INORGANIC ADSORPTION PAPER CHROMATOGRAPHY

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The pioneering work of SCHOENBEIN who studied the movement of inorganic salt solutions along strips of paper has developed into the modern technique of inorganic paper chromatography. The many complex factors which are involved in the separation of inorganic compounds by this technique were discussed by POLLARD AND McOMIE[1].

One important consideration is the role of the paper. As well as being a convenient mode of support for a fixed liquid phase, the paper may influence the distribution of ions by direct participation in the equilibrium processes. Several mechanisms have been proposed to explain the behaviour of the paper.

A useful hypothesis is that of HANES AND ISHERWOOD[2] who suggested that imbibed water molecules become linked to the paper in the form of a water–cellulose complex. Solute molecules and polar solvents may then compete with water for a position in this cellulose complex. BURMA[3] regards the distribution of a solute between the "non-solvent water" (*i.e.* water chemically bound to cellulose) and free adsorbed water as an adsorption process.

Other workers[4,5,6] have attributed the adsorption of cations by paper to ion exchange. It is suggested that the ions of a solute exchange with the ions of Na, K, Ca, Mg etc. which may be found on paper bound to carboxyl groups, silicates and other insoluble material.

Experimental evidence for some of the theories is limited and hence this study has been initiated. This paper records the results of a chromatographic investigation of the movement of cations using aqueous solvents of different pH values.

PROCEDURE

Spots of approximately 0.02 ml of either molar or deci-molar solutions of the nitrates of twelve common cations were placed near one edge of rectangular strips of Whatman No. 1 Filter Paper. These paper strips were suspended in enclosed glass vessels with the "spotted" end dipping into the developing solution.

Solutions of pH 1, 4, 7, 10 and 13 were prepared by adding either nitric acid or sodium hydroxide to distilled water and a constant ionic strength of 0.1 was maintained by the addition of potassium nitrate.

These solutions were used as the developing media for the series of chromatograms. After the liquid had ascended to a chosen height, the papers were removed
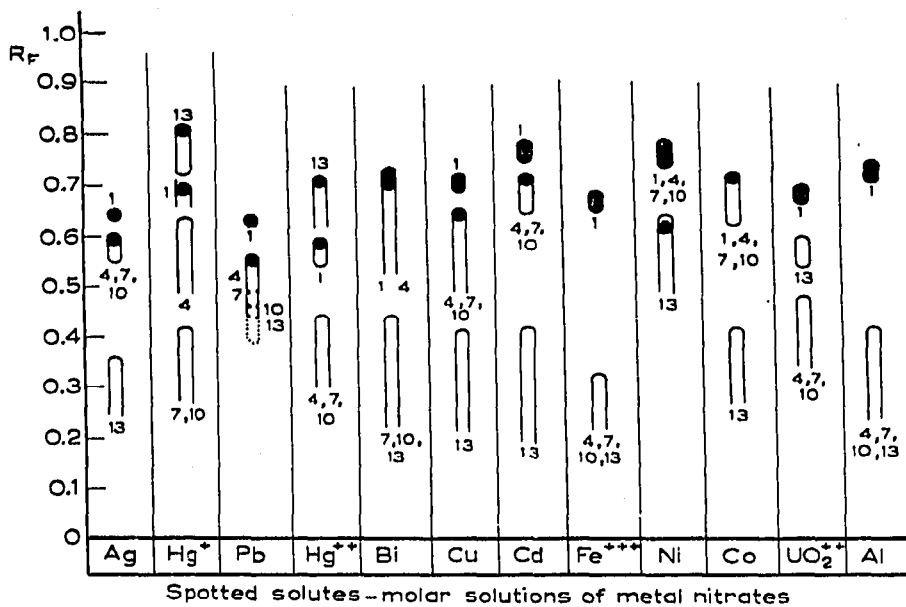
Spotted solutes – molar solutions of metal nitrates

