Journal of Chromatography, 114 (1975) 488–490

CHROM. 8543

Note

Paper partition chromatography of inorganic ions

XX. The behaviour of copper(I), silver(I) and iron(II) in butanol–hydrochloric acid mixtures

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(Received June 26th, 1975)

In the separation of inorganic ions, butanol–hydrochloric acid–water mixtures are among the most used solvents. A survey of the movement of numerous metal ions was published by Guedes de Carvalho[1], and this was completed by Clanet[2] for the transuranium elements. Korkisch *et al.*[3] recently reported that copper could be concentrated on Dowex-1 in dilute hydrochloric acid by reducing it to the monovalent state by addition of ascorbic acid.

Except for two preliminary reports on separations of Cu(I) from Cu(II) with rather unusual solvents[4,5], no data for paper partition chromatography were known to us, and we thought that it would be interesting to investigate the movement of Cu(I) in partition systems for which the movement of many other ions has been recorded.

MONOVALENT COPPER, Cu(I)

Preliminary experiments with butanol–hydrochloric acid mixtures showed that copper travelled rather quickly, irrespective of whether it was reduced by ascorbic acid, stannous chloride or sulphur dioxide. We therefore think that ascorbic acid is unlikely to complex Cu(I) and that the compound that migrates is presumably $HCuCl_2$. During development, the Cu(I) is oxidised more or less quickly, depending on the concentration of reductant in the original mixture and that of hydrochloric acid in the solvent.

The use of an inert atmosphere (carbon dioxide or nitrogen) did not reduce this effect to a satisfactory degree, so we tried butanol–hydrochloric acid mixtures to which ascorbic acid was added. This helped in some systems, but complete stabilisation in longer chromatograms could only be achieved by impregnating the paper with a 5% aqueous solution of ascorbic acid and subsequently drying it and incorporating 5% of ascorbic acid into the solvent.

As ascorbic acid does not move immediately with the solvent front, the spots to be chromatographed are placed "behind the solvent front", *i.e.*, the sheet of paper is developed for 4 cm with the solvent, then taken quickly out of the jar, and the spots are placed on the paper, which is returned to the development jar. Under these circumstances, the chromatograms shown in Fig. 1 were obtained.

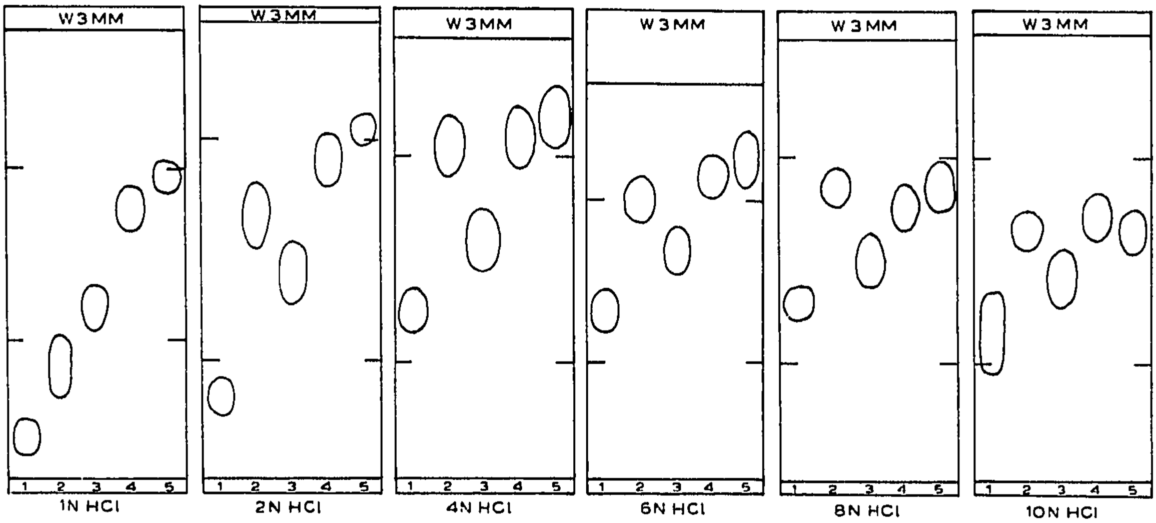

Fig. 1. Chromatograms of Pb(II), Cd(II), Bi(III), Hg(II) and Cu(I) (shown as 1–5, respectively, on the chromatograms) developed in the following manner: Whatman 3MM paper was impregnated with a 5% aqueous solution of ascorbic acid and air dried; butanol–aqueous hydrochloric acid (1:1) mixtures (the normality of the acid is indicated below each chromatogram) containing 5% of ascorbic acid were allowed to ascend for 4 cm on the paper, then the paper was withdrawn and a spot of the metal ion solution in dilute hydrochloric acid was placed 4 cm behind the liquid front. The strips were then replaced in the development jars and the solvent was allowed to migrate another 10 cm (5–7 h).

