

## SOLVENT EFFECTS IN INORGANIC CHROMATOGRAPHY

## I. FACTORS AFFECTING THE ADSORPTION FRONT

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## INTRODUCTION

ZIMMERMANN<sup>1</sup> and SOMMER<sup>2</sup> have investigated the effect of varying the concentration and type of acid and alcohol in various solvent mixtures employed in the determination of the  $R_F$  values of a number of metal ions. They also investigated the influence of the variation in the physical properties of various types of papers commonly used in paper chromatography. KERTES AND LEDERER<sup>3</sup> and DECARVALHO<sup>4</sup> have extended their work and have shown the relationship between the  $R_M$  value and alcohol concentration, on the one hand, and water concentration on the other. No other significant quantitative approach to the effect of these factors appears in the literature. This paper describes part of an attempt to link the effects of acid concentration, water-alcohol ratio, nature of the acid anion, and the identity of the alcohol (and the interactions between these) on the  $R_F$  values of a selected group of metal ions. As there is evidence that at least some metal ions move in a way which is governed by the acid adsorption front, the first step was to study the above effects on the  $R_F$  value of this front, and this report is confined to that aspect of the investigation; the  $R_F$  value being the ratio—height of adsorption front/height of liquid front—as proposed by POLLARD *et al.*<sup>5</sup>.

The approach is through a factorial design, in a series of experiments, in which the above-mentioned factors were varied in a regular manner and the results treated by analysis of variance. This allows the variations in the property of interest (here the  $R_F$  value) to be assigned to the different causes of variation and allows the variability due to particular causes to be compared with the experimental error. Unless this is done on a statistical basis interesting effects may not be observed because of the magnitude of uncontrolled experimental variation. The overall design of the experiment and method of treating the data are described in greater detail below.

## EXPERIMENTAL

*Apparatus and technique employed*

Cylindrical glass jars of approximately 30 cm height and 13.5 cm diameter with ground edges and fitted with heavy glass plates as covers were used as development tanks for the running of the chromatograms. The alcohol component of the solvent was used to saturate the vapour of the tank prior to the running of the chromatograms. An empty Petri dish, of approximately 70 ml capacity, was placed in the

alcohol on the bottom of the tank in such a way that the alcohol surrounded it. The tank was covered with the glass plate and allowed to stand for one hour. The solvent was then added to the Petri dish. The chromatograms were made with sheets of Schleicher and Schüll No. 598 paper, 31 × 21 cm formed into a cylinder 21 cm high. The paper was immersed to a depth of 1 cm in the solvent. The tank was covered and left for ¼ to 12 hours depending on the nature of the solvent used. The chromatograms were run to a uniform height of 18 cm above the surface of the solvent pool using the ascending technique of WILLIAMS AND KIRBY<sup>6</sup>. The temperature throughout the experiments was 25 ± 3°. The papers were not equilibrated before the chromatograms were made as MARTIN<sup>7</sup> has shown this to be unnecessary.

Metal ions were also run in these chromatograms but details of the results with these ions will be reported later.

#### *Solvent reagents employed*

The first four alcohols of the aliphatic series, methanol, ethanol, propan-1-ol and butan-1-ol and their four isomers, propan-2-ol, 2-methylpropan-1-ol, butan-2-ol, 2-methylpropan-2-ol, were used as the basis of the solvents.

The acids chosen were hydrochloric, hydrobromic, nitric and perchloric. All the alcohols were anhydrous and all the reagents were of A.R. grade.

Individual mixtures of each alcohol, each acid, and water, were made so that the following ratios were obtained:

*Alcohol/water*: 0.30, 0.35, 0.40, and 0.45 mole fraction of water. To these sufficient of each acid was added to make solutions which were 0.30, 0.60, and 0.90 *M* with respect to the added acid. The water in these mixtures included the water normally present in each acid used. A minimum accuracy of ± 1.0 % was used in all measurements of volume in the preparation of the solvents. The  $R_F$  values of all these solvents are given in Table I.

#### *Design of the experiment*

A factorial design was adopted for the experimental arrangement, since this permits not only the average effects of the factors to be determined but also their "interactions" *i.e.* effects due solely to particular combinations of factors. These experimental designs are described in works on statistical analysis and methods<sup>8</sup>.

