CHROMATOGRAPHY ON PAPER IMPREGNATED WITH ION-EXCHANGE RESINS

PART VIII. SOME TEMPERATURE EFFECTS IN PARTITION AND ION-EXCHANGE PAPER CHROMATOGRAPHY

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INTRODUCTION

Numerous authors have measured and discussed the effect of temperature on R_F values in partition chromatography (for summaries see ref. 1), and it is generally agreed that a constant temperature is essential for reproducible R_F values and that the variation in R_F values due to changes in the temperature are rather small. The effect of temperature on ion exchange equilibria has been studied by KRAUS AND RARIDON[2] over a wide range of temperatures, however no data are available so far for papers loaded with ion-exchange resins. Since in such papers not only the equilibrium constant but also the ratio of solvent to resin may change with temperature, it was decided to investigate the effect of temperature on the R_F values on such ion-exchange papers. Experiments with some partition systems were also carried out in order to permit a comparison of the relative temperature effects.

In addition to the work undertaken on constant temperatures, we also investigated the effect of variations of temperature during development. This was suggested to us by the spectacular success of temperature programmed gas chromatography on the one hand and the statement of RITCHIE[3] that under field conditions without temperature control improved separations were sometimes noted in paper chromatograpy.

TECHNIQUE

The chromatograms were developed in jars 25 cm high and 14 cm diameter, tightly closed with a rubber stopper, which carried a thermometer. Development at 35° and 50° was carried out in a thermostatically controlled oven and a refrigerator was used for development at 4°. The temperature of the laboratory was air-conditioned to 20° (± 1°) for the chromatograms carried out at 20°. The solvents were equilibrated at the temperature of development, *viz.* those for development at 4° were equilibrated in the refrigerator and those for 35° and 50° at the corresponding temperature in the oven.

The solvent (aqueous or otherwise) was usually added to the container at the desired temperature and left for several hours until it had acquired the temperature of its surroundings. The paper was then introduced into the container and allowed to

hang from a glass hook in the rubber stopper for at least 30 min and then lowered into the solvent for development. With partition solvents the container also held a 150 ml beaker containing the aqueous phase of the solvent mixture. For experiments with temperature changes during development, the equilibration of the solvent was carried out at a chosen temperature and a different temperature for the development then obtained by placing the colder (or warmer) container into a new ambient temperature. Development was then started after 30 min in the new ambient temperature.

RESULTS

(*a*) *Ion exchange papers*

Figs. 1 and 2 show the temperature variation of R_F values on the cation resin paper SA-2 (Rohm and Haas) from 4° to 50° plotted against the normality of HCl in Fig. 1, and against the temperature in Fig. 2. Three ions taken at random were studied, namely Cu (II), UO_2^{2+} and Fe (III). It is evident from Fig. 1 that each ion has a different temperature variation, *i.e.* the temperature effect on the ion-exchange equilib-

