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## ION-EXCHANGE PAPER CHROMATOGRAPHY OF INORGANIC IONS

## IXV. SOME CONSIDERATIONS ON THE DETERMINATION OF THE "CHARGE" OF A METAL ION BY ION-EXCHANGE EQUILIBRIA

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## SUMMARY

Ion exchangers with few reactive groups such as cellulose sulphonic acid paper do not distinguish between ions of different charges in the law of mass action equation. It is suggested that this is due to the large distance between the exchange groups. Similar results are obtained with papers impregnated with very dilute solutions of liquid ion exchangers.

## INTRODUCTION

BOYD *et al.*<sup>1</sup> reviewed the question of ion-exchange equilibria in 1947 and pointed out that the equilibria may be considered as a type of law of mass action equation although other approaches are also possible (*e.g.* the Freundlich isotherm). From this paper it was however clear that the charge of the adsorbed cation can influence adsorption as in a law of mass action equation. TOMPKINS AND MAYER<sup>2</sup> have shown that law of mass action equations may also be used for complexing equilibria on ion exchangers, *e.g.*, for the elution of rare earth ions with citrate solution.

Since then confirmation of this principle in ion exchange has been obtained several times, not only with the usual ion-exchange resins but also with inorganic ion exchangers<sup>3</sup>; liquid ion exchangers also behave in the same way. A simple equation relating the  $R_F$  value, the "charge" of the ion and the concentration of the eluent electrolyte was proposed for ion-exchange resin papers<sup>4</sup>.

$$\alpha \text{ pH} = R_M + \text{constant}$$

Usually the concentrations were not "corrected" by multiplication with the activity coefficient as this was deemed presumptive in a system where there are certain to be concentration gradients and mass gradients along the paper strip. In spite of the rather empirical approach straight line relationships between  $-\log [\text{H}^+]$  and  $R_M$  were obtained with ion-exchange resin papers<sup>4</sup>, zirconium phosphate papers<sup>5</sup>, ammonium tungstophosphate paper<sup>6</sup>, papers impregnated with liquid ion exchangers<sup>7</sup>, and alginic acid thin layers<sup>8</sup>, to mention a few.

In all these cases the tangent which should indicate the "charge" of the cation was usually around 1 for monovalent cations, 1.4 to 2 for divalent cations, 2 to 2.7 for trivalent cations and 3 to 3.7 for tetravalent ones.

To summarise: all the evidence seems to indicate that the cations combine with the cation exchangers by a mass action type of equation where the charge of the cation can be considered identical with the charge exhibited in simple solid salts.

We have recently found one exception to this rule.  $\text{Co}(\text{NH}_3)_6^{3+}$ , on sulphonic resin papers, behaves like a pentavalent cation<sup>9</sup>. This could be explained by assuming outer-sphere complex formation between the sulphonic groups of the resin and the

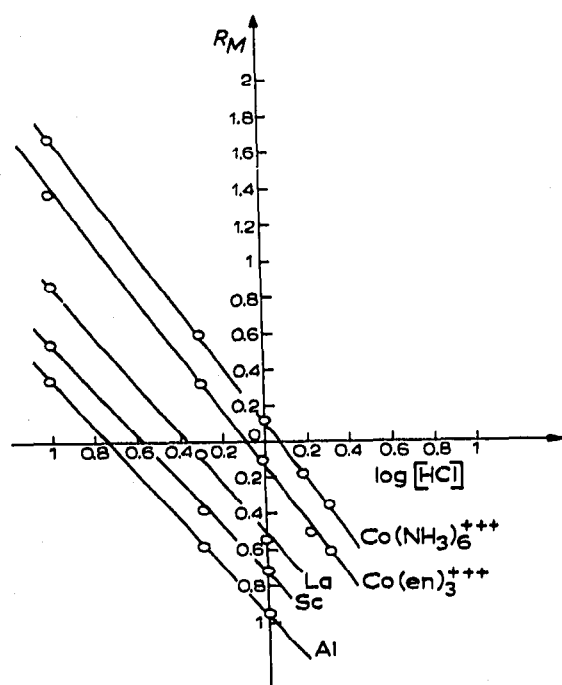


Fig. 1.  $R_M$  versus  $\log [\text{HCl}]$  plots for Macherey-Nagel sulphonic acid cellulose papers. Slopes for  $\text{Co}(\text{NH}_3)_6^{3+} = 1.59$ ;  $\text{Co}(\text{en})_3^{3+} = 1.57$ ;  $\text{La} = 1.2$ ;  $\text{Sc} = 1.27$ ; and  $\text{Al} = 1.31$ .