In this investigation the characteristics of the experimental design are:

(i) Four factors designated for convenience by capital letters, *viz.*,  $A$  = alcohols,  $B$  = acid anions,  $C$  = water content, and  $D$  = acid concentration.

(ii) Several levels of each factor (by variation of which the effect of the factor as such is determined) designated by a number with a lower case letter for generality, *viz.*,  $a = 1, 2 \dots 8$  for eight individual alcohols,  $b = 1, 2, 3, 4$  for the anions,  $c = 1, 2, 3, 4$  for the water contents, and  $d = 1, 2, 3$  for the acid concentrations.

(iii) Single replication, by which one value of the property of interest ( $R_F$ ) is obtained for each and every combination of factor levels,  $8 \times 4 \times 4 \times 3 = 384$  in all.

(iv) A "fixed effect" or "regression" model, interest being devoted to the actual factor levels tried, *i.e.* the specific alcohols, anions and concentrations.

According to the model adopted we may write for any individual value in any such table:

$$X_{abcd} = \mu + \alpha_a + \beta_b + \gamma_c + \delta_d + (\alpha\beta)_{ab} + \dots + (\alpha\beta\gamma)_{abc} + \dots + \epsilon_{abcd}$$

TABLE I

 $R_p$  VALUES FOR ALL SOLVENTS

The letters *A*, *B*, *C*, *D*, refer to, *A* identity of alcohol, *B* identity of anion, *C* mole fraction of water in solvent, and *D* molar concentration of acid in solvent. The alcohols are given in the following order indicated under the heading "Solvent reagents employed": 1 = methanol; 2 = ethanol; 3 = propan-1-ol; 4 = propan-2-ol; 5 = butan-1-ol; 6 = 2-methylpropan-1-ol; 7 = butan-2-ol and 8 = 2-methylpropan-2-ol.