Fig. 1

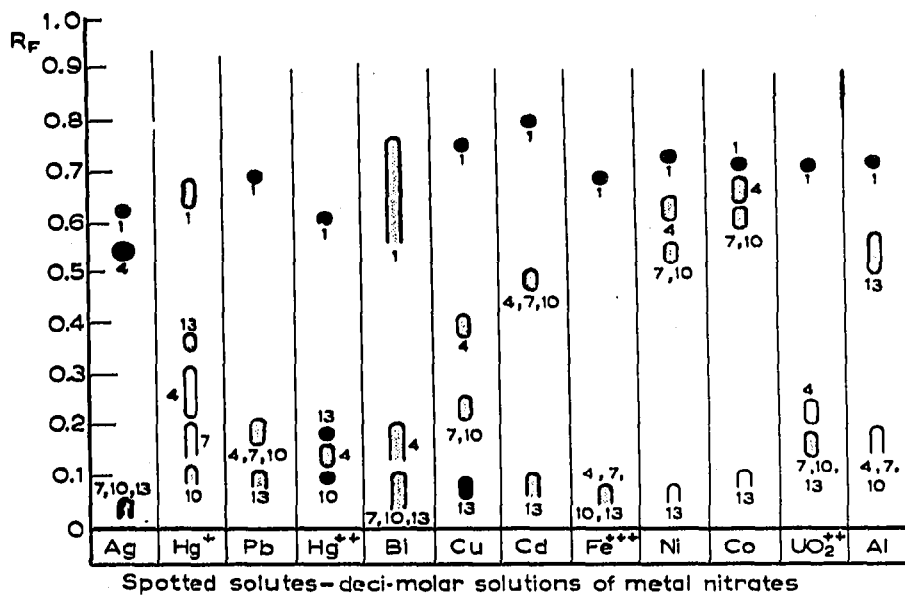
Spotted solutes – deci-molar solutions of metal nitrates

Fig. 2

Figs. 1 and 2. Movement of cations in aqueous solutions. The size of the symbols ●, ▤ etc. represents the relative increase in the area of the original spot during development. Tailing back to the starting line is shown by an opening at the lower edge, ⊓. A localised concentration of cation is shown by a darkened area within an elongated zone, ▮. With elongated areas, the leading edge indicates the approximate R_F of the centre of the most concentrated zone. The numerals 1, 4, 7, 10 and 13 indicate the pH of the solvents used.

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and the cations were located by exposure to H_2S or treatment with some other suitable reagent.

In many cases the cations diffused over a wide area of paper and there was often tailing from the original spot. This effect was most marked when molar salt solutions were spotted on the paper. A symbolic representation of the results is shown in Figs. 1 and 2. The smallest circles on these figures represent spots which did not increase to more than five times their original size during development. An enlarged symbol of double or triple this area illustrates that the solute diffused into an area approximately ten or fifteen times (respectively) greater than the original spot. Elongated symbols designate tailing and where this tailing extended to the original spot, the lower edge of the symbol has been left unclosed. With molar "spots", cations became concentrated near the leading edge and this is shown by a darkened area in this zone. Because of the tailing and general diffusion, accurate calculation of R_F values was not possible and hence the relative movements of the cations indicated in Figs. 1 and 2 are of comparative value only. The numerals shown on these diagrams represent the pH values of the solvents responsible for the movement.

In a second series of tests, strips of filter paper were dipped into solutions containing varying concentrations of nitric acid or sodium hydroxide. After the liquid
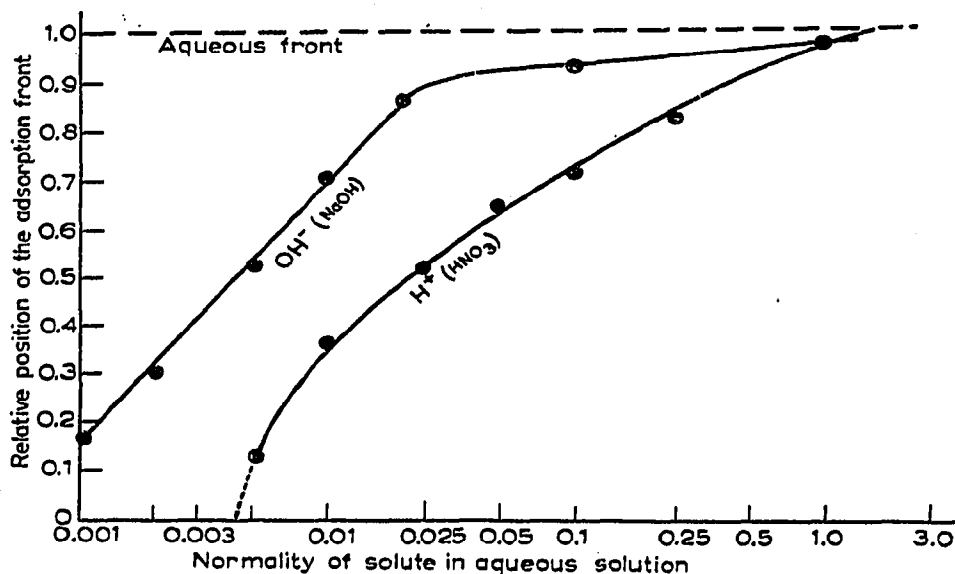

Fig. 3. The adsorption of acid or alkali by filter paper during chromatographic development with aqueous solvents.

had ascended the paper to a chosen height, the position of the acid or alkali front was located by moistening the paper with Universal Indicator. The results are recorded in Fig. 3.

