THE CHROMATOGRAPHIC PROCESS IN A REVERSED-PHASE SYSTEM FOR THE SEPARATION OF SOME METAL IONS, BY ION-ASSOCIATION DISTRIBUTION

L. S. BARK

Department of Chemistry and Applied Chemistry, University of Salford, Salford, Lancs. (Great Britain)

AND

G. DUNCAN

Department of Chemistry and Biology, Manchester Polytechnic, Manchester (Great Britain)

(First received November 20th, 1969; revised manuscript received February 7th, 1970)

SUMMARY

After a consideration on the distribution of metal ions in reversed-phase systems consisting of tri-n-butyl phosphate and 3–9 M hydrochloric acid, a general equation relating the partition coefficients of the metal ions in the system and their R_F values is proposed

$$\alpha^1 = A \left\{ 1/(R_F - 1) \right\} - B$$

where α^1 is the experimentally determined partition coefficient of a solute. A is a volume ratio term, not necessarily the ratio of the amount of reversed-phase material to the amount of solvent covering a particular area of the plate, and being concerned with the intermixing of the phases and the use of part of the stationary phase in binding to the cellulose layer. B is a term related to the interaction of the mobile and stationary phases. In systems where no interaction occurs and the stationary phase is all chromatographically active, the equation reduces to the ideal equation of chromatography, *viz.* the MARTIN relationship.

INTRODUCTION

The use of reversed-phase systems for the chromatographic separation of compounds is widespread, in both organic and inorganic fields. The mechanism of the separation is generally regarded as partition of a solute between two liquid phases, one a mobile phase and the other the stationary phase. These phases are generally regarded as independent and discrete and the various chromatographic equations such as that derived by MARTIN and co-workers[1], which have served as the basis of much of the present theoretical knowledge of chromatography, assume this to be self

evident. One result of this assumption is that the mechanism of chromatography is often assumed to be simple partition between two distinct well defined phases because the MARTIN or a similar relationship is valid for the system. This assumption is not necessarily correct, and it was thus decided to investigate systems in which the phases were not necessarily discrete and could have mutual interaction and thence to evolve a more general relationship than that indicated by MARTIN. However, we must first consider the processes by which distribution of solutes takes place in systems in which the MARTIN relationship is known to be valid. These usually involve a relatively non-polar organic phase and an aqueous phase and the solute to be distributed between these phases has no discrete charge, but may contain groups, usually the chromatographically functional group, which is polarised or is capable of being so. The molecules of the solvents of the two phases may exert a dipole-induced dipole attraction on each other, but this is not of sufficient magnitude to cause dissolution of any one phase in the other to such an extent that discrete phases are not discernible. Thus solution of an organic solute in a non-polar organic phase occurs because the solute units fit into the solvent molecular pattern and little or no electronic disturbance is thereby caused, and the induced dipole caused in the solute by the dipole of the molecules of the aqueous phase is insufficient to give a complex of the type (organic solute–aqueous solvent) sufficiently stable to exist in the aqueous phase as a solvated (aquated) species.

In the case of inorganic metal complexes, which may possess an electric charge and which are distributed between a stationary phase containing polar groupings and a mobile phase, which is generally ionic or has at least a relatively high dipole or dielectric constant, then solution occurs because of somewhat different mechanisms to those postulated above. In some systems it is possible to get partition of an inorganic species between a non-aqueous stationary phase and an aqueous mobile phase, by an ion-association mechanism[2] or by a somewhat related ion-exchange system[3]. In both cases, to a large extent there is a similarity of the various species involved; and the mechanisms are somewhat analogous. We considered that it is possible to have the solute species occurring in the two phases, in different chemical entities. These may have electrical properties differing only in degree but not in type. Furthermore the similarity in the electrical nature of the two phases may be such that there could be some doubt concerning the absolute chromatographic and physical boundaries of the two phases. It was thus decided to use some ion-association systems and to investigate the relationship between the partition coefficients of substances distributed between various chromatographic phases and the R_F values of these substances in the same chromatographic phases. Although CERRAI[3] had postulated an ion-exchange mechanism for the separation of metal chlorides on a reversed-phase system with a stationary phase of HDEHP (di-(2-ethylhexyl) orthophosphoric acid) supported on cellulose paper, using various molarities of hydrochloric acid as the eluent, in his derivation of working equations he used the same considerations regarding the separation of the phases as did MARTIN, except that he did not assume that the whole of the HDEHP was necessarily chromatographically involved, and related the quantity $1/(R_F-1)$ to the effective concentration of HDEHP on the impregnated paper. He did not, however, explain the various deviations which occurred, nor did he explain why the effective concentration was not the sum total concentration of HDEHP. The support was assumed to have no chromatographically functional role.