| <i>A</i> | <i>B</i>         | <i>C</i> = 0.35 |      |      | 0.40 |      |      | 0.45 |      |      | 0.50 <i>mf</i> |      |              |
|----------|------------------|-----------------|------|------|------|------|------|------|------|------|----------------|------|--------------|
|          |                  | <i>D</i> = 0.3  | 0.6  | 0.9  | 0.3  | 0.6  | 0.9  | 0.3  | 0.6  | 0.9  | 0.3            | 0.6  | 0.9 <i>M</i> |
| 1        | Cl               | 0.85            | 0.86 | 0.95 | 0.83 | 0.85 | 0.88 | 0.85 | 0.82 | 0.81 | 0.85           | 0.88 | 0.90         |
|          | Br               | 0.85            | 0.84 | 0.86 | 0.86 | 0.90 | 0.89 | 0.88 | 0.88 | 0.86 | 0.83           | 0.88 | 0.90         |
|          | NO <sub>3</sub>  | 0.84            | 0.87 | 0.92 | 0.94 | 0.95 | 0.89 | 0.86 | 0.93 | 0.92 | 0.83           | 0.92 | 0.93         |
|          | ClO <sub>4</sub> | 0.83            | 0.96 | 0.88 | 0.85 | 0.87 | 0.88 | 0.93 | 0.86 | 0.86 | 0.85           | 0.91 | 0.88         |
| 2        | Cl               | 0.80            | 0.88 | 0.88 | 0.90 | 0.85 | 0.88 | 0.85 | 0.85 | 0.88 | 0.88           | 0.84 | 0.86         |
|          | Br               | 0.89            | 0.87 | 0.90 | 0.85 | 0.84 | 0.87 | 0.85 | 0.84 | 0.87 | 0.82           | 0.86 | 0.88         |
|          | NO <sub>3</sub>  | 0.82            | 0.88 | 0.92 | 0.93 | 0.88 | 0.93 | 0.84 | 0.88 | 0.92 | 0.88           | 0.90 | 0.90         |
|          | ClO <sub>4</sub> | 0.87            | 0.89 | 0.94 | 0.88 | 0.91 | 0.92 | 0.88 | 0.90 | 0.97 | 0.85           | 0.88 | 0.90         |
| 3        | Cl               | 0.80            | 0.83 | 0.80 | 0.73 | 0.80 | 0.83 | 0.76 | 0.79 | 0.82 | 0.78           | 0.80 | 0.83         |
|          | Br               | 0.75            | 0.83 | 0.87 | 0.80 | 0.81 | 0.82 | 0.77 | 0.87 | 0.88 | 0.81           | 0.86 | 0.89         |
|          | NO <sub>3</sub>  | 0.77            | 0.90 | 0.86 | 0.86 | 0.85 | 0.90 | 0.80 | 0.85 | 0.92 | 0.81           | 0.85 | 0.87         |
|          | ClO <sub>4</sub> | 0.83            | 0.92 | 0.97 | 0.80 | 0.90 | 0.91 | 0.86 | 0.88 | 0.91 | 0.90           | 0.88 | 0.94         |
| 4        | Cl               | 0.74            | 0.82 | 0.83 | 0.80 | 0.83 | 0.82 | 0.76 | 0.82 | 0.88 | 0.81           | 0.88 | 0.87         |
|          | Br               | 0.77            | 0.80 | 0.92 | 0.74 | 0.81 | 0.90 | 0.82 | 0.90 | 0.89 | 0.77           | 0.87 | 0.93         |
|          | NO <sub>3</sub>  | 0.78            | 0.87 | 0.91 | 0.84 | 0.89 | 0.90 | 0.80 | 0.85 | 0.88 | 0.82           | 0.88 | 0.96         |
|          | ClO <sub>4</sub> | 0.84            | 0.94 | 0.96 | 0.87 | 0.92 | 0.95 | 0.92 | 0.92 | 0.95 | 0.90           | 0.95 | 0.96         |
| 5        | Cl               | 0.65            | 0.75 | 0.82 | 0.66 | 0.70 | 0.83 | 0.72 | 0.77 | 0.84 | 0.68           | 0.72 | 0.87         |
|          | Br               | 0.76            | 0.74 | 0.77 | 0.70 | 0.75 | 0.77 | 0.68 | 0.83 | 0.75 | 0.73           | 0.76 | 0.79         |
|          | NO <sub>3</sub>  | 0.72            | 0.79 | 0.85 | 0.73 | 0.88 | 0.92 | 0.76 | 0.88 | 0.93 | 0.84           | 0.81 | 0.83         |
|          | ClO <sub>4</sub> | 0.77            | 0.88 | 0.81 | 0.78 | 0.86 | 0.90 | 0.81 | 0.87 | 0.86 | 0.79           | 0.85 | 0.88         |
| 6        | Cl               | 0.65            | 0.68 | 0.73 | 0.66 | 0.67 | 0.78 | 0.62 | 0.68 | 0.75 | 0.67           | 0.70 | 0.78         |
|          | Br               | 0.72            | 0.70 | 0.75 | 0.66 | 0.74 | 0.77 | 0.70 | 0.73 | 0.77 | 0.65           | 0.73 | 0.76         |
|          | NO <sub>3</sub>  | 0.72            | 0.77 | 0.83 | 0.84 | 0.79 | 0.84 | 0.80 | 0.78 | 0.81 | 0.76           | 0.84 | 0.82         |
|          | ClO <sub>4</sub> | 0.77            | 0.85 | 0.92 | 0.78 | 0.87 | 0.87 | 0.79 | 0.82 | 0.88 | 0.78           | 0.84 | 0.89         |
| 7        | Cl               | 0.76            | 0.74 | 0.82 | 0.63 | 0.72 | 0.78 | 0.69 | 0.73 | 0.79 | 0.69           | 0.82 | 0.79         |
|          | Br               | 0.78            | 0.76 | 0.84 | 0.72 | 0.77 | 0.86 | 0.72 | 0.77 | 0.86 | 0.73           | 0.88 | 0.82         |
|          | NO <sub>3</sub>  | 0.83            | 0.82 | 0.88 | 0.78 | 0.83 | 0.88 | 0.76 | 0.82 | 0.86 | 0.80           | 0.85 | 0.87         |
|          | ClO <sub>4</sub> | 0.83            | 0.90 | 0.95 | 0.84 | 0.88 | 0.95 | 0.82 | 0.90 | 0.94 | 0.84           | 0.89 | 0.94         |
| 8        | Cl               | 0.70            | 0.77 | 0.70 | 0.72 | 0.73 | 0.91 | 0.72 | 0.78 | 0.90 | 0.76           | 0.80 | 0.88         |
|          | Br               | 0.72            | 0.87 | 0.96 | 0.75 | 0.83 | 0.93 | 0.80 | 0.87 | 0.95 | 0.78           | 0.85 | 0.94         |
|          | NO <sub>3</sub>  | 0.79            | 0.88 | 0.96 | 0.80 | 0.92 | 0.94 | 0.81 | 0.88 | 0.94 | 0.83           | 0.93 | 0.70         |
|          | ClO <sub>4</sub> | 0.83            | 0.95 | 0.98 | 0.87 | 0.94 | 1.00 | 0.85 | 0.94 | 1.00 | 0.82           | 0.92 | 1.00         |

