CHROMATOGRAPHY ON PAPER IMPREGNATED WITH ION EXCHANGE RESINS

V. THE STUDY OF COMPLEX EQUILIBRIA

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INTRODUCTION

The possibilities of using ion exchange resin papers for the separation of metal ions were described in previous papers of this series[1-4]. In complex chemistry these papers were applied mainly to determine the charge on stable Rh (III) complexes[5,6] and to examine the adsorbability of cations from an HF solution[4].

Resin papers may, of course, also be used instead of columns for the study of complex equilibria, and we have employed them here in the study of the complexes formed by Al (III) in mixtures of HCl–HF.

From previous work[4] it was already known that Al(III) does not adsorb on Dowex-50 paper from 2 % HF, and NELSON, RUSH AND KRAUS[7] have observed that Al(III) does not adsorb on Dowex-2 (anionic resin) from HCl–HF mixtures, *e.g.* I M HF–0.01 M HCl. Work on the reaction of Al (III) solutions with CaF_2 and pH studies suggested that the main complex formed is AlF_2^+, which could be confirmed with chromatograms, while other studies led to the assumption of equilibria in which all complexes from AlF^{2+} to AlF_6^{3-} are involved[10].

In this study it was decided to employ for the first time a commercially prepared cationic resin paper instead of the home-made Dowex-50 papers[1-4]. A comparison of this paper with the home-made paper led to quite interesting observations on the effect of the relative amount of resin incorporated in the paper. It seems to be impossible to talk of an optimum amount. Rather a range of resin contents should be available so that the paper most suitable for a given purpose can be selected.

EXPERIMENTAL

Throughout this work the Amberlite ion exchange paper SA-2 containing about 45 % of a strong cation exchanger (sulphonic resin in the sodium form) was employed; it was washed with N HCl and water and air-dried before use.

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(1) *Comparison of the Amberlite SA-2 paper with the Dowex-50 paper previously used*

Figs. 1 (a–c) show some R_F values on SA-2 paper with aqueous HCl as developer. Figs. 1 (d–f) show the R_F values on both kinds of paper for Ni^{2+}, Cu^{2+} and Al^{3+}.

It is evident that since the SA-2 paper contains 45 % resin and our Dowex-50 paper only 10 % of resin, the R_F values with SA-2 paper should be lower. This has, however, several consequences. Certain mixtures may be separated at a certain
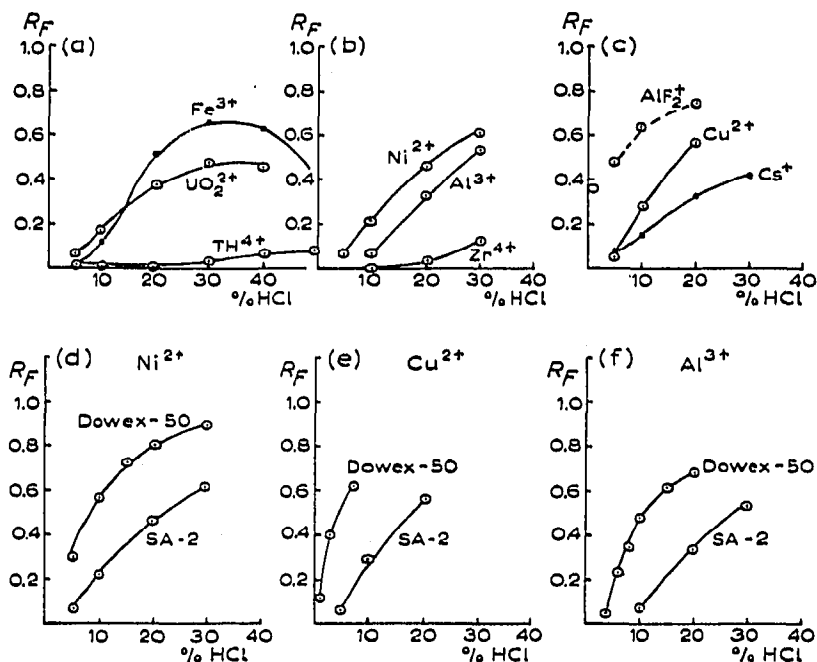

Fig. 1. Graphical representation of the change of R_F value with the concentration of HCl used as solvent. (a–c) R_F values of various metal ions on Amberlite SA-2 paper. (d–f) Comparison of the R_F values on Dowex-50 paper and Amberlite SA-2 paper for Ni^{2+}, Cu^{2+} and Al^{3+}. The Dowex-50 paper contains about one fifth of the amount of resin that the SA-2 paper contains.