With acid solvents there was a distinct break between the red acid zone (pH < 3) and the slightly acidic (pH 6) reaction of the remaining sections of the paper strip. With dilute alkaline solvents there was a transition of alkalinities from the purple band (pH 10) recorded in Fig. 3 to the slight acidity of the solvent front.

DISCUSSION

This study confirmed that paper has a retarding effect on the movement of cations and is in agreement with the work of MILIĆEVIĆ[7] who separated groups of cations and anions with aqueous solvents. The results recorded in this paper can be interpreted by assuming an operating procedure similar to displacement analysis in chromatographic columns.

The developing solvents were all of equal ionic strength yet the presence of decinormal nitric acid in the solvent caused greater movement and less tailing than an equivalent amount of potassium nitrate (cf. symbols marked "1" and "7", Figs. 1 and 2).

One explanation for the effect of the acid in the solvent would be that the acid inhibits hydrolysis of the salts. Alternately, this effect can be attributed to hydrogen ions being more strongly adsorbed by the paper than most other cations. The acid would thus displace the cations and cause them to move as compact zones. Using a nitric acid solvent of pH 1, the R_F values of many of the cations were similar to the R_F value of the acid front for the same solvent. The tailing of bismuth and mercury salts using this solvent may indicate an adsorptive strength similar to the hydrogen ion. The reduced movement on substituting potassium ions in the solvent could illustrate its weaker adsorptive capacity.

With spotted solutes of molar concentration, the system is analogous to overloading an adsorption column with solutes. The paper in the path of the solute becomes saturated with cation and permits the bulk of the salt to move with the solvent. This leads to concentrated leading zones and extensive tailing. However, the presence of sufficient protons in the solvent will still cause displacement of the cation as a regular zone.

The observed movement of cations using solvents of pH 13 can be attributed to the adsorption of hydroxyl ions by the paper. During development of the chromatogram, the solvent at the liquid front would be virtually freed of hydroxyl ions before reaching the spot of metal salt. This salt would then move up the paper with the liquid front unless retarded by adsorption. Precipitation of the retarded ions would occur as they were overtaken by the following alkali front. When the paper is overloaded with solutes (i.e. molar solutions) considerable movement may occur before the leading edge is overtaken by the alkali. This would yield the marked tailing from the original spot detected with most salts.

Using solvents containing concentrations of acid and base corresponding to pH's of 4 and 10, there was no movement of the acid or alkali front above the point of immersion. The liquid flowing over the spotted solute will therefore be virtually neutral and the movement of the cations should be similar in both cases to results obtained with the solvent of pH 7. This similarity of behaviour is shown by the results recorded in Figs. 1 and 2. It has been shown[8] that cellulose adsorbs less acid from a solution containing acid and salt than from a solution containing acid only of the same pH. Thus the KNO_3 present in the solvent of pH 4 may be responsible for the slightly greater movement of some deci-molar solutes at this pH.

Extrapolation of the hydrogen ion adsorption curve (Fig. 3) indicates that acid adsorption ceases in solutions of pH greater than 2.5. This corresponds approximately to the iso-electric point of cellulose and is in accordance with an observation of GAVORET[9] that purified cotton had a threshold of adsorption for Pb, Th and Cu salts at a pH of 2.7.

An inspection of the relative movements of the cations under the different conditions indicates that the approximate order of adsorption of the metal nitrates by Whatman No. 1 filter paper is Ni, Co, Cd < Cu < Ag, U, Hg, Pb < Al < Bi < Fe.

CONCLUSIONS

In the absence of a lipoid solvent, the movement of cations on paper chromatograms appears to be controlled by a process of adsorption and displacement. The adsorption could be due to a form of ion exchange but this study was not suitable for confirming such a theory.

SUMMARY

Inorganic chromatograms were developed using aqueous solvents of different pH. The results obtained have been interpreted in terms of a process of adsorption and displacement.

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