where  $\mu$  is a general constant estimated by the grand mean of all the values in the table,  $\alpha_a$  etc. are particular corrections for individual factors,  $(\alpha\beta)_{ab}$  etc. are corrections for particular combinations of factors (there are six such first order interaction terms),  $(\alpha\beta\gamma)_{abc}$  etc. are corrections for particular combinations of levels of three factors (there are four such second order interaction terms), and  $\varepsilon_{abcd}$  is a random error distributed normally with zero mean and a variance ( $\sigma^2$ ), which is independent of particular factor levels. In the analysis of the data, the total variability of the values

of  $X$ , measured by the sum of the squares of their deviations from the grand mean *i.e.*  $\Sigma(X_{abcd} - \bar{X})^2$ , is divided into parts which can be attributed to the factors alone and in combination, and a remainder which cannot be so accounted for and is largely due to ordinary experimental errors of measurement. The analysis of variance table (Table II) illustrates this partitioning. A comparison of the mean variability due to change of levels within a factor with the mean residual variability (an estimate of the distribution of errors,  $\sigma^2$ ) indicates whether or not such changes in factor levels have a significant effect (*i.e.* greater than can be explained by random variation) on the values of the variable of interest.

#### DISCUSSION OF THE EXPERIMENT

The main restriction on the observations which could be made was the desire to work within a single batch of paper. This limited the number of separate chromatograms to about 400, but it permitted a considerable number of interesting alcohols to be included as well as several different acids. In the case of quantitative factors, such as  $C$  and  $D$ , three equally spaced levels are sufficient to detect a curvilinear relationship and this was the number of acid concentrations adopted, but four different water contents were included because it was desired to cover the range of water content as well as possible and it was not certain that the top level could be achieved in all cases. Testing for every combination of the eight alcohols, four anions, four water concentrations and three acid concentrations involved 384 individual chromatograms. These were run in random order of time (the order being taken from a table of non-repeating random numbers<sup>9</sup>) so as to prevent minor variations in experimental conditions from influencing the effects of the actual factors under investigation.

##### *Choice of experimental pattern*

The general pattern of inorganic chromatography has been formed around a choice of organic solvents in which a considerable amount of water (at least 10%) would dissolve and which, on the addition of an acid or complexing agent, would differentiate between some inorganic cations. This pattern has been continued in this study with certain limitations imposed partly by the nature of the materials chosen and partly by the necessity of keeping the experimental design within bounds which could be handled with reasonable ease.

The first four of the saturated aliphatic alcohols and their isomers were chosen as they were readily available in a high degree of purity and have a suitable solvency for water. Other types of solvent (*e.g.* ketones and ethers) were excluded so as to avoid too diverse a range of chemical effects and to limit these to purely structural changes. Moreover alcohols have been the basis of most solvents. The ratio of water to alcohol was limited, at the highest concentration by mutual solubility and at the lowest by the maximum concentration of acid which could be obtained. It did, however, cover the range of the majority of normal solvents.

Acid concentration was limited by the experimental design, as the strongest aqueous hydrobromic acid was only 8M solution and so did not permit of much greater concentration in the solvent than the 0.9M solution used. The limitations of the experimental framework still permitted the ratio of water to acid to range from 57 to 1 down to 6 to 1 on a molar basis.

The four acids were all "strong" acids. The halogen acids were capable of forming anionic complexes with some of the metals chosen while in the case of nitric and perchloric this was not likely.

## DISCUSSION OF RESULTS

We concentrate on the  $R_F$  value here, since the complete treatment of the  $R_F$  has not yet been undertaken, nor have we yet investigated the relationship between the  $R_F$  and the  $R_P$  values.