It was thus decided to investigate systems having a stationary phase of tri-*n*-butyl phosphate (TBP) supported on a thin layer of cellulose powder and a mobile phase of hydrochloric acid of various molarities. The solutes were the appropriate ionic species containing cadmium, cobalt(II), copper(II), manganese(II), palladium(II), and zinc.

MUSIL et al.[4] had previously reported chromatographing some metal chlorides on paper impregnated with a TBP–methanol mixture using various molarities of hydrochloric acid as eluent, and had attempted to find a relationship between the R_F value of the metal chlorides and their partition between TBP and hydrochloric acid. No interpretation of their results was attempted. Before any systematic study can be made of the relationship between partition coefficients and chromatographic parameters for all kinds of systems it is necessary to examine the equation postulated by MARTIN, who was concerned only with relatively simple non-polar organic systems. Thus he postulated the relationship:

$$\alpha = \frac{A_L}{A_S} \cdot \left(\frac{1}{R_F} - 1 \right)$$

where

α = the partition coefficient for the distribution of the solute between the mobile and stationary phases (of the chromatographic system).

A_L = the cross-sectional area of the mobile phase (of the chromatographic system)

A_S = the cross-sectional area of the stationary phase (of the chromatographic system)

R_F is defined as the ratio of the distance moved by the solute and that moved by the mobile phase.

(It is generally assumed that these terms refer to the whole system.)

Each of these terms must be examined in conditions practically identical with those appertaining to the actual chromatographic system. In addition, it is considered necessary to examine physically the phases during the development of the chromatogram so that any changes occurring may provide further data.

Many of the previous workers on such relationships have either assumed values for either A_L or A_S or determined them using simple non-polar organic reversed-phase systems. These approaches are exemplified respectively by the work of MULVANEY et al.[5] and COPIUS PEEREBOOM[6]. Any slight deviations from the MARTIN relationship have generally been attributed to experimental error.

The purpose of the work was to establish experimentally a more general equation which would be valid for both polar and non-polar systems.

EXPERIMENTAL

Chromatography

The TBP was purified by a method reported previously[5,7] using a batch process. All the batches were recombined to give a homogenous material.

The method and apparatus used for the chromatography of the metal ions was reported previously[2], and is summarised as follows: Purified and sieved cellulose powder was mixed with a solution of TBP in carbon tetrachloride and used to coat

glass plates. The carbon tetrachloride was caused to evaporate and to the pure TBP layers solutions of metal chlorides were applied. The plates were placed in a small-volume double saturation chamber[8], pure hydrochloric acid of known molarity (3.0; 4.0; 4.5; 5.0; 6.0; 7.0; 7.5; 8.0; 9.0 M) was used as the mobile phase, and the chromatograms were developed by an ascending technique under controlled temperature conditions (25 $\pm$ 0.5°). The eluent was allowed to move a fixed distance (12.5 $\pm$ 0.25 cm) from the point of application of the metal ions. The development times ranged from 1 to 3 h, depending on the molarity of the acid. There was an increase in time of development with the increase in the acid molarity.

After very rapid removal of most of the TBP and the acid (achieved by using temperatures in excess of 120°), the plates were sprayed with various chromogenic reagents[9], and the R_F values were determined.

Each R_F value reported is the mean of at least four values obtained on different plates, and differing by not more than $\pm$ 0.01 R_F units from the arithmetic mean. (This precision was possible only since the chromatography was done under strictly standardised conditions. Very slight variations in the purity of the TBP gave variations greater than $\pm$ 0.01 R_F units—see DISCUSSION OF THE RESULTS.)

The molarity of each of the hydrochloric acid solutions was determined titrimetrically.