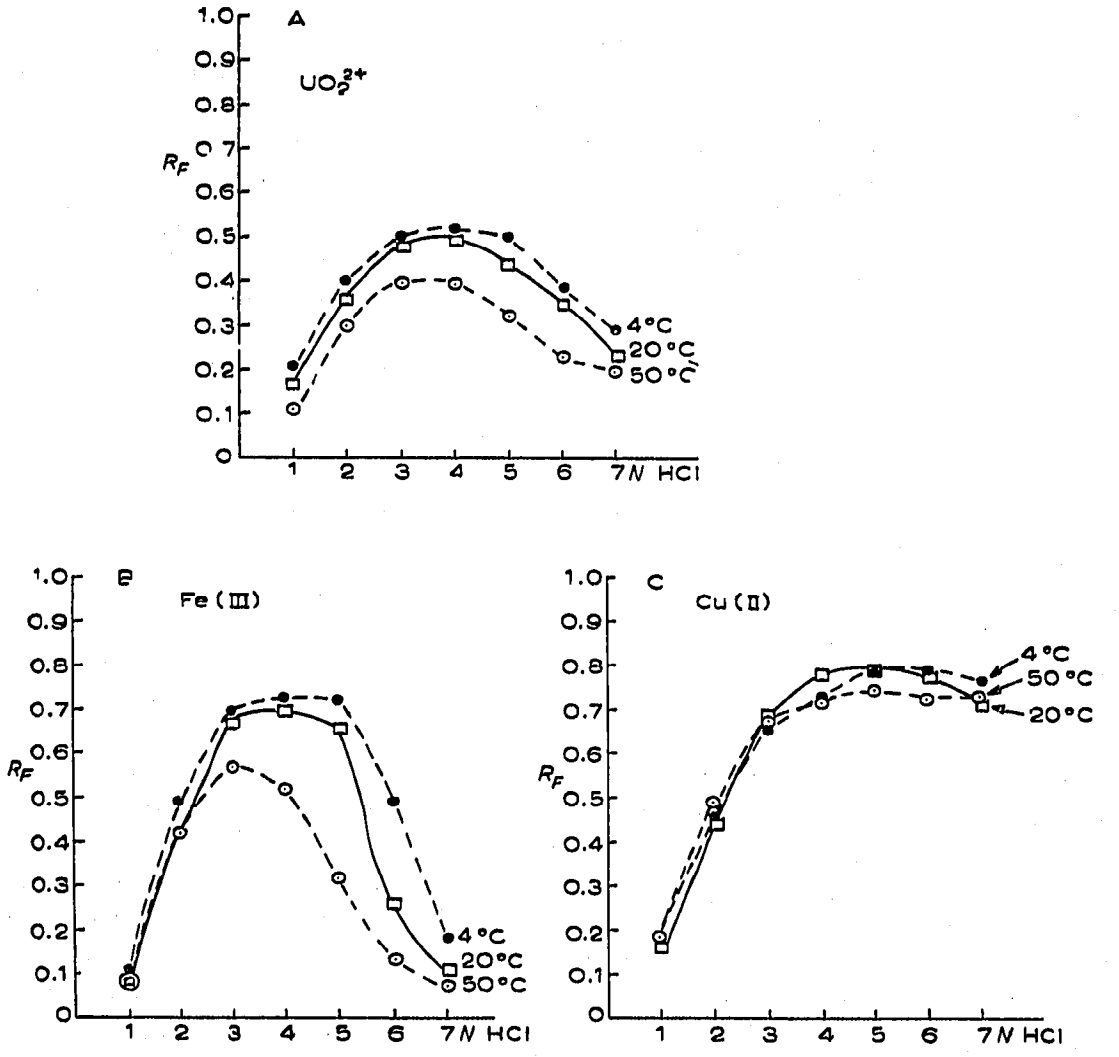

Fig. 1. R_F values of some metal ions on SA-2 cation resin paper plotted against the normality of HCl at 4°, 20° and 50°. (a) Uranyl ion; (b) ferric ion and (c) cupric ion.

