the monovalent and alkaline earth ions, lower values have been found on CMCNa than on Dowex.

The values reported in Table IV refer to a gluconate buffer solution of pH 4.15. The selectivity coefficients at the pH values of acetate and lactate buffer solutions are different for some ions, mostly on CMCNa layers. The greatest difference is observed for Be(II), whose K_s value, when eluting with acetate buffer solutions, is 15.3 instead of the reported value of 12.2.

The increase in the selectivity coefficients on changing from Dowex layers containing cellulose to those containing microcrystalline cellulose and, overall, the different sequence observed for some ions, indicate the necessity of knowing the "conditional" value of the selectivity coefficients for a given exchanger. It is particularly useful to know these values relative to the ionic strength (1 in this work) and to the pH at which the chromatographic process occurs.

Stability constants

From an analytical point of view, it is useful to know the value of the stability constants under the conditions at which the chromatographic process occurs other than the "conditional" selectivity coefficients. The chromatographic behaviour of the ions on the different exchangers and the possibilities of their separation can be predicted *a priori* on the basis of the knowledge of these two parameters. Such predictions, at least from a quantitative point of view, are very difficult to make on the basis of the values of the stability constants reported in the literature, as such values generally refer to an ionic strength of zero and, for a given ion, often differ from each other owing to the different techniques used in their determination.

The calculation of the stability constants has been carried out by means of the following relationship:

$$\alpha = l_0 \cdot \frac{1 + l[\mathrm{A}^-]}{1 + \sum_1^n \beta_n [\mathrm{A}^-]^n} \tag{1}$$

where l is calculated on the basis of the Fronaeus method[5], which has already been applied to ion-exchange papers by Grimaldi *et al.*[4].

This method, critically revised by Marcus[6], is limited in the determination of higher stability constants owing to the uncertainty of the extrapolations that involve the use of auxiliary functions involving subtractions of closely similar numbers. For this reason, only the values of β_1 and β_2 are reported in Table V. It should be noted that for some ions the β values are reported for only one exchanger. The non-determination of the stability constants is due, for Pb(II) and Cu(II) on CMCNa, to the impossibility of obtaining a finite value of l_0 and, for Ba(II) on Dowex, to the high affinity of this ion for the exchanger so that the influence of the complex formation on the R_F value is negligible. As regards the numerical values of the stability constants, good agreement is observed between the results obtained on the two exchangers with the exception of Cd(II) and, to a lesser extent, of Zn(II) and Be(II). Such differences can be attributed to the incomplete reversibility of the exchange reaction of these ions with CMCNa[2].

TABLE V

STABILITY CONSTANTS OF THE ACETATE (β), GLUCONATE (β') AND LACTATE (β'') COMPLEXES OF MONO- AND DIVALENT IONS CALCULATED ON THE BASIS OF THE R_F VALUES ON (*a*) CMCNa AND (*b*) DOWEX 50-X4 (Na+) THIN LAYERS

Ion	β_1		β_2		β'_1		β'_2		β''_1		β''_2	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
Tl(I)	0	0	0	0	0.5	0.7	0	0	0	0	0	0
Ag(I)	2.0	1.4	0	0	2.8	2.4	1.4	0	3.0	2.8	1.7	0
Hg(I)	–	–	–	–	75	–	0	–	–	–	–	–
Pb(II)	–	126	–	4500	–	126	–	4500	–	101	–	1500
Cu(II)	–	44.5	–	700	–	–	–	–	–	–	–	–
Cd(II)	24.7	20	102	235	43.6	20	310	235	58.5	20	610	235
Zn(II)	4.2	6.9	19	35	31	31	293	420	51.5	36.5	950	1100
Mn(II)	4.9	4.3	8	7	6.2	6.4	21	15	11.5	10.2	82	35
Co(II)	5.0	6.6	11	7	19	17.6	120	198	29.1	21	390	330
Ni(II)	6.2	6.6	14	7	28	27.3	340	270	44.2	–	1200	–
Ba(II)	1.2	–	0.7	–	5.6	7.2	16	12	5.0	–	7	–
Sr(II)	2.0	1.9	1.1	0.8	6.0	7.2	18	11	5.4	2.8	16	2
Ca(II)	3.0	2.6	4	4	14.2	12	59	38	8.7	7.4	35	21
Mg(II)	3.7	3.8	6	6	3.2	3.85	8	4	5.75	5.45	23	14
Be(II)	26	24	220	295	18	20.8	52	141	31.3	22.8	222	180

