

CHROMATOGRAPHIC BEHAVIOUR OF BORATES AND THEIR
HETEROPOLYACIDS

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INTRODUCTION

Paper chromatography has proved successful for the separation of inorganic polyacids such as polyphosphates or silicates. It was thus decided to investigate whether separations of the various borates (meta-, tetra- and perborates) were possible by paper chromatography. Our results described in Part I of this paper indicate that no chromatographic distinction between the various borates could be observed probably owing to their ready interconversion to the stablest ionic form under given conditions. Even additions of *cis*-dihydroxy compounds (except for high concentrations of tartaric acid) did not influence the R_F values of borates indicating that its movement is most likely already determined by a complexation equilibrium with the cellulose surface.

On the other hand the R_F values of borates mixed with inorganic acids known to form heteropolyacids are not the same as those of pure borate indicating that complex formation does take place and is sufficient to change the partition equilibria of the borate. Part II of this paper describes our results with borate-tungstate and borate-molybdate mixtures.

Throughout this work the ascending technique of development was used with Whatman No. 1 paper which was washed free of impurities with HCl before use.

PART I. - CHROMATOGRAPHIC BEHAVIOUR OF BORATES

We determined the R_F values of aqueous saturated solutions of H_3BO_3 , $Na_2B_4O_7 \cdot 10H_2O$ and $NaBO_3 \cdot 4H_2O$ with many solvent mixtures as eluants. None of the solvents gave a separation of the three anions used: BO_3^{-3} , $B_4O_7^{-2}$ and BO_3^{-} . Table I shows the R_F values obtained.

The similar behaviour of the three compounds tried led us to suppose that they have the same anions in solution. This agrees with several authors^{1, 2} whose opinions are that in dilute solutions of borates only $H_2BO_3^{-}$ and BO_2^{-} exists, and the obtention of anion aggregates (isopolyacids) when borate solutions are progressively acidified are not to be expected.

The hydrolysis of the monoborate ion



can perhaps explain some of the figures obtained.

References p. 51.

In acid or neutral medium the reaction is displaced to the right and probably H_3BO_3 predominates (experiments 5 to 14) with high R_F values. In alkaline medium the reaction will be displaced to left and BO_2^- ions will predominate (experiments 15, 16, 17 (a) and 18 (a)) with lower R_F values.

In all these experiments R_F values seem to be only influenced by the acidity of the medium, the anions present not altering those values, so that complex ions formed by borates and these anions are not to be expected.