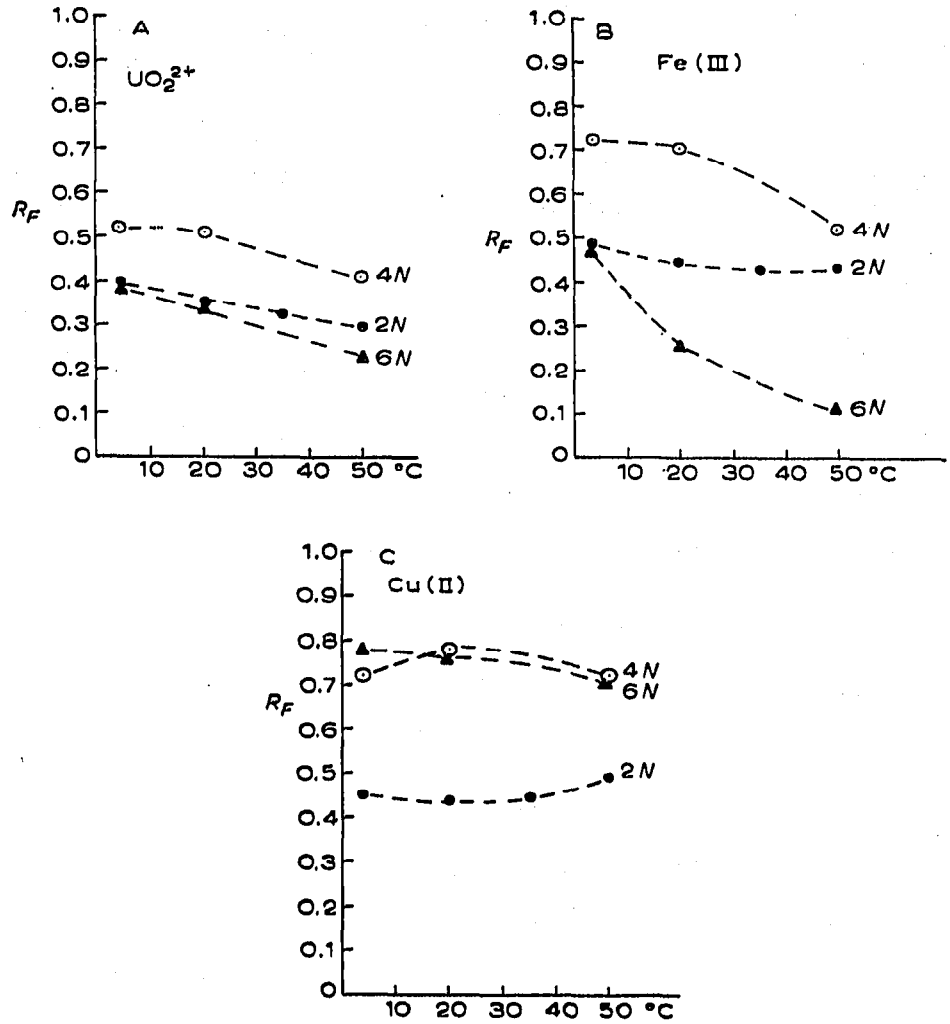

Fig. 2. R_F values of some metal ions on SA-2 cation resin paper developed with HCl. The R_F values are plotted against the temperature for $2N$, $4N$ and $6N$ HCl. (a) Uranyl ion, (b) ferric ion and (c) cupric ion.

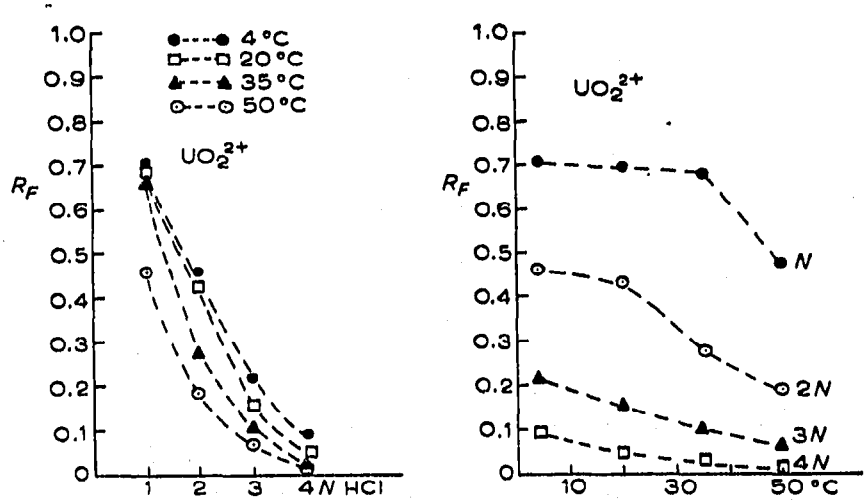

Fig. 3. R_F values of uranyl ion on SB-2 anion resin paper developed with HCl. (a) Plotted against the normality of HCl for 4°, 20°, 35° and 50°; (b) plotted against the temperature for N, $2N$, $3N$ and $4N$ HCl.

rium is probably the preponderant factor. Fig. 2 also shows that except under some conditions, *e.g.* Fe(III) in $5N$ and $6N$ HCl the temperature variation is very small, for example the R_F value of Cu(II) in HCl remains practically constant from 4° to 50°.