Determination of the cross-sectional area of the stationary phase

This was done at only two different molarities of hydrochloric acid (6 M and 8 M). Coated plates were placed in a saturation chamber, the atmosphere of which was saturated with the vapours of either 6 M or 8 M acid, and the plates were allowed to stand for approximately 2 h in the appropriate atmosphere. (This time was chosen as being a median between the times taken for plates to run under normal conditions and as being sufficient to allow for any gravitational drainage of the stationary phase to occur.) After standing, the plates were removed from the saturation chamber, and were divided into bands parallel to the upper edge of the plate, viz. what would be the solvent front under development conditions. For the distribution of the phosphate on the layers the bands were transferred to dry tared sintered glass crucibles, and the crucibles and contents were weighed. Carbon tetrachloride was then passed through the cellulose to remove the TBP. The crucibles were then dried in an air oven, to constant weight. The process was repeated until constant weight was obtained between two successive washings with carbon tetrachloride. Control experiments using non-impregnated cellulose layers were done using the same total volume of carbon tetrachloride. This enabled corrections to be made for any material other than the phosphate which may have been washed out of the cellulose by the carbon tetrachloride. The results are shown in Table I.

The values quoted for the weight of TBP found were obtained from plates taken at random from alternate batches of plates made and used in subsequent experiments. By this method it was thought possible to eliminate errors caused by the operator during the spreading of the plates.

To see if the TBP was moved up the plate by the flow of HCl, a small series of plates was developed at 6 M HCl and the TBP was measured in strips parallel to the solvent front as before (except that the bands were only measured at 4–6 cm, 8–10 cm, and 12–14 cm from the point of application). The results obtained were within the

range of results obtained for the above experiments. It was thus concluded that although there would be dissolution of the TBP by the HCl, saturation conditions were established and thus no TBP was effectively transported by the HCl at this molarity and under these experimental conditions. Thus the amount of TBP covering a particular area of the plate remains experimentally constant at this molarity of HCl.

Distribution of hydrochloric acid on the eluted layers

The plates, already impregnated with the TBP, were eluted with two different concentrations of HCl (6 M and 8 M) to a distance of 14 cm from the point of application of the solutes. The chromatoplate was removed from the saturation chamber, and the layer was removed in bands (2 cm wide) using a specially designed scraper. The acid was leached from the cellulose with water and the amount of acid was determined titrimetrically using NaOH (0.5 M) as the titrant and screened Methyl Orange as a visual end point indicator.

TABLE I

A_L/A_S RATIOS AT 6 M AND 8 M HCl

Distance from line of application (cm)	Amount of TBP (mg)[a]	A_L/A_S, 6 M[b]	A_L/A_S, 8 M[b]
0–2	109.6		
2–4			
4–6	108.0	9.21	6.38
6–8		8.85	6.16
8–10	108.5	7.16	6.06
10–12		6.79	5.81
12–14	117.9	6.31	5.05
14–16		4.51	4.02
16–18	117.7	—	—
18–20		—	—

[a] Amount of TBP in a band of 18 × 2 cm.

[b] The A_L/A_S ratio for a given band was calculated from the measured volumes of stationary phase and mobile phase in that band, corrected for the acid extracted by the TBP and the increase in volume of the stationary phase as a result of this extraction. The values quoted for this ratio are the mean of at least four determinations.

The cellulose above the apparent solvent front was also treated in the above manner to determine its acid content. The means of at least four determinations for each acid concentration were used to calculate the A_L/A_S ratios given in Table I.

In separate experiments the total amounts of acid left after developing the plates were determined by titrating not only the acid on the layer (over the whole length of the plate) but also that remaining in the bottom of the saturation chamber and on the walls of the vessel. The differences in the amounts of acid introduced into the chamber and the amounts recovered were not sufficiently great (less than 2%) to indicate that any significant hydrolysis of the TBP by the HCl had occurred and we thus concluded that the layers were substantially chemically unchanged during the development of the chromatogram.