HCl concentration on paper with 10 % resin but are not separated with 45 % resin (for example Th–Fe–UO_2 in 0.5 N HCl). Separations may be obtained on the SA-2 paper by increasing the HCl concentration, but then also an inversion of the sequence of Fe^{3+} and UO_2^{2+} occurs.

In the study of complexes, such as the rhodium (III) hexaquo-, monochloro- and dichloro-complexes, separations may be obtained on 10 % resin paper in acidities in which these complexes are stable (*e.g.* up to 1 N HCl), while this would not be the case on papers containing more resin.

Continuing our mathematical treatment of chromatography on resin papers[2] it was possible to obtain a relation between the amount of resin in the paper and the R_M value:

$$K_e = \log \frac{[RM]}{[M^x]} + x\log [H^+] - x\log [RH] \tag{1}$$

where K_e is the exchange constant, M^x the cation of charge x, and RM and RH the amount of the resin in the metal salt and hydrogen forms respectively.

The conditions for obtaining good chromatograms with narrow zones are that RM should be relatively small in comparison with RH and that RH can thus be considered independent of RM. The ratio $\log([RM]/[M^x])$ (usually called R_M in paper chromatography) will thus vary directly with $\log[RH]$ and the difference between the R_M values of two papers will depend on $\log[RH]$ or the log of the ratio of the resin contents of the two papers.
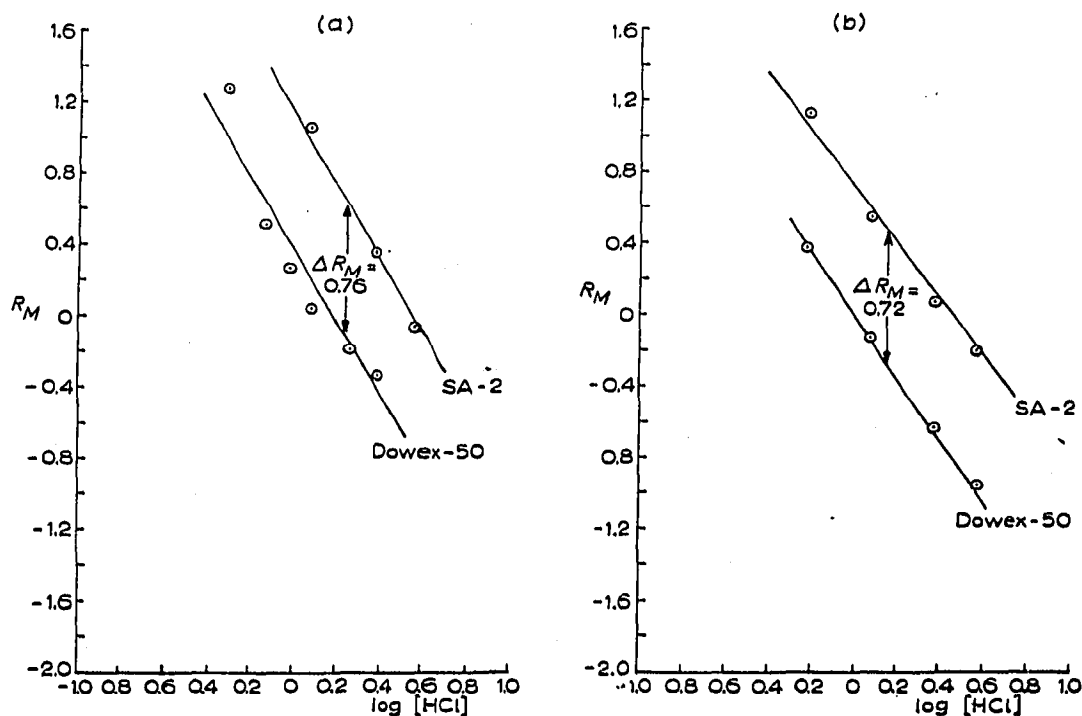

Fig. 2. R_M–log [HCl] relationship for (a) Al^{3+} and (b) Ni^{2+} on Dowex-50 paper and on Amberlite SA-2 paper. The $\varDelta R_M$ value obtained is used for calculating the relative exchange capacities of the two papers.