$\text{Co}(\text{NH}_3)_6^{3+}$ . It should be mentioned here that anomalous results with certain ions have been observed previously, *e.g.*, the strong adsorption of  $\text{Rh}(\text{H}_2\text{O})_6^{3+}$  on sulphonic resin papers and the seemingly irreversible adsorption of  $\text{Fe}(\text{III})$  on cellulose phosphate papers. However in both cases complex formation between the resin and the metal ions seemed evident.

While studying the remarkable behaviour of  $\text{Co}(\text{NH}_3)_6^{3+}$  we discovered another exception to the usual adsorption of cations on ion exchangers. This behaviour is exhibited by ion exchangers with only a few ion-exchange groups on a non-exchanging surface and is the topic of the present paper.

## RESULTS

While working with  $\text{Co}(\text{NH}_3)_6^{3+}$  we thought that it would be interesting to examine its behaviour on cellulose sulphonic acid paper (Macherey-Nagel): the results

TABLE I

THE SLOPES OF THE  $R_M$  versus LOG  $[\text{HClO}_4]$  PLOTS FOR THE MACHEREY-NAGEL CELLULOSE SULPHONIC ACID PAPERData from F. SARACINO<sup>11</sup>.

Metal ion	Slope
Al(III)	1.65
Sc(III)	1.22
Y(III)	1.7
La(III)	1.3
Co(II)	1.1
Ni(II)	1.07
Cu(II)	1.36
Zn(II)	1.0
Mn(II)	1.04
Cd(II)	1.23
$\text{UO}_2^{2+}$	1.24

were very different from those on sulphonic resin papers, namely the "charge" obtained was around 1.6 instead of 4.75. Unexpectedly low results were also obtained for the slopes of the  $R_M$  versus log  $[\text{HClO}_4]$  plots, derived from the  $R_F$  data, for several multivalent cations eluted on cellulose sulphonic acid papers with perchloric acid (results already published by SARACINO<sup>11</sup>). An example of such plots is shown in Fig. 1, while Table I collects all the results for di- and trivalent ions. It can be seen that the slopes obtained are much lower (in absolute values) than expected. These substituted cellulose papers have one obvious difference in their properties from the resins, namely, the few sulphonic groups are spaced rather far apart (one on each sugar moiety). We thought therefore that the abnormal results obtained could be attributed to this property.

In order to confirm this assumption, two series of experiments were carried out. Rare earths (known to be "uncomplexed" by chloride ions) were eluted with hydrochloric acid on Macherey-Nagel (MN) cellulose sulphonic acid paper and on Whatman

TABLE II

SLOPES OF THE  $R_M$  versus LOG  $[\text{HCl}]$  PLOTS ON MACHEREY-NAGEL CELLULOSE SULPHONIC ACID PAPER

Metal ion	Slope
La(III)	1.4, 1.2
Ce(III)	1.3
Pr(III)	1.45
Nd(III)	1.8
Sm(III)	1.4
Eu(III)	1.4
Gd(III)	1.7
Tb(III)	1.8
Dy(III)	1.3
Ho(III)	1.8
Er(III)	1.9
Tm(III)	1.3
Yb(III)	1.85
Lu(III)	1.6