Determination of the partition coefficients of the metal ions

The amounts of HCl and TBP having been determined, the same ratios of metal ion, HCl and TBP were shaken together in a separating funnel (approximately 20–30 ml portions were used). After allowing equilibrium to be established, the funnel was placed in an air oven at 25 ± 0.5° for 30 min and the two phases were allowed to separate. When separate, the lower aqueous phase was removed and the metal concentration determined either by atomic absorption or titrimetrically. In the case of cadmium, no hollow cathode lamp was available and the concentration of the metal ion remaining in the aqueous phase was generally too small to give a good visual end point in the titration with EDTA. Thus the metal ion was re-extracted from the non-aqueous phase by shaking the phase with distilled water (two aliquots of 15 ml were used). The combined extracts were then titrated at pH 5.0 using EDTA and pyridyl-azonaphthol (0.1% w/v ethanolic solution) as the visual indicator.

The metals which had been determined by means of atomic absorption methods were assayed on various commercial instruments, the choice of instrument being governed by the availability of the various hollow cathode lamps required. In all the determinations using atomic absorption methods, it was necessary to prepare standard calibration graphs using hydrochloric acid solutions of the same molarity as that used in each particular determination. It was also necessary to shake this acid with TBP
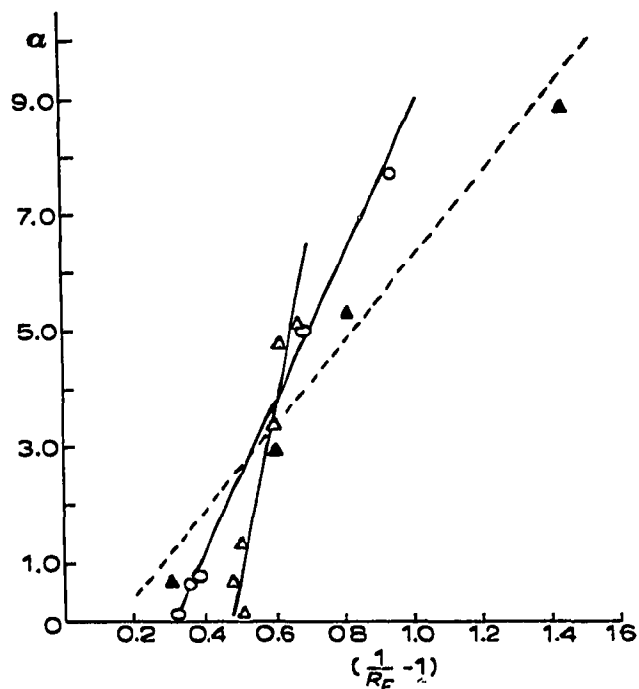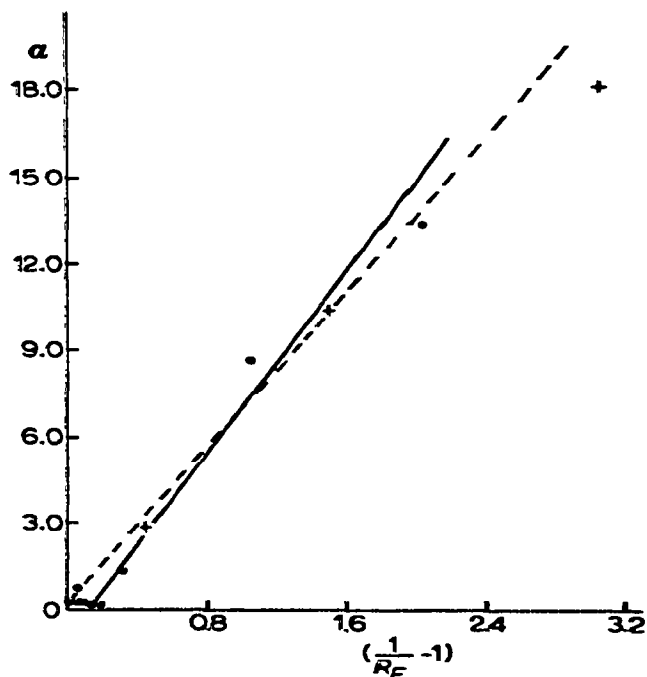
Fig. 1   Fig. 2

Plot of the variation of $1/(R_F - 1)$ *vs* the partition coefficients for the various molarities of acids used. Fig. 1. △—△, 9 M, ○—○, 8 M; ▲————▲, 7.5 M. Fig. 2. ————+————, 5 M HCl; ——·————, 6 M HCl.