An interesting parameter, which seems to have a constant value for each type of ligand, is the ratio

$$\frac{l_1}{l_0}=\frac{l}{\beta_1}$$

where

$$l_1=\frac{[\mathrm{MeA}^+]_R}{[\mathrm{MeA}^+]_{\mathrm{sol}}} \quad \text{and} \quad l_0=\frac{[\mathrm{Me}^{2+}]_R}{[\mathrm{Me}^{2+}]_{\mathrm{sol}}}.$$

On both exchangers, for the monodentate ligands the l_1/l_0 values are virtually the same for the different ions, *viz.*, 0.28±0.12 (acetate), 0.20±0.10 (lactate) and 0.16±0.06 (gluconate). It is interesting to note that the value of 0.28±0.12 for acetate is similar to that found by Marcus[6] for the same ligand (0.30±0.1). It should be noted, furthermore, that the l_1/l_0 values decrease as the ligand size increases; in fact, the l_1/l_0 values for chloride, whose size is much smaller than that of the ligands we used, are 0.75 and 0.92 in 0.691 *M* $HClO_4$ solution. These values were calculated on the basis of the data of Morris and Short[7,8] on Amberlite IR-120 (H^+) relative to the Mn(II) and Co(II) chloro-complexes.

Greater reliability of the values of the stability constants obtained with the chromatographic method is achieved when the ligand charge is equal to or higher than that of the cation. In this case, eqn. 1 becomes

$$\frac{l_0-\alpha}{\alpha[\mathrm{A}^-]}=\beta_1+\beta_2[\mathrm{A}^-]+\beta_3[\mathrm{A}^-]^2+\ldots \qquad (2)$$

and the calculation of the constants is greatly simplified, as α and l_0 can easily be obtained from the chromatographic data. Eqn. 2 is similar to that used for the calculation of the stability constants obtained by the standard methods. The values of the stability constants relative to oxalate and calculated by means of eqn. 2 are reported in Table VI. These values do not refer to the analytical concentrations, but

TABLE VI

STABILITY CONSTANTS FOR THE OXALATE COMPLEXES WITH MONO- AND DIVALENT IONS

Ion	*Ion-exchange TLC*			*Other investigations*			
	Log β_1	*Log β_2*	*Log β_3*	*Log β_1*	*Log β_2*	*Log β_3*	*Ref.*
Tl(I)	0.23	–	–	–	–	–	
Ba(II)	0.81	–	–	0.58	–	–	9
Sr(II)	1.65	–	–	1.25	1.90	–	10
Mg(II)	2.06	–	–	2.00	–	–	11
Mn(II)	2.30	3.90	–	–	–	–	
Ni(II)	3.31	4.89	6.31	–	–	–	
Co(II)	3.15	4.75	–	–	–	–	
Zn(II)	3.20	4.49	7.0	3.44	6.48	7.24	12
Cd(II)	2.60	3.75	4.23	2.61	4.11	5.06	13
				3.0	4.7	–	14

to the actual oxalate concentrations on the layer. The pH on the layer, determined as previously described[3], is about 5.90 for almost the whole of the concentration range investigated. At this pH value, the ratio $C_2O_4^{2-}/HC_2O_4^-$ is 50:1 instead of 1:2 in the eluent. On the basis of these results, the formation of complexes such as $[Me(HC_2O_4)_n]^{x-n}$ can be excluded.

As regards the accuracy of the results, the comparison of our results with those of other workers using different techniques at an ionic strength of unity may be interesting (see Table VI). It should be noted that the same order of magnitude is found and, for Mg(II), there is good agreement between the numerical values.

For Cd(II) and Zn(II), for which the incomplete reversibility of the exchange reaction on CMCNa has been pointed out, the constants have only an analytical interest with regard to this layer.

Differences between the pH on the layer and that in solution have been pointed out both on Dowex and CMCNa layers when eluting with acetate, gluconate and lactate buffer solutions. With such ligands, however, the pH on the layer is tending towards that of the solution as the buffer concentration increases and its influence on the value of the stability constants does not seem to be determined, as the good agreement between our values and those of Fronaeus for the copper–acetate[5] and nickel–acetate[15] systems shows.

Affinity and complex formation in ion-exchange analysis

The influence of both the affinity of the ions for the exchanger and the concentration and type of ligand enables criteria to be fixed such that the best separations among two or more elements may be obtained.