The analysis of variance table (Table II) shows that the  $R_P$  values are very considerably affected by changes in alcohol, in anion, in acid concentration, and to a lesser extent in water concentration. There is a dubious connection between anion and water concentration, but the effect of acid concentration varies, highly significantly, from alcohol to alcohol (alcohol-acid concentration interaction).

TABLE II

ANALYSIS OF VARIANCE OF  $R_P$  VALUES

The level of significance is indicated by the number of asterisks. One asterisk (\*) indicates significance at better than the 5% level, two asterisks at better than the 1% level, and three asterisks at better than the 0.1% level.

| Source of variation | Sum of squares | Degrees of freedom | Mean square | Ratio to residual | Significance |
|---------------------|----------------|--------------------|-------------|-------------------|--------------|
| A Main effect       | 5994.33        | 7                  | 856.33      | 109.1             | ***          |
| B Main effect       | 5500.35        | 3                  | 1833.45     | 233.6             | ***          |
| C Main effect       |                |                    |             |                   |              |
| linear              | 73.63          | 1                  | 73.63       | 9.381             | **           |
| quadratic           | 0.85           | 1                  | 0.85        | 0.108             |              |
| cubic               | 0.25           | 1                  | 0.25        | 0.032             |              |
| D Main effect       |                |                    |             |                   |              |
| linear              | 4865.06        | 1                  | 4865.06     | 619.8             | ***          |
| quadratic           | 18.75          | 1                  | 18.75       | 2.389             |              |
| AB Interaction      | 1349.99        | 21                 | 64.29       | 8.191             | ***          |
| AC Interaction      | 188.44         | 21                 | 8.97        | 1.143             |              |
| AD Interaction      |                |                    |             |                   |              |
| linear              | 855.56         | 7                  | 122.22      | 15.57             | ***          |
| quadratic           | 47.54          | 7                  | 6.79        | 0.865             |              |
| BC Interaction      |                |                    |             |                   |              |
| linear              | 55.72          | 3                  | 18.57       | 2.365             |              |
| quadratic           | 48.84          | 3                  | 16.28       | 2.074             |              |
| cubic               | 77.86          | 3                  | 25.95       | 3.306             | *            |
| BD Interaction      | 31.28          | 6                  | 5.21        | 0.664             |              |
| CD Interaction      | 56.58          | 6                  | 9.43        | 1.201             |              |
| ABC Interaction     | 459.07         | 63                 | 7.29        | 0.929             |              |
| ABD Interaction     | 466.64         | 42                 | 11.11       | 1.415             |              |
| ACD Interaction     | 335.50         | 42                 | 7.99        | 1.018             |              |
| BCD Interaction     | 254.83         | 18                 | 14.16       | 1.804             | *            |
| Residual            | 988.92         | 126                | 7.85        |                   |              |
| Total               | 21670.00       | 383                |             |                   |              |

Fig. 1 (a) shows the overall variation of  $R_P$  values from alcohol to alcohol. The values are much lower for the butanols (except *tert.*-butanol) than for the remainder. This is believed to be related to the fact that *n*-butanol, isobutanol and *sec.*-butanol are only partly miscible with water, while all other alcohols are completely miscible.