Equations to lines: 9 M, α = 28 80 $\{1/(R_F - 1)\}$ — 14.12
8 M; α = 12.37 $\{1/(R_F - 1)\}$ — 3 80
7 5 M, α = 7 45 $\{1/(R_F - 1)\}$ — 2.42
6 M, α = 6.81 $\{1/(R_F - 1)\}$ — 0.97
5 M; α = 5.97 $\{1/(R_F - 1)\}$ — 0.08

TABLE II

PARTITION COEFFICIENTS AND CHROMATOGRAPHIC PARAMETERS

Metal	Acid molarity	R_F value	$1/(R_F - 1)$	α
Cadmium	3	0.18	4.56	22.40
	4	0.22	4.45	19.75
	5	0.24	3.17	18.05
	6	0.32	2.13	13.16
	7.5	0.41	1.44	8.83
	8	0.52	0.94	7.74
	9	0.59	0.68	5.12
Cobalt	3	0.96	0.04	0.00
	4	0.95	0.05	0.00
	5	0.95	0.05	0.00
	6	0.85	0.18	0.03
	7	0 83	0.20	0.38
	8	0.72	0.38	0.77
	9	0.65	0.52	1 27
Copper	3	0.96	0.04	0.075
	4.5	0.95	0.05	0.14
	5	0.91	0.10	0.37
	6	0.82	0.22	0.51
	7.5	0.76	0.32	0.635
	8	0.74	0.35	0.64
	9	0.67	0.49	0.67
Manganese	4	0.95	0.05	0.03
	5	0.93	0 08	0.04
	6	0.89	0.13	0.05
	7	0.87	0.15	0.075
	8	0.76	0.315	0.11
	9	0.66	0.52	0.16
Palladium	5	0.70	0.43	2.6
	6	0.67	0.49	2.8
	7.5	0 63	0.59	2 9
	8	0.63	0.59	3.5
	9	0.63	0 59	3 2
Zinc	4.5	0.36	1.78	11 80
	5	0 40	1.50	10.40
	6	0.47	1.13	8 33
	7.5	0.55	0.82	5.27
	8	0.59	0.69	5.02
	9	0 62	0.62	4.83

before adding the appropriate metal salt. (This is necessitated by the enhancement of the absorption caused by some chloride complexes, and the suppressive effects of the pyrolysis products of TBP contained in the aqueous phases.)

The results are reported in Table II with the appropriate R_F values.

Graphical relationships

The relationships between the partition coefficients and the R_F values were obtained by plotting the variation of $1/(R_F-1)$ against the partition coefficients for the various molarities of acids used. The method of least mean squares was used to obtain the best fit to the experimental values.

The lines obtained are shown as Figs. 1 and 2.

DISCUSSION OF THE RESULTS

The R_F values and partition coefficients

The values quoted here are those obtained using an "homogenised" sample of TBP. We have used on other occasions single batches of TBP, purified by a method similar to that quoted here, and have obtained R_F values and partition coefficients which gave relationships as linear as those reported here but with noticeable and significant variations. This lack of agreement in the values for a particular ion in the supposedly same "TBP/HCl" systems is evident throughout the literature[9-11].

It has been shown[12] that these differences are caused by the varying amounts of the lower butyl phosphates (and in some cases *n*-butanol) which were not completely removed by the purification processes. These lower butyl phosphate esters are reported to cause synergistic effects with TBP[13,14]. Thus to obviate any variations in the particular coefficient measurements and in the R_F values, it is necessary to use a completely homogenous sample of purified TBP throughout. As mentioned above, the values obtained are only strictly comparable when *inter alia*. However, the same overall conclusions may be deduced from any such system; the shapes of the graphs relating the chromatographic parameters and the distribution parameters are comparable. The order of R_F values is in good agreement with those values previously reported with analogous systems[4,15,16] and the partition coefficients follow the same patterns as those previously reported[12,16,17], although the variations throughout the literature make it impossible to have direct and strict comparisons.

The partition coefficients cannot be determined *in situ* on the plate because of the practical difficulties involved, and the exact conditions cannot be duplicated in bulk, since the amount of cellulose needed to represent the support would render impossible the mixing of the phases by agitation.