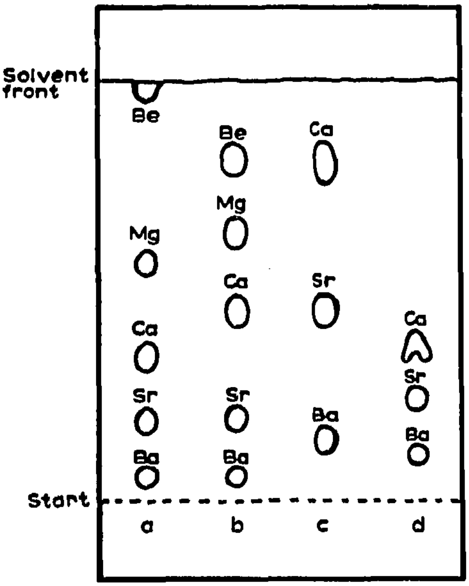

Fig. 2. Thin-layer chromatograms of Be(II) and alkaline earth ions on Dowex 50-X4 (Na+) when eluting with buffer solutions containing (a) 1 *M* sodium acetate; (b) 0.5 *M* sodium lactate; (c) 1 *M* sodium lactate. Chromatogram (d) refers to the results of Berger *et al.*[16] when eluting with 0.75 *M* ammonium lactate.

Such criteria are: (a) the affinity sequence of the ions for the exchanger must be opposite to that of their stability constants with the ligand; and (b) the differences in R_F values among the different ions may be increased because, if point (a) applies, the difference is a function only of the ligand concentration.

The validity of these two criteria in order to obtain good separations is demonstrated by the chromatograms in Fig. 2.

Apart from Be(II), whose affinity is intermediate between that of Ca(II) and Sr(II) and whose behaviour is determined by the high stability of its acetate and lactate complexes, the alkaline earth ions show a decreasing affinity for the Dowex layer from Ba(II) to Mg(II). The sequence of the complexes of these ions with acetate and lactate is opposite to that of the affinities, with the exception of Mg(II) whose stability constants with lactate are lower than those of Ca(II). The complexes with acetate of these five ions are less stable than those with lactate. On this basis, it is possible to obtain: (a) a separation with acetate of the five ions; (b) a good separation of the same ions with a lactate concentration equivalent to half of that of acetate; and (c) a better separation among Ba(II), Sr(II) and Ca(II) by simply doubling the lactate concentration.

In Fig. 2 (d), there is also reported the separation of Ba(II), Sr(II) and Ca(II) obtained by Berger *et al.*[16] on Dowex 50-X2 (H^+) layers when eluting with 0.75 *M* ammonium lactate. From a comparison of the chromatograms, it seems that the criteria we have put forward have great importance in the improvement of the separations on these layers when eluting with the same ligand agents.

REFERENCES

1 L. Lepri, P. G. Desideri and R. Mascherini, *J. Chromatogr.*, 70 (1972) 212.
2 L. Lepri, P. G. Desideri, V. Coas and D. Cozzi, *J. Chromatogr.*, 47 (1970) 442.
3 D. Cozzi, P. G. Desideri and L. Lepri, *J. Chromatogr.*, 42 (1969) 532
4 M. Grimaldi, A. Liberti and M. Vicedomini, *J. Chromatogr.*, 11 (1963) 101.
5 S. Fronaeus, *Acta Chem. Scand.*, 5 (1951) 859.
6 Y. Marcus, in J. A. Marinsky (Editor), *Ion exchange*, Vol. 1, Marcel Dekker, New York, 1966, p. 111.
7 D. F. C. Morris and E. L. Short, *J. Chem. Soc.*, (1961) 5148.
8 D. F. C. Morris and E. L. Short, *Electrochim. Acta*, 7 (1962) 385.
9 T. Sekine, M. Sakairi and Y. Hasegawa, *Bull. Chem. Soc. Jap.*, 39 (1966) 2141.
10 Y. Hasegawa, K. Maki and T. Sekine, *Bull. Chem. Soc. Jap.*, 40 (1967) 1845.
11 J. Lefebvre, *J. Chim. Phys. Physicochim. Biol.*, 54 (1957) 567.
12 Y. Kanemura and J. I. Watters, *J. Inorg. Nucl. Chem.*, 29 (1967) 1701.
13 D. L. Masters, J. C. DiRaimondo, L. H. Jones, R. P. Lindley and E. W. Zeltmann, *J. Phys. Chem.*, 66 (1962) 249.
14 H. E. Hellwege and G. K. Schweitzer, *J. Inorg. Nucl. Chem.*, 27 (1965) 99.
15 S. Fronaeus, *Acta Chem. Scand.*, 6 (1952) 1200.
16 J. A. Berger, G. Meyniel and J. Petit, *J. Chromatogr.*, 29 (1967) 190.