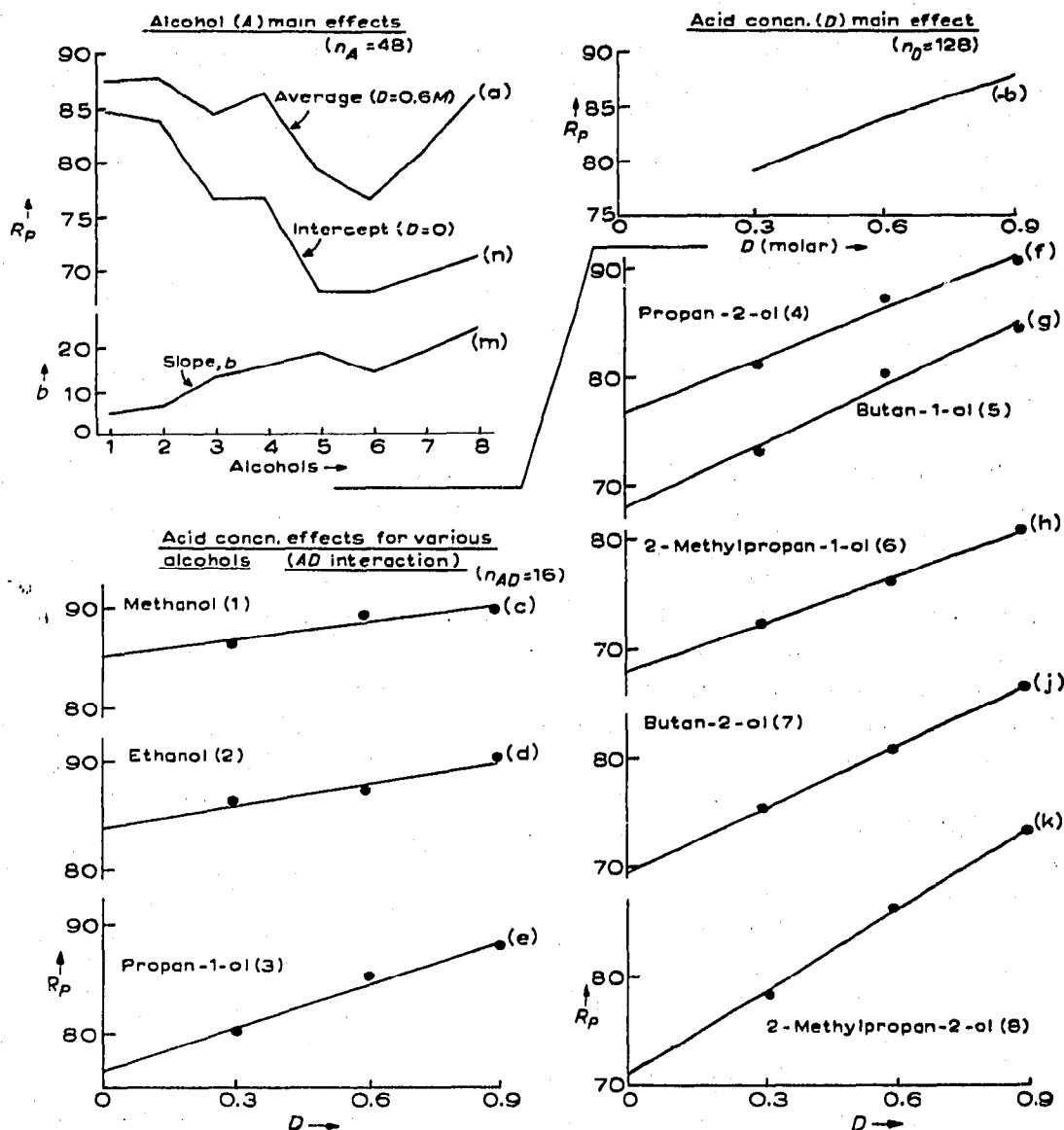


Fig. 1. Graphical representation of the  $R_P$  values showing the effects of (a) change in alcohol (means of 48 values for each of the eight alcohols in order: methanol, ethanol, propan-1-ol, propan-2-ol, butan-1-ol, 2 methylpropan-1-ol, butan-2-ol, 2 methylpropan-2-ol); (b) acid concentration (means of 128 values for each of three concentrations); (c) to (k) acid concentration for individual alcohols (means of 16 values); (n)  $R_P$  values extrapolated to zero acid concentration for the eight alcohols (intercepts of curves (c) to (k)); (m) rate of change of  $R_P$  with acid concentration for the eight alcohols (slopes of curves (c) to (k)).

The upper right-hand curve, Fig. 1 (b), shows the average effect of acid concentration, the relationship to  $R_P$  being strictly linear over the range of concentration studied. The analysis of variance indicates, however, a very strong interaction between alcohol and the linear component of acid concentration which means that the actual slope of the  $R_P$  versus concentration lines varies significantly from alcohol to alcohol. The eight lines, Fig. 1 (c) to Fig. 1 (k), are shown on the lower part of the figure. The intercepts (in effect  $R_P$  extrapolated to zero acid concentration) and the slopes of these significantly different lines are plotted in the upper left-hand graph of Fig. 1. The

intercepts, curve Fig. 1 (n), show the same kind of general variation from alcohol to alcohol as the overall averages, except that all the butanol values are now low by comparison with the simpler alcohols. The slopes, curve Fig. 1 (m), on the other hand show a general rise over the alcohol series. That is to say, the effect of higher concentration in raising the acid front is the greater, the greater the complexity of the alcohol molecule.