The relationship between the R_F values and the experimentally determined partition coefficients

Although various workers have investigated the distribution process in partition chromatography from various aspects, for example as a discontinuous system[1] or kinetic equilibria[3,18-20], or involving steady state phenomena[21], all the equations derived are almost identical and reduce effectively to the MARTIN equation. Only CERRAI[3] has indicated that the volume of the organic phase which should be considered is not necessarily the total volume of the substance present. He reported that he could find no direct proportionality between the molarity of the impregnant (HDEHP) used to treat the paper and the effective concentration of this taking part in the chromatographic process. However, his method of estimating that amount which is present in the partition process is based on the absorption of one metal into one system.

From considerations of the plots of the experimentally determined partition coefficients of the metals studied here, and the term $1/(R_F-1)$ (Figs. 1 and 2), it appears that there is a linear relationship of the following type

$$\alpha^1 = A \left(\frac{1}{R_F} - 1 \right) - B$$

where

α^1 is the experimentally determined partition coefficient of the solute between

TABLE III

EQUATIONS FOR THE GENERAL EXPRESSION $\alpha' = A\{1/(R_F - 1)\} - B$

Molarity (M)	A term	B term
5	5.97	0.08
6	6.91	0.97
7.5	7.45	2.42
8	12.37	3.80
9	28.80	14.12

the two phases "in bulk", which need not necessarily be the same thermodynamic function as envisaged by MARTIN and others;

A is a function for a particular system involving the ratio of the actual volumes of the phases concerned in the partition of the solute on the chromatogram; and

B is a term related to the interaction of the two phases in a particular system.

We regard this as the general equation of any chromatographic process, and suggest that where there is no interaction between the phases, which can then be considered to be discrete, $B = 0$, and the equation becomes essentially of the same form as the MARTIN equation. If we assume that the volumes of the two phases measured experimentally are identical with those taking part in the distribution process, then the equation becomes identical with the MARTIN equation.

However, in the systems considered here, there are not ideal conditions. This is made evident if we consider Table III, which collects the equations calculated from the results given in Table II and shown graphically in Figs. 1 and 2. (Although R_F values greater than 0.85 units and less than 0.1 units are not sufficiently precise to

TABLE IV

COMPARISON OF A_L/A_S RATIOS

Ion	R_F value[a]	A_L/A_S (exptl.)[b]	A_L/A_S (calc.)[c]	A term[d]
Using 6 M HCl as the eluent				
Cd	0.32	9.6	6.2	
Co	0.85	6.6	0.2	
Cu	0.82	6.8	2.3	6.81
Mn	0.89	6.4	0.4	
Pd	0.67	7.8	5.7	
Zn	0.47	8.9	7.4	
Using 8 M HCl as the eluent				
Cd	0.52	5.8	8.3	
Co	0.72	6.0	2.1	
Cu	0.74	6.0	1 8	12.37
Mn	0.76	5.9	0.35	
Pd	0.63	6.1	6.0	
Zn	0.59	6.1	7.3	

[a] Values are the mean of at least four results.
[b] Obtained by graphical interpretation of results in Table I
[c] Calculated from $A_L/A_S = \alpha/\{1/(R_F - 1)\}$.
[d] Obtained from slopes of graphs given in Figs. 1 and 2.

be used in calculations, they are given in Table II to indicate the orders of separation of the various ions; they have not been used for the calculation of the equations to the experimental values.) Thus we can see that the A terms vary from approximately 6 to 30 and the B term from 0.08 to approximately 14. Within a particular system the variation between theory (i.e., no interaction of phases) and practice (i.e., probable interaction between phases) is well illustrated by Table IV. The lack of correlation between the observed and the calculated values for the A terms leads us to consider whether or not there were definable chromatographic layers in the systems studied.

The discreteness of the two phases

In the course of the investigation we observed that as the concentration of the acidic phase increased the developed plates appeared progressively drier, although the volume of acid used as the solvent was kept constant, and the same length of chromatographic run was allowed. This apparent lack of mobile phase we attributed to increased dissolution of the mobile phase into the stationary phase. Previous workers on TBP/HCl systems have studied the mutual solubility of the two substances. HARDY[22] reported that if equal volumes of TBP and water (or dilute acid solutions) are equilibrated, the resulting ratio of organic phase to inorganic phase will be 1.13. This ratio progressively increases with increase in acid concentration, until at 11 M HCl the ratio is 1.90, thus corresponding to an increase of 33% in the organic phase. In the systems reported here (TBP/5 M–9 M HCl) the value of B increases from 0.08 to 14.12. This we regard as an indication of the amount of the HCl entering the TBP phase.