Preliminary experiments in which the temperature was varied during development indicated that there is no marked effect due to temperature variation. It seems then that little can be gained by programming, or by raising or lowering of the temperature with these papers.

The behaviours of UO_2^{2+} on the anion resin paper SB-2 (Rohm and Haas) shows a similar trend to that on the cation exchange paper with perhaps a more pronounced temperature effect. It appears that essentially the same results can be expected within the usual range of room temperatures, as is shown in Fig. 3.

(b) Partition chromatography

Tables I and II show the variation of the R_F values of some inorganic ions in butanol–$3N$ HCl and butanol–$1.5N$ NH_4OH on Whatman No. 1 paper. Similar results with other solvents have been observed previously[1]. We would, however, like to point out that the variations noted are much greater than the variation of the solubility of butanol in water and of water in butanol which varies over this range of 45° by approximately 3%[4], and hence are probably due to variations of the ratio of the

TABLE I

R_F VALUES OF SOME ANIONS

Solvent: *n*-butanol–$1.5N$ NH_4OH (1:1). Paper: Whatman No. 1. Development: ascending.

Temperature of solvent equilibration	4°	20°	50°	20°	20°
Temperature of development	4°	20°	50°	4°	50° (3 chromatograms)
Anions			R_F values		
Cl^-	0.08	0.10	0.14	0.07	0.26, 0.15, 0.29
Br^-	0.14	0.16	0.20	0.13	0.37, 0.24, 0.43
I^-	0.22	0.25	0.28	0.21	0.55, 0.38, 0.60
CNS^-	0.37	0.37	0.45	0.32	0.73, 0.53, 0.80

two phases (A_L/A_S) as well as variations in the partition coefficients of the ions. However, all these effects are small. Unexpectedly high variations due to temperature were obtained with partition chromatograms where the solvent was equilibrated at room temperature and the development carried out at 50°. The R_F values obtained can be as much as double those obtained with solvents equilibrated at 50° as shown in Tables I and II. When chromatograms are carried out at a temperature lower than that at which the solvent was equilibrated the effect is minimal.

The general conclusion from these observations is that while the actual temperature for development is not of great importance in paper partition chromatography, temperature variations during development are of consequence.

In ion-exchange paper chromatography neither the actual temperature nor

variations during development will have a great effect within the usual range of room temperatures.

The marked variations obtained when the temperature is changed for development in partition chromatography can be explained by the fact that if the solvent and the aqueous phase are not quite in equilibrium the amount of evaporation from the paper can be considerable, owing to the extremely large surface in relation to its liquid content. The increased movement of ions may be accounted for if we imagine

TABLE II

R_F VALUES OF SOME METAL IONS

Solvent: *n*-butanol–3*N* HCl (1:1). Paper: Whatman No. 1. Development: ascending.

Temperature of solvent equilibration	4°	20°	50°	20°	20°
Temperature of development	4°	20°	50°	4°	50°
Metal			R_F *values*		
Cu(II)	0.16	0.26	0.27	0.17	0.47
Fe(III)	0.18	0.28	0.42	0.19	0.86
Cd(II)	0.66	0.91	0.77	0.66	0.93
Bi(III)	0.50	0.66	0.62	0.50	0.84

that there is continuous evaporation from the liquid front as well as from the surface of the paper, which is then compensated by new solvent moving over the paper. Most publications reporting R_F values at various temperatures show a greater variability of results at room temperature, where variation is greatest, than with temperatures maintained in ovens.

Finally, we should like to raise the question of whether it is in general advisable to carry out paper chromatography at room temperature, which is difficult to maintain at a constant level and where the opening of a door may cause temperature gradients from one side of the development vessel to the other. It may be rather an advantage to work at a given oven temperature *e.g.* 35° where variations can be kept to a minimum.

SUMMARY

The effect of temperature variation in paper partition and ion exchange paper chromatography of some inorganic ions was studied. While the temperature coefficient is rather small, variations of the temperature during development were found to have a considerable effect in partition chromatography but only little effect in ion exchange paper chromatography.

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