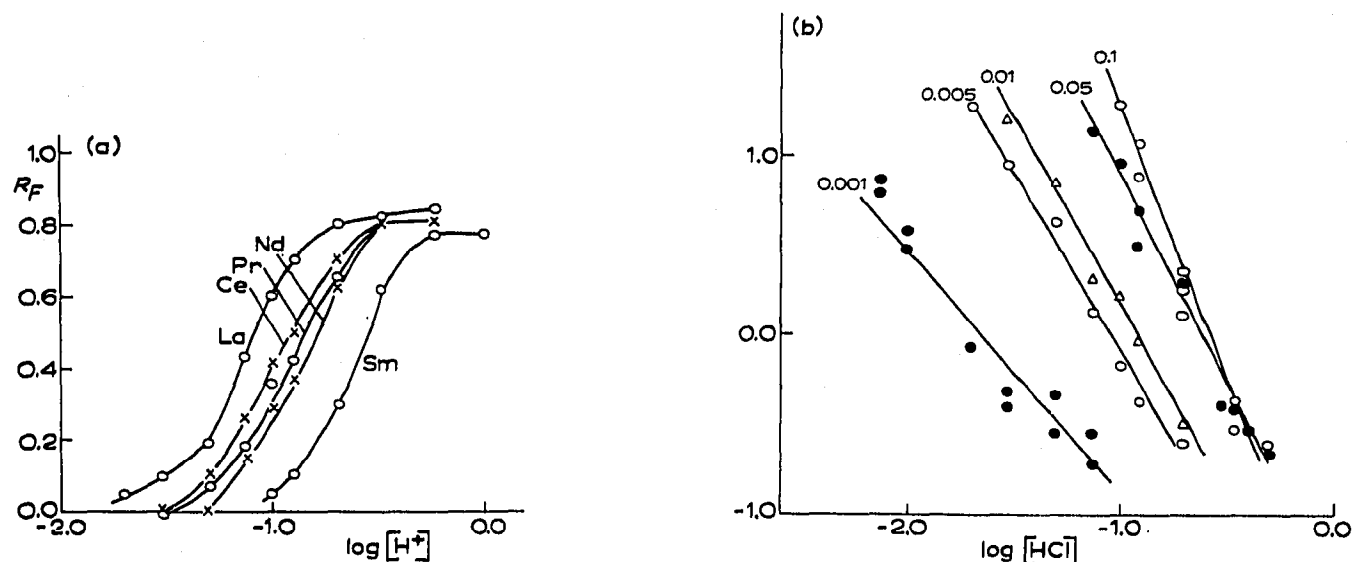


Fig. 2. (a)  $R_F$  versus  $\log [H^+]$  plots for papers impregnated with 0.005 M HDEHP. (b)  $R_M$  versus  $\log [H^+]$  plots for papers impregnated with various concentrations of HDEHP. Data for La(III) as given in Table III.

No. 1 paper loaded with very low amounts of di-(2-ethylhexyl)orthophosphoric acid (HDEHP), a well-known liquid cation exchanger extensively used in reversed-phase chromatography<sup>7</sup>.

The reversed-phase experiments were carried out on paper treated with HDEHP solutions down to 0.001 M in cyclohexane. Although the actual amount of extractant loaded on the paper was unknown, it was reasonably assumed to be roughly proportional to the concentration used, so that the surface density of active exchange groups on the paper increases as the concentration of HDEHP decreases in the treating solution.

The slopes of the straight lines which best fitted the  $R_M$  versus  $\log [HCl]$  plots for the MN paper and HDEHP-treated paper are reported in Tables II and III, respectively, for the latter together with their confidence limits, calculated from a statistical approach at the 95% probability level. A representative plot for HDEHP-treated paper is shown in Fig. 2. While the MN paper results confirm that the "charges" for the rare earths are far below 3, the HDEHP-treated paper results show