To some extent, this will account for the discrepancy between the volume ratio (A) calculated from the graph and that calculated from the experimentally determined amounts of TBP and HCl present on a plate, since in the latter case it has been tacitly assumed that each substance was contained in a separate layer.

Other factors, such as the mechanisms of the mutual dissolution of hydrochloric acid and TBP, and of the partitioning of the metal species, must also be considered when seeking an explanation of the variations in the volume ratio term.

In a review[23] of the use of TBP in the solvent extraction of metal ions from mineral acids, MARCUS discussed the extraction of HCl by TBP and indicated the probable composition of some of the extracted species existing in the organic phase. The species are mainly partly dissociated ion pairs of the type $[(BuO)_3 \cdot POH]^+$ $[(H_2O)_n \cdot Cl^-]^-$, which co-exist in the TBP phase with other neutral species containing TBP, viz. $[TBP(H_2O)_x]$ and $[TBP(HCl)_y]$, the former being more prevalent in low acidity conditions, the latter being found mainly at high molarities. Various solvation ratios have been reported[24-26] and the most probable composition of the complex has a 1:3 ratio of TBP:H_2O. The consequent transfer of both water and acid into the organic phase will inevitably cause relatively large volume changes in both phases, and the differences in the chemical natures of the two phases will also be reduced.

Other factors play a part in this alteration in the phases. It has been reported[27,28] that the amount of HCl extracted into TBP, when metal ions are present, is greater than that extracted from solutions not containing metal ions. This synergistic increase is to some extent a result of the composition of the extracted, metal-containing species. If we consider the extraction of cobalt from hydrochloric acid solutions, we find that in the aqueous phase the cobalt(II)-containing species is an ion-association system

of the type $(H_3{}^+O)_2[(H_2O)_2 \cdot CoCl_4]^{2-}$. When some dissociation takes place there can be some replacement of the water by the TBP, to give an ion pair of the type $[(BuO)_3POH]^+{}_2 \cdot [H_2O \cdot TBP \cdot CoCl_4]^{2-}$, which is preferentially extracted into the TBP layer.

The degree of dissociation of an ion pair depends on the dielectric constant of the solvent medium, and hence, since the electrical conductance of hydrochloric acid solutions rapidly decreases with increase in the molarity of the HCl[20], there will be a decrease in the dielectric constant of the aqueous phase. This means that there will be a very little tendency for the cobalt(II) ions to be pulled from the TBP layer, and hence the R_F values will decrease with increase in molarity of the HCl layer.

The role of the cellulose

The cellulose substrate is a relatively polar part of the system and its role must be considered. As we have previously reported[30], some of the TBP will be held in the amorphous regions of the cellulose and it is possible that some or all of these TBP molecules are not available for protonation or for forming complexes with the metal species. The TBP is held to the cellulose by hydrogen bonds formed between the polar hydrogen atoms of the hydroxyl group of the cellulose molecule and the oxygen of the phosphorus ester. This bond must be relatively strong since it is through such bonds that the TBP is held to the so-called inert support. Although there is a possibility that the polar groups of the cellulose could take part in the formation of the complexes, we consider this to be unlikely since the amount of TBP present will probably cover all the available polar sites. It is thus probable that we can regard the cellulose as playing no part in the partition process involving the metal-containing species.

CONCLUSION

In systems such as those investigated here, it is considered that the mechanism of the partition of the solute between the TBP and the HCl, and the mutual solubility by extraction or otherwise of these two latter substances, make it probable that no definable phase interface exists, where there is only one or other of the two substances. However, from the linearity of the relationship between the observed partition coefficients and the term $1/(R_F-1)$ for such systems it is apparent that there exists an equation of the type

$$\alpha^1 = A \left(\frac{1}{R_F} - 1 \right) - B,$$

similar to the MARTIN equation and related equations. However, the volume ratio term (A) cannot be determined experimentally because of the impossibility of exactly defining the phases or their boundaries. Although the total amount of the impregnant is not used in the partition process, there is no chemical distinction between the impregnant so used and that used in the partition process. The deviation of the A term from the experimentally determined ratio of the impregnant and solvent is probably a measure of both the interaction of the two phases and the bonding of the stationary phase to the cellulose support.