TABLE I

| Experiment | Eluant | Phases | R_F | Observations |
|------------|---|--------|--|---------------------------|
| 1 | Water | 1 | 0.87-0.90 | |
| 2 | Pyridine | 1 | 0.88 | tails with borates |
| 3 | <i>n</i> -Butanol | 1 | Retention at the origin and tails until 0.85 | |
| 4 | Aniline | 1 | Retention and light tails | |
| 5 | <i>n</i> -Butanol + water (1:1) | 2 | 0.50-0.55 | |
| 6 | <i>n</i> -Butanol + HCl, <i>N</i> (1:1) | 2 | 0.53-0.57 | |
| 7 | <i>n</i> -Butanol + HNO ₃ , <i>N</i> (1:1) | 2 | 0.51-0.54 | |
| 8 | <i>n</i> -Butanol + H ₂ SO ₄ , <i>N</i> (1:1) | 2 | 0.51 | |
| 9 | <i>n</i> -Butanol + HCH ₃ COO, <i>N</i> (1:1) | 2 | 0.52-0.58 | |
| 10 | <i>n</i> -Butanol + HClO ₄ , 0.1 <i>N</i> (1:1) | 2 | 0.51-0.53 | |
| 11 | <i>n</i> -Butanol + H ₃ PO ₄ , 0.1 <i>N</i> (1:1) | 2 | 0.51-0.53 | |
| 12 | <i>n</i> -Butanol + satd. salicylic acid (1:1) | 2 | 0.47-0.48 | |
| 13 | <i>n</i> -Butanol + satd. succinic acid (1:1) | 2 | 0.51-0.52 | |
| 14 | <i>n</i> -Butanol + satd. oxalic acid (1:1) | 2 | 0.48-0.49 | |
| 15 | <i>n</i> -Butanol + (NH ₄ OH + NH ₄ Cl) (1:1) | 2 | 0.20-0.23 | pH ~ 9 |
| 16 | <i>n</i> -Butanol + NH ₄ OH (1:1) | 2 | 0.10-0.12 | |
| 17 (a) | <i>n</i> -Butanol + (citric acid (10%) + NH ₄ OH) (1:1) | 2 | 0.21-0.24 | pH ~ 9 |
| (b) | <i>n</i> -Butanol + citric acid (10%) (1:1) | 2 | 0.48-0.52 | |
| (c) | <i>n</i> -Butanol + citric acid (sat.) (1:1) | 2 | 0.96 | |
| 18 (a) | <i>n</i> -Butanol + (tartaric acid (10%) + NH ₄ OH) (1:1) | 2 | 0.18-0.20 | pH ~ 9 |
| (b) | <i>n</i> -Butanol + tartaric acid (10%) (1:1) | 2 | 0.42-0.50 | |
| (c) | <i>n</i> -Butanol + tartaric acid (20%) (1:1) | 2 | 0.45-0.50 | two spots are revealed |
| (d) | <i>n</i> -Butanol + tartaric acid (40%) (1:1) | 2 | 0.15-0.23 | revealed |
| (e) | <i>n</i> -Butanol + tartaric acid (60%) (1:1) | 2 | 0.47-0.50 | two spots are revealed |
| (f) | <i>n</i> -Butanol + tartaric acid (80%) (1:1) | 2 | 0.22-0.33 | revealed |
| (g) | <i>n</i> -Butanol + tartaric acid (100%) (1:1) | 2 | 0.56-0.58 | two spots are revealed |
| 19 | <i>n</i> -Butanol + hexamethylenetetramine (16%) (1:1) | 2 | 0.49 (tail) | revealed |
| 20 | <i>n</i> -Butanol + mannitol (10%) (3:1) | 2 | 0.48-0.50 | two spots are revealed |
| 21 | <i>n</i> -Butanol + glucose (10%) (1:1) | 2 | 0.48 | slight tails with borates |
| 22 | <i>n</i> -Butanol + urea (50%) (3:1) | 2 | 0.47 | slight tails with borates |
| 23 | <i>n</i> -Butanol + tannic acid (25%) (4:1) | 2 | 0.42 | slight tails with borates |
| 24 | <i>n</i> -Butanol + diphenylamine (20:1) | 1 | origin retention and tails | |
| 25 (a) | <i>n</i> -Butanol + glycerol (10:1) | 1 | origin retention and tails | |
| (b) | <i>n</i> -Butanol + glycerol + water (2:1:1) | 2 | 0.42-0.53 | |
| 26 (a) | <i>n</i> -Butanol + phenol (100:6) | 1 | origin retention and tails | |
| (b) | <i>n</i> -Butanol + phenol + water (50:44:6) | 2 | 0.42-0.46 | |
| 27 (a) | <i>n</i> -Butanol + aniline (5:1) | 1 | origin retention and tails | |
| (b) | <i>n</i> -Butanol + aniline + water (5:1:1) | 1 | 0.53 | |

As several complexes between borates and some amines, sugars, etc. are known, we investigated this in experiments 19 to 27. However no change of R_F values was observed; once again the behaviour was similar to that obtained with only *n*-butanol + water.

With all the eluants without water (experiments 24, 25 (a), 26 (a) and 27 (a)) only a slight tailing is observed.

With tartaric acid in concentrations over 10%, two spots are observed: one in the aqueous zone and other in the alcoholic zone, the separation line of the two zones being clearly noted between the two spots (see Fig. 1). In this case a complexation

