

CHROMATOGRAPHY ON ION EXCHANGE PAPERS

XIV. SOME GENERAL REMARKS ON FRONTAL ANALYSIS PHENOMENA DURING DEVELOPMENT

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(Received June 25th, 1964)

INTRODUCTION

It has been shown repeatedly that ion exchange papers may yield the same information as batch equilibration or column experiments and that D values can be calculated from R_F values by the simple relation:

$$D = \left(\frac{1}{R_F} - 1 \right) \frac{A_L}{A_S}$$

The values so obtained are (within the accuracy of the measurements) identical to those obtained by other methods. A comparison has also been reported between instability constants measured with ion exchange papers and those by other methods with very satisfactory results¹.

There are however differences between ion exchange papers and column experiments which are due to differences in technique and not to differences in principle, and work had been reported which claimed that no analogy can be drawn between the two techniques².

It is well known that oxidation reactions may take place on paper strips which cannot occur inside columns. Most workers can also detect at sight when a substance, after being spotted on the paper and dried, crystallises out instead of remaining "in solution". A further factor whose effect was known to us and automatically accounted for, but for which no data have been collected so far, must be considered, namely the front effects of the various constituents of the eluant. In column chromatography it is usual to wash the column with the eluant in order to have a certain ionic form of the resin and a certain solution in which the ions to be studied will be placed. In ion exchange paper chromatography it is possible to convert the paper to a certain form, however the sample to be run is usually placed on a dry paper and the solvent front is then allowed to run over it. If some constituents of the solvent are then retained by the ion exchange paper, the ions placed on the paper will not be in contact with the bulk eluant but with the solvent at the liquid front which may be altered by moving over the paper. In order to assess the magnitude of such front phenomena we have carried out a number of typical elution experiments in which the heights of the fronts were recorded.

EXPERIMENTAL

Amberlite resin papers SA-2 and SB-2 were washed twice with 2 *N* HCl and distilled water and then converted to the required form by leaving for 30 min in a normal solution of the required salt, washing with water and repeating the equilibration. The paper was then air dried overnight and developed by the ascending method in small volume jars. Hydrogen ions were detected by spraying with universal indicator and the other ions with suitable reagents or by their colour. Usually very sharp fronts were obtained which were readily reproducible.

RESULTS

(i) Monovalent ion–monovalent ion equilibria

Fig. 1 shows the H⁺ ion front when the chloride form of the anionic SB-2 paper is developed with HCl solutions. There is practically no retention of H⁺ ions and the H⁺ front moves with or closely behind the solvent front. Fig. 2 shows the movement of the H⁺ front when the sodium form of the cationic SA-2 paper is developed with HCl. The sodium ions are eluted and replaced by H⁺ ions. Below 0.5 *N* HCl the H⁺ front is surprisingly low and ions which are chromatographed in such a system and which are not very strongly adsorbed will move in a neutral medium and probably never come in contact with the HCl.

(ii) Monovalent ion–divalent ion equilibria

We chose as typical example the movement of a Ni⁺⁺ front on the H⁺ form of the sulphonic SA-2 paper, because Ni⁺⁺ is little complexed in HCl and readily detected with ammonium sulphide. Fig. 3 shows the movement of the Ni⁺⁺ front in the presence of varying amounts of HCl in the solvent. Even with 1 *N* NiCl₂ in the presence of 3 *N* HCl (which should displace the Ni⁺⁺ ions considerably) the *R_F* value of the Ni⁺⁺ front is only about 0.7. We should also like to emphasise that with very dilute solutions, *e.g.* 0.1 *N* Ni⁺⁺ in the absence of H⁺ in the solvent, the nickel hardly moves along the paper.

Another interesting example of a divalent–monovalent equilibrium is the movement of H₂SO₄ on the neutral sulphate form of the SB-2 paper. The sulphonic acid converts the neutral sulphate into HSO₄⁻ and as shown in Fig. 4 the H⁺ front in very dilute solutions moves to about *R_F* 0.1 leaving the upper portion of the paper with water as the eluant. Here we also noted the curious behaviour of Fe⁺⁺⁺ when chromatographed in this system. Fe⁺⁺⁺ yields a narrow compressed band which coincides with the H⁺ front. Two spots of Fe⁺⁺⁺ placed 1 cm above each other were found at the same height after development, *i.e.* it is impossible to speak of *R_F* values of Fe⁺⁺⁺ under these conditions and evidently the movement of Fe⁺⁺⁺ on the resin paper will bear no relation to the behaviour of Fe⁺⁺⁺ in batch or column experiments.

The oxalate form of the SB-2 paper developed with oxalic acid behaves similarly. The undissociated H₂Ox is adsorbed on the resin and the H⁺ front is still lower than with the sulphate form and sulphuric acid as shown in Fig. 5. Another example, namely the movement of chromate on the chloride form of SB-2 paper, is given in Fig. 6.