It is suggested that the MARTIN equation is essentially the ideal form of the

more general equation and that the smaller is the interaction between the two chromatographically active layers for any system, the nearer will be the experimental equation to the ideal MARTIN equation.

REFERENCES

1 R. CONSDEN, A. H. GORDON AND A. J. P. MARTIN, *Biochem. J.*, 38 (1944) 224.
2 L. S. BARK, G. DUNCAN AND R. J. T. GRAHAM, *Analyst*, 92 (1967) 347.
3 E. CERRAI, *CISE Documentation 103*, 1966, and references contained therein.
4 A. MUSIL, W. HAAS AND G. WEIDMANN, *Mikrochim. Acta*, (1962/3) 883.
5 P. K. MULVANEY, H. D. AGAR, Q. P. PENISTON AND J. L. MCCARTHY, *J. Am. Chem. Soc.*, 73 (1951) 1255.
6 J. W. COPIUS PEEREBOOM, *Rec. Trav. Chim.*, 84 (1965) 659.
7 K. ALCOCK, S. S. GRIMLEY, T. V. HEALEY, J. KENNEDY AND H. A. C. MCKAY, *Trans. Faraday Soc.*, 52 (1956) 39.
8 L. S. BARK, R. J. T. GRAHAM AND D. MCCORMICK, *Talanta*, 12 (1965) 122.
9 I. J. GAL AND A. RUVARAC, *Bull. Inst. Nucl. Sci. "Boris Kidrich" (Belgrade)*, 8 (1958) 67.
10 H. IRVING AND D. N. EDGINGTON, *J. Inorg. Nucl. Chem.*, 15 (1960) 159.
11 T. B. PIERCE, P. F. PECK, *Analyst*, 89 (1964) 662.
12 H. IRVING AND D. N. EDGINGTON, *J. Inorg. Nucl. Chem.*, 10 (1959) 306.
13 D. H. LIEM, D. DRYSSEN, *Acta Chem. Scand.*, 20 (1966) 272.
14 Y. MARCUS AND A. S. KERTES, *Ion Exchange and Solvent Extraction of Metal Complexes*, Wiley–Interscience, London, 1969, pp. 836–848.
15 L. S. BARK, G. DUNCAN AND R. J. T. GRAHAM, *Analyst*, 92 (1967) 31.
16 V. J. J. AARSTEN AND A. E. KORVEZEE, *Trans. Faraday Soc.*, 60 (1964) 510.
17 T. ISHIMORI, K. WATANABE AND E. NAKAMURA, *Bull. Chem. Soc Japan*, 33 (1960) 636.
18 J. C. GIDDING, in E. HEFTMANN (Editor), *Chromatography*, Reinhold, New York, 1961, p. 181.
19 A. WAKSMUNDSKI AND E. SOCZEWINSKI, *Roczniki Chem.*, 32 (1958) 863; *ibid.*, 33 (1959) 1423.
20 E. CERRAI AND G. GHERSINI, *J. Chromatog.*, 13 (1964) 211.
21 D. MCCORMICK, *M. Sc. Thesis*, University of Salford, 1967.
22 C. J. HARDY, *Brit. Rept. AERE*, R.3124 (1959) .
23 Y. MARCUS, *Chem. Rev*, 63 (1963) 139.
24 A. S. KERTES, *J. Inorg. Nucl. Chem.*, 14 (1960) 104.
25 K. NAITO AND T. SUSUKI, *J. Phys. Chem.*, 66 (1962) 983.
26 J. A. APRAKSIN, S. S. KOROVIN, A. M. REZNIK AND A. M. ROZEN, *Zh. Neorgan. Khim.*, 8 (1963) 137.
27 S. KATO AND K. ISHI, *Sci. Papers Inst. Phys. Chem. Res. (Tokyo)*, 36 (1939) 82.
28 E. RABINOWITCH AND W. C. STOCKMEYER, *J. Am. Chem. Soc.*, 64 (1942) 335.
29 *International Critical Tables*, Vol. 6, McGraw-Hill, New York, 1926, p. 241.
30 L. S. BARK, G. DUNCAN AND R. J. T. GRAHAM, *Analyst*, 92 (1967) 31.