The linear relationship of  $R_P$  to acid concentration is explicable on the assumption that the range of concentrations used lies on a linear or nearly linear portion of a Langmuir isotherm (MARTIN<sup>10</sup>).

The upper left-hand graph, Fig. 2 (a), shows the very marked differences in the overall averages for the four anions of the acids employed, the values following the lyotropic series, frequently quoted from ZECHMEISTER<sup>11</sup>, except that the positions of  $\text{Cl}^-$  and  $\text{Br}^-$  are in reverse of the usual order (which goes  $\text{Br}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$  in strengths of adsorption). Nor does the order found quite agree with the relative strengths of the acids in glacial acetic acid as reported by BELL<sup>12</sup> although in this case it is the nitrate and bromide which are transposed.

The effect of changes in the water to alcohol ratio (in the regions investigated) is relatively slight, although statistically very significant by comparison with the random error. The overall averages change linearly with  $R_P$ , curve Fig. 2 (b). The analysis shows, however, a significant anion-water concentration (cubic) interaction. This means that the up-down alternation, rather than slope or curvature, of the averages for the four concentrations differ between anions by more than can be explained by the random error. In spite of this statistical significance we incline to the belief that the effect is actually spurious and can offer no explanation for such behaviour.

Lastly, the analysis indicates a highly significant alcohol-anion interaction, *i.e.* the effect of a particular anion on  $R_P$  value differs from alcohol to alcohol and *vice versa*. The lower curves, Fig. 2 (c) and (d), attempt to show this. The values plotted are not the actual average  $R_P$  for particular alcohol-anion combinations, but those values adjusted for general alcohol and general anion variations. These represent particular discrepancies due to the isolated effect of alcohol-anion combinations above and below the grand mean (centre lines). The lines equidistant above and below the grand mean line represent the extent of variations which could be accounted for by ordinary experimental error. The nature of the interaction can be clearly seen—a fall over the 8 alcohols in the presence of chloride changing over to a rise in the presence of perchlorate—a fall over the four anions, in the presence of methanol and ethanol, changing over to a rise in the presence of the more complex butanols.

Attention must again be drawn to the proportions of the solvent constituents, there being a 10-fold range of water to acid when considered in molar proportions. There seems little doubt that the proton will have at least one molecule of water associated with it, and previous work (MARTIN<sup>10</sup>) indicates that it may be greater than one in the case of *n*-butanol. Of the total quantity of water in the solvent some is directly adsorbed by the cellulose. A further indefinite quantity accompanies the proton or hydronium ion or hydrated hydronium ion. This leaves a greatly diminished quantity available for hydration of the anion with the possible situation of this position of the solvent being solvated partly by water and partly by alcohol. This may explain the very significant alcohol-anion type interaction (*A-B* interaction) and the alcohol-anion concentration interaction (*A-D* interaction).