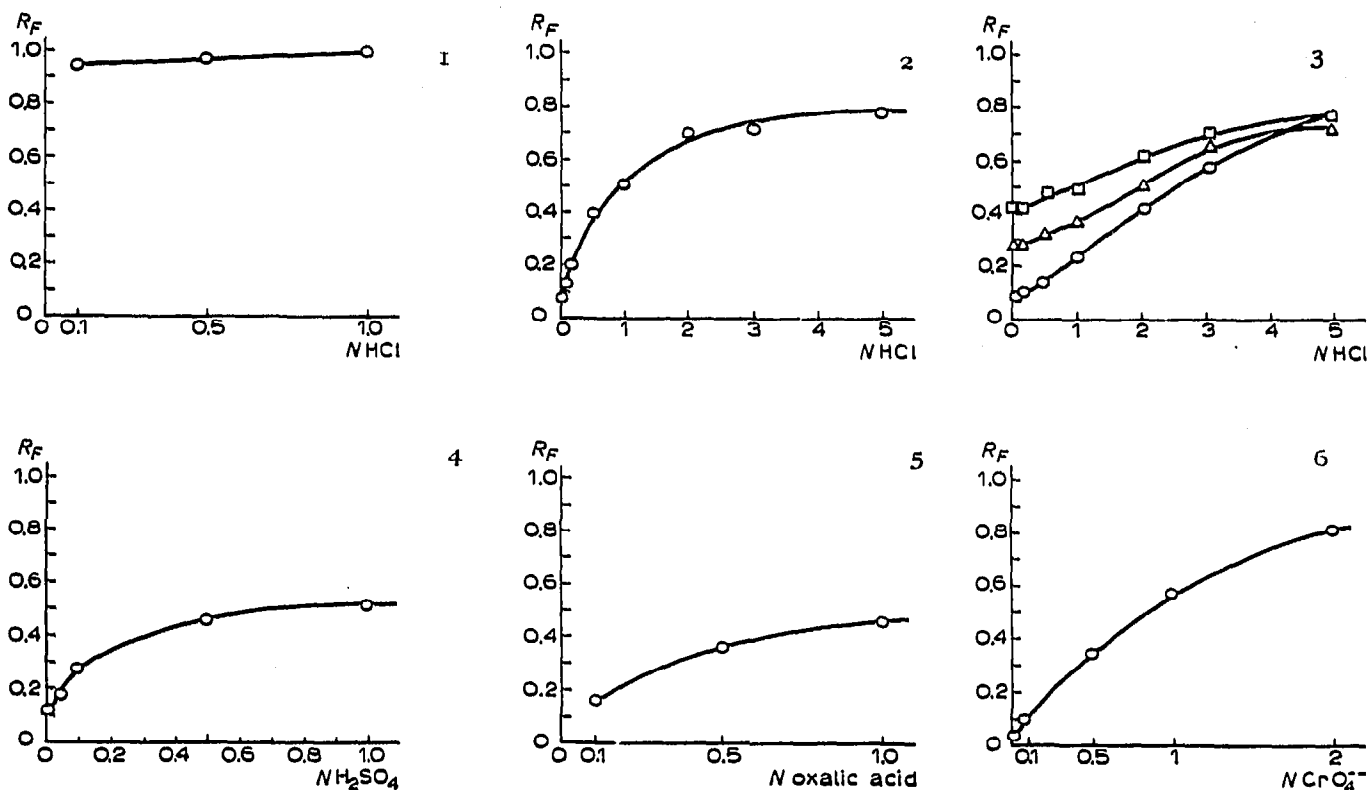


Fig. 1. The R_F values of the H^+ front plotted against HCl concentration on the Cl^- form of the basic SB-2 paper.

Fig. 2. The R_F values of the H^+ front plotted against the HCl concentration on the Na^+ form of the acidic SA-2 paper.

Fig. 3. The R_F values of Ni^{++} front plotted against the concentration of HCl (*i.e.* mixtures $NiCl_2$ and HCl as solvent) on the H^+ form of the acidic SA-2 paper. \circ — \circ = 0.1 N $NiCl_2$, \triangle — \triangle = 0.5 N $NiCl_2$, and \square — \square = 1.0 N $NiCl_2$.

Fig. 4. The R_F values of the H^+ front plotted against the concentration of H_2SO_4 on the SO_4^{2-} form of the basic SB-2 paper.

Fig. 5. The R_F values of the H^+ front plotted against the concentration of oxalic acid on the oxalate form of the basic SB-2 paper.

Fig. 6. The R_F values of the CrO_4^{2-} front plotted against the concentration of K_2CrO_4 on the Cl^- form of the basic SB-2 paper.

DISCUSSION

For practical purposes we can offer a few suggestions to overcome these effects.

1. The front effect can be ignored for systems such as the HCl-chloride form of the SB-2 paper.

2. When the front moves sufficiently fast, the spots to be chromatographed can be placed behind the front, *i.e.* the solvent is allowed to run for 5 or 10 cm and the spot is then placed at a measured distance behind the solvent front and this distance is subtracted when R_F values are determined.

3. When the front moves slowly, as for example with oxalate buffers of low

ionic strength, it would appear impossible to obtain equilibrium conditions by the usual development techniques. The technique of placing the samples behind the liquid front can be applied if the solvent is allowed to run over the paper by descending development for a considerable time (*e.g.* overnight) and if experimental evidence is obtained to show that the sample is really placed behind the front.

4. One useful criterion for suitable development conditions may be found in the shape of the developed spot. It should be somewhat larger than the original spot owing to diffusion etc. but should have retained the approximate shape of the original zone. Elongated comets or compressed narrow zones should be taken as evidence for non-equilibrium conditions and the technique should be suitably modified.

SUMMARY

The importance of the frontal separation of the eluants in ion exchange paper chromatography is demonstrated and several examples are discussed.

REFERENCES

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