Figs. 2 (a) and (b) show the R_M–log[H+] relationship for Ni^{2+} and Al^{3+} for both papers; the ratio of resin contents calculated from these graphs is 5.3 and 5.7 respectively, while by weighing (for the Dowex-50 paper) the result obtained was 7.7, which, however, does not take into account the differences in exchange capacities of the two resins.

Equation (1) may also be used to predict the R_F values for a given resin content of the paper.

(2) *The study of complex equilibria*

By again using eqn. (1) it is possible to study two properties of complexes in solution, namely the charge on the complex (= x) at a given concentration of the complexant by varying the concentration of HCl, and secondly the change of charge on the complex by changing the concentration of the complexant and working at a constant HCl concentration.

In order to confirm the validity of the equation for determining the charge on a cation, we determined the R_M–log HCl slopes for mono-, di-, tri- and tetravalent cations

taking the values from Fig. 1, as well as determining the R_F values for ^{137}Cs (carrier-free). The results are shown in Fig. 3 and Table I. Most slopes are somewhat below the theoretical value owing to some complexation with HCl, changes of the activity coefficients (which were not taken into consideration in order to simplify the treatment) and probably also the amount of swelling of the paper support with higher concen-

TABLE I

TANGENTS OF THE R_M–log [HCl] RELATIONSHIP FOR
IONS OF VARIOUS IONIC CHARGES

Ion	Charge	Tangent
(a) On Amberlite SA paper		
Zr	4	3.7
Fe	3	2.75
Al	3	2.4
UO_2	2	1.4
Ni	2	1.5
Cu	2	2.08
Cs	1	1.14
(b) On Dowex-50 paper		
La	3	2.31
Ni	2	1.67
Te (VI)	1	1.06

trations of HCl. However, it is always possible to distinguish the charge on the various cations. The ion for which the slope is closest to the theoretical value is Cs^+, which is little hydrated; it was therefore employed as a carrier-free tracer and thus any inaccuracies due to the concentration of the cation on [RH] in eqn. (1), were eliminated.

Fig. 4 shows the R_F and R_M values of Al(III) in HCl (0.1 to 1 N) containing 0.1 N HF. The slope of the R_M–log [H^+] curve is 0.82, thus the aluminium is present as a monovalent cation. Since in absence of HF, Al(III) behaves as a trivalent cation the loss of charge must be ascribed to the addition of F^- and not to hydrolysis, and we must conclude that the predominant species is AlF_2^+ (as was also observed in previous work[8, 9]).

In these chromatograms a mixture of Al(III) and Zr(IV) was chromatographed. Zr moved always very fast (R_F 0.83) presumably as ZrF_6^{2-}.