We had placed on the same sheet the other metal ions of the second analytical group for comparison, and they all move more or less as in the corresponding butanol–hydrochloric acid mixtures in absence of ascorbic acid. Monovalent copper moves faster than Hg(II) and thus belongs to the fastest moving metal ions in the butanol–hydrochloric acid system. The only other metal ions that move so close to the solvent front are Tl(III), Au(III) and Po(IV).

We have thus observed here a new property of Cu(I), which we believe has not been recorded before, namely, its tendency to favour the non-polar phase in partition systems. We think that this should have some meaning in biological chemistry, as aqueous solutions of ascorbic acid exist in intra- and extra-cellular environments accompanied by the necessary amount of chloride ions. Under these conditions, Cu(I) should favour the lipid phase of a biological system such as the cell wall.

SILVER(I) IONS

Monovalent silver the next higher element to Cu(I) in group IB of the periodic table was recorded by Guedes de Carvalho[1] as having in all mixtures of butanol–hydrochloric acid an $R_F = 0$. This is correct if silver nitrate solutions are placed on the paper. The butanol–hydrochloric acid solvent is relatively poor in acid in the first few millimetres of development, and all Ag^+ is precipitated as AgCl. However, Ag(I) is quite soluble in concentrated hydrochloric acid and in butanol–concentrated hydrochloric acid mixtures; if the latter (which is less liable to destroy the paper) is

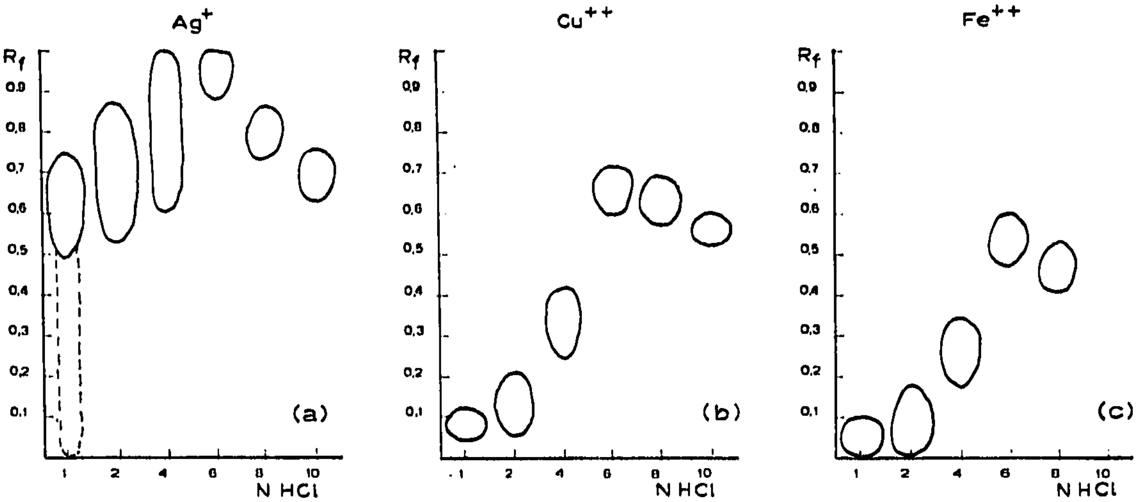

Fig. 2. Schematic R_F–concentration of hydrochloric acid diagrams for butanol–aqueous hydrochloric acid (1:1) mixtures on Whatman 3MM paper. (a) Silver nitrate dissolved in butanol–10 N hydrochloric acid (1:1); the spot size, R_F value, etc., is plotted against the normality of acid in butanol–hydrochloric acid mixtures (1:1). (b) Cupric chloride: this salt was re-examined in order to compare it with Cu(I) under the same conditions as shown in Fig. 1. (c) Ferrous chloride; here a spot of Fe(III) could also be detected, but it is not shown.

placed on the paper and developed with butanol–hydrochloric acid, we obtain movement of the $HAgCl_2$ complex. This is shown in Fig. 2a.

In the butanol-1 N hydrochloric acid mixture, Ag^+ leaves a slight trail of AgCl. While $HAgCl_2$ also moves considerably, it is not as well extracted as Cu(I) in mixtures containing low concentrations of hydrochloric acid.

FERROUS IRON

As the work of Guedes de Carvalho[1] does not give any R_F values for Fe(II), we wanted to complete his tables by recording the behaviour of this species; Figs. 2b and 2c show Cu(II) and Fe(II), respectively. The curves of R_F *vs.* hydrochloric acid concentration are very similar (as they are also on cation exchangers). In all systems, there is some oxidation to a faster moving Fe(III) spot. In butanol–10 N hydrochloric acid, all the Fe(II) was converted into Fe(III) and no R_F value could be recorded.

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