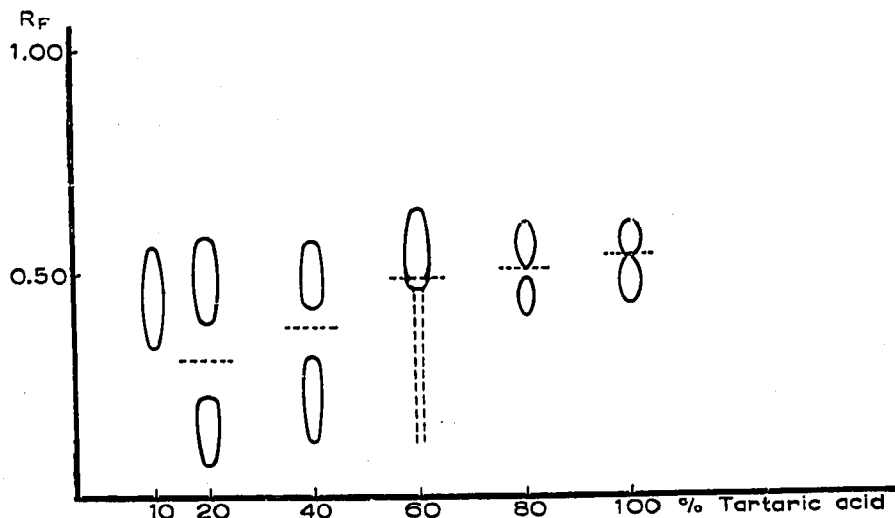


Fig. 1. Graphical results of experiments 18(b)–18(g).

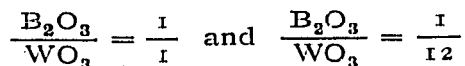
seems to exist. In all cases the lower spot (aqueous zone) was much weaker than the upper one.

PART II. A – CHROMATOGRAPHIC BEHAVIOUR OF BOROTUNGSTATES

We decided to study acid eluant mixtures of ketone and diluted sulphuric acid (1:1), because, among many kinds of eluants tried, those gave the highest R_F for tungstates. As alkaline eluants we used mixtures (1:1) of ketone and diluted ammonia.

In each experiment we chromatographed side by side four spots: one of H_3BO_3 , one of Na_2WO_4 and two of a mixture of $H_3BO_3 + Na_2WO_4$. After development borate was detected in its isolated spot and in one of the mixed spots by an alcoholic solution of turmeric. Tungstate was detected in the other two spots by $SnCl_2$ solution. In this manner we detected the position of both borate and tungstate ions either isolated or in a mixture.

Two borate–tungstate mixtures with the following composition were used:



Two series of experiments were conducted with each one of the mixtures. The first series was in normal Whatman No. 1 paper, and the second in paper washed by

acids. As the figures obtained in the four series were similar, we took in each case the mean of the four values determined. These values are graphically represented in Fig. 2.

Some inferences can be obtained from this figure:

(a) Spots of isolated borate have, essentially, the same R_F in the acid solvents. In the solvents of pH 9 to 11 the spots are longer and the R_F values decrease. For the

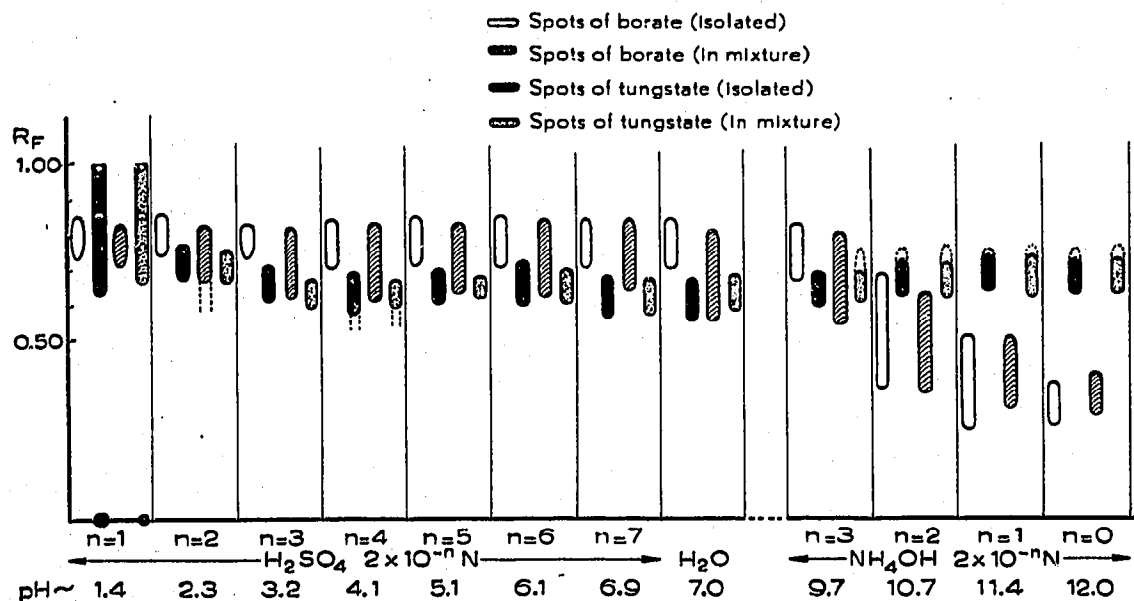


Fig. 2. Spots of borates and tungstates after chromatography with *n*-butanol + H_2SO_4 or NH_4OH .

zone of pH higher than 11 to 12 the spots became round again and the R_F remains low.