TABLE III

SLOPES OF  $R_M$  versus LOG [HCl] PLOTS FOR PAPER IMPREGNATED WITH VARIOUS AMOUNTS OF HDEHP

Metal ion HDEHP concentration in the impregnating solution

	0.1 M	0.05 M	0.01 M	0.005 M	0.001 M
La(III)	$-3.02 \pm 0.47$	$-2.29 \pm 0.23$	$-2.12 \pm 0.46$	$-1.99 \pm 0.26$	$-1.34 \pm 0.18$
Ce(III)	$-2.82 \pm 0.58$	$-2.68 \pm 0.21$	$-2.40 \pm 0.35$	$-2.17 \pm 0.51$	$-1.40 \pm 0.18$
Pr(III)	$-2.98 \pm 0.37$	$-2.47 \pm 0.36$	$-2.20 \pm 0.56$	$-2.10 \pm 0.43$	$-2.06 \pm 0.30$
Nd(III)	$-3.08 \pm 0.61$	$-2.40 \pm 0.41$	$-2.28 \pm 0.73$	$-2.00 \pm 0.41$	$-2.27 \pm 0.52$
Sm(III)	$-3.11 \pm 0.69$	$-2.69 \pm 0.35$	$-2.66 \pm 0.53$	$-2.12 \pm 0.62$	$-1.71 \pm 0.48$

TABLE IV

DISTANCES MOVED BY METAL IONS IN  $\text{HClO}_4$  BY HIGH VOLTAGE ELECTROPHORESISPaper: Whatman No. 1. Experiments conducted at  $3-4^\circ$  for 2 h at 300 V. Camag apparatus.

Metal ion	Distance in mm corrected for electro-osmotic flow (with $\text{H}_2\text{O}_2$ )		
	0.1 N $\text{HClO}_4$	0.5 N $\text{HClO}_4$	1.0 N $\text{HClO}_4$
Al(I)	93	76	61
$\text{UO}_2^{2+}$	45	35	35
Bi(III)	46	49	50
Co(II)	60	56	52
Cd(II)	74	57	57
Cu(II)	61	47	50
Fe(III)	52	45	47
Co(II)	61	56	51
Li(II)	62	56	51
In(II)	70	57	50
Mn(II)	62	57	51
Ni(III)	69	56	49
Pb(III)	67	59	52
La(III)	75	65	58
Pr(IV)	28 comet	37 comet	38 comet
Th(IV)	49	55	55

That such "charges" actually decrease as the HDEHP loading is lowered, ranging from about 3 for the greatest HDEHP amounts to below 2 for paper treated with 0.001 M HDEHP solutions.

Two hypotheses could explain such a decrease in the observed "charges" with decreasing surface density of the active exchange groups. On the one hand, the distance among the groups may be large enough to prevent a cation from interacting with the number of active groups as required by its actual ionic charge.

On the other hand, the relatively few groups may be insufficient to destroy the outer-sphere complexes built around the multivalent cations in the original solution. Paper electrophoretic experiments have repeatedly shown that in hydrochloric acid solutions<sup>10</sup> there is little difference in speed between trivalent metal ions such as Al(III), and divalents such as Cu(II), Ni(II) or Co(II). This cannot be entirely explained by chloride complexes such as  $\text{AlCl}_2^{2+}$  since the same behaviour was observed in other, certainly non-complexing, media; results obtained with perchloric acid are reported in Table IV.

Either being the reason, the data reported above show that a slope very different from that expected can be obtained with ion exchange materials, under suitable circumstances. We should not be surprised if an analogous situation is soon found with the very similar extraction equilibria.

In planning the above experiments, we also hoped to demonstrate an effect on the slopes due to the increasing size of the hydrated radius of the different rare earths. Unfortunately, the results obtained suffer from too large an uncertainty for this purpose, as, probably due to the non-uniformity of both the stationary phases and to their low capacity, either the detection or shape determination of the eluted spots were often impaired.

Larger differences among hydrated ion sizes will probably make ions behave

in rather different ways and this could improve separation factors. That is why we believe that systems such as those considered in this work are rather promising, in spite of the low ion-exchange capacities.

Finally, we would like to propose a new nomenclature for ion-exchange systems. Exchangers having active sites far enough apart as to show such effects as the ones dealt with in this work should be called "dilute" exchangers, while those which actually differentiate between different valencies in the law of mass action should be called "concentrated" ones. This still leaves the terms strong and weak, for denoting the strength of the reactive group as is the usual practice.

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