To investigate the change of complexation with a change of the HF concentration, Al(III) was developed with HCl–HF mixtures that were N with respect to HCl and 0.025, 0.05, 0.1 and 0.2 N with respect to HF. The R_F and R_M values are shown in Fig. 5, where we have plotted R_M against log[HF]. From other studies[8, 9] as well as from the solution chemistry of HF[11] we have assumed that (a) unionised HF participates in the complexing reaction and (b) the amount of dissociated and associated ions (F^-, HF_2^-) amounts to less than 20 % of the total HF concentration and does not vary appreciably with the pH or with the dilution of the HF.
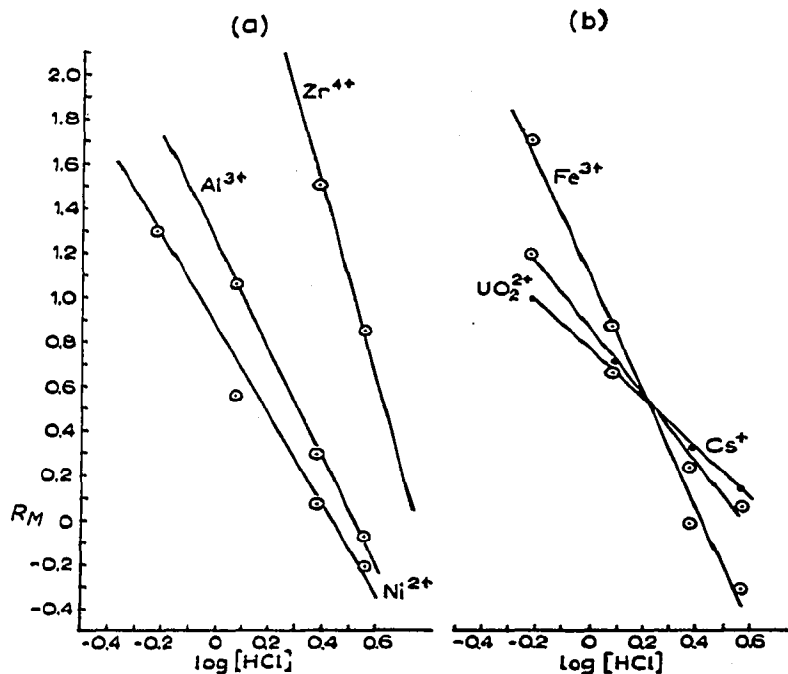
Fig. 3. (a) R_M–log [HCl] graphs for Ni, Al and Zr on Amberlite SA-2 paper. (b) R_M–log [HCl] graphs for UO_2, Fe(III) and Cs on Amberlite SA-2 paper.
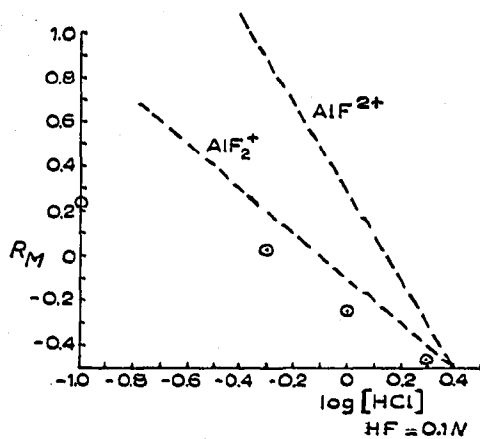

Fig. 4. R_M–log [HCl] graph for Al(III) in HCl–HF mixtures containing 0.1 N HF and varying amounts of HCl. The dotted lines are the theoretical slopes for AlF_2^+ and AlF^{2+}.
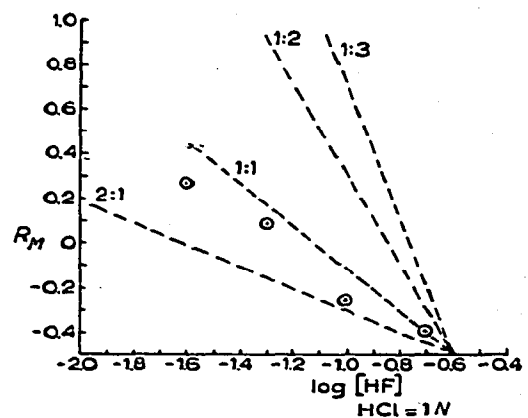
Fig. 5. R_M–log [HF] graph for Al(III) in HCl–HF mixtures containing 1 N HCl and varying amounts of HF. The dotted lines indicate the theoretical curves for the reactions Al(III) + x F$^-$ for x = 1/2, 1, 2, 3.

These assumptions are of course only approximations and the treatment given here is inadequate for the measurement of any precise values. However, as can be seen in Fig. 5 the slope of the R_M–log [HF] curve approximates 1; thus, unless the above assumptions are wrong, the complexation reaction in the range of concentrations studied involves one single HF.

Since the average charge at the second-highest HF concentration is one, *i.e.* the complex is presumably AlF_2^+, we must conclude that in concentrations below 0.025 N HF in N HCl a complex of the type AlF^{2+} exists also.

It is not feasible to study solutions containing still less HF because preferential adsorption of HF and reaction with impurities in the paper etc. would make the results unreliable. Already all the chromatograms with Al(III) in HCl–HF mixtures yield elongated spots when compared to pure HCl, which is probably due to the change in HF concentration when the solvent moves over the Al(III) zone. It would also not be feasible to study higher concentrations of HF as the precision of high R_F and R_M values is insufficient.

SUMMARY

The use of resin papers permits an extremely fast and simple determination of the charge on a complex as well as an estimation of the type of complexing reaction. The method is limited to those concentrations which yield intermediate R_F values on the resin paper. It was possible to confirm previous work indicating that AlF_2^+ is the main species present in HCl–HF mixtures; however, evidence was obtained that also AlF^+ should exist in solutions containing only very little HF (0.025 M and less).

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