(b) Spots of tungstate (isolated or in mixture) present essentially the same R_F from pH 1 to 12. In the alkaline zone the spots show a tendency to give forward tails.

(c) Spots of borate in mixtures are longer than those of isolated borate and they comprise all the zone of isolated tungstate and borate spots. It seems that a retention of borate by tungstate exists from pH 1 to 10. With solutions of higher pH no retention occurs and the spots are perfectly separated.

If the observed retention is due to a borotungstic heteropolyacid, we can infer that that complex would be stable only in a zone of pH lower than 10, which is in agreement with the literature.

B - CHROMATOGRAPHIC BEHAVIOUR OF BOROMOLYBDATES

In a similar study we obtained the results condensed in Fig. 3.

(a) A sharp decrease in the R_F values of molybdates with a pH increase can be observed. However at pH 9 the spots are already very elongated and for solutions of higher pH, the R_F increases and remains constant. The decrease of R_F values in the acid zone could be explained by the formation of distinct isopolymolybdates in different zones of pH, which is well known³. Further work is being done in order to clear up this point.

(b) We can see that in all the experiments borate is sharply retained by molybdate.

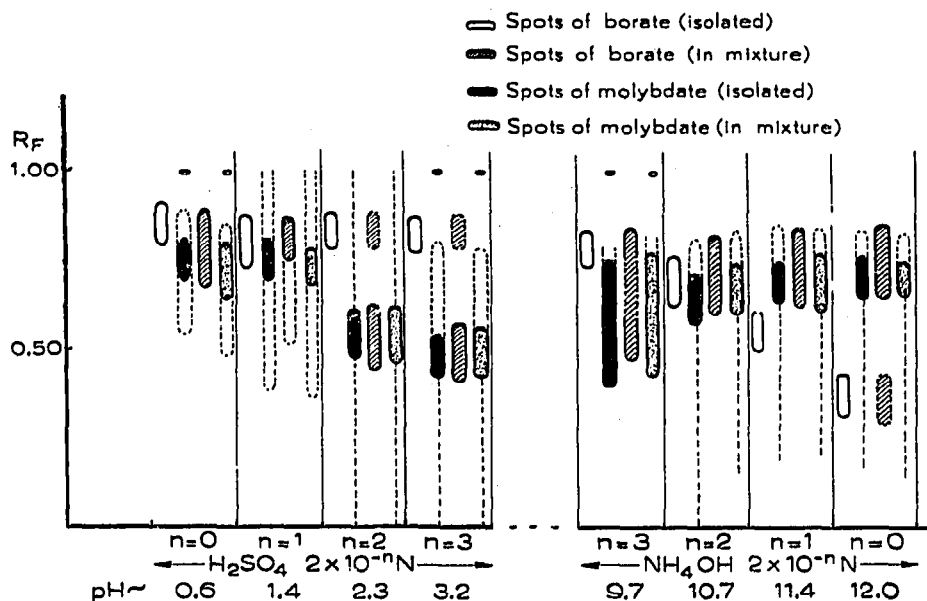


Fig. 3. Spots of borates and molybdates after chromatography with *n*-butanol + H_2SO_4 or NH_4OH .

When R_F values of borate and molybdate are very different (zones of pH 2 to 9 and 11) we observe a strong borate spot retained by molybdate and a weak spot of free borate.

(c) If this retention is due to the formation of a boromolybdic heteropolyacid, we see that the complex is stable in all the solutions studied, i.e., in a pH zone 0.6 to 12.

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SUMMARY

R_F values of borates (meta-, tetra- and per-) are determined in a great number of solvents.

Chromatographic behaviour of borate-tungstate and borate-molybdate mixtures was studied using sulphuric acid solutions + ketone (1:1) and ammonia solutions + ketone (1:1) as solvents. R_F variations in function of pH of solvents are interpreted as being due to the formation of isopoly- and heteropolyacids.

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