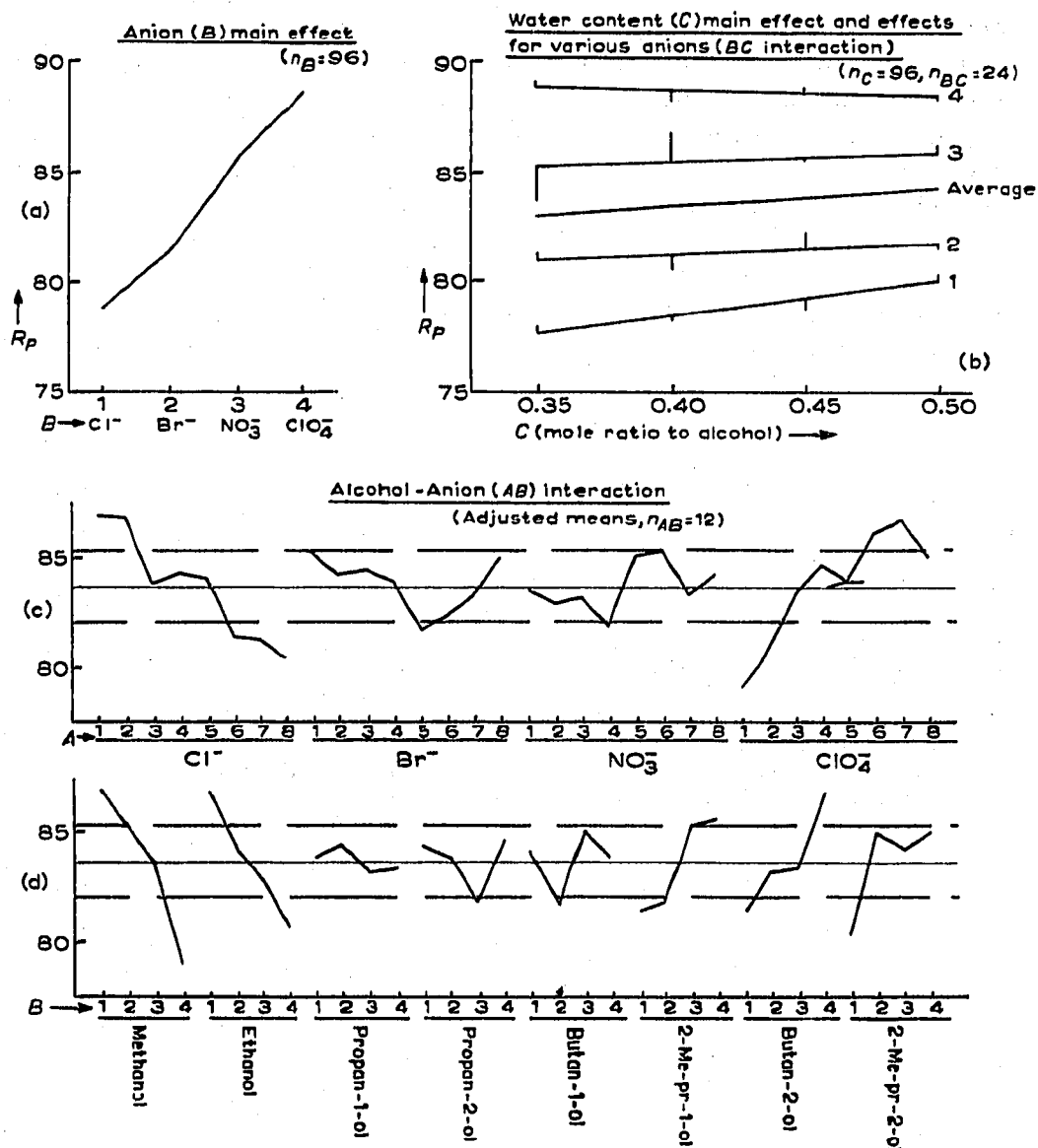


Fig. 2. Graphical representation of the  $R_p$  values showing the effects of (a) change in acid anion (means of 96 values for the four acid anions in order:  $Cl^-$ ,  $Br^-$ ,  $NO_3^-$ ,  $ClO_4^-$ ); (b) water/alcohol ratio (means of 96 values showing overall variation (central curve) and means of 24 values for each of the four anions (1= $Cl^-$ , 2= $Br^-$ , 3= $NO_3^-$ , 4= $ClO_4^-$ )); (c) change in alcohol for individual anions (adjusted means of 12 values); (d) change in anion for individual alcohols (adjusted means of 12 values).

The type of experimental design adopted is that best fitted for elucidating the average changes in values of a property caused by changes in factors and for distinguishing those changes from the effects of combinations of factors. In this case the most significant features revealed are:

- (i) the close interdependence of the effects of anions of the acids and the alcohols,
- (ii) the variation of the effect of acid concentration from alcohol to alcohol.

SUMMARY

This paper describes a series of tests designed to elucidate the effects of varying the



alcohol and acids as well as the concentration of water and acid on the  $R_F$  value of solvents consisting of these three constituents. The first four aliphatic alcohols and their four isomers propan-2-ol, 2-methylpropan-1-ol, butan-2-ol, 2-methylpropan-2-ol, and hydrochloric, hydrobromic, nitric, and perchloric acids were used. The acid concentration was varied from 0.3 to 0.9M and the water to alcohol ratio from 0.35 to 0.50 mole fraction. The results obtained from 384 chromatograms were treated by analysis of variance to show that the  $R_F$  value was linearly related to the acid concentration and water concentration although the latter had little effect on the result. The interactions between the acid anion and the alcohol and the acid concentration and the alcohol were highly significant.

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