



Since ions are now directly involved in the partition of the acid between the two phases, possible differences in electric potential will affect the equilibria. Such potential can be expected to occur generally when electrolytes are added to the solvent system. This can be illustrated for the case where a base BOH is present in the solvent. Then the following equations will hold for the thermodynamic equilibrium:

$$\mu_{0,B^+,s} + RT \ln c_{B^+,s} + FE_s = \mu_{0,B^+,m} + RT \ln c_{B^+,m} + FE_m \quad (1)$$

$$\mu_{0,OH^-,s} + RT \ln c_{OH^-,s} - FE_s = \mu_{0,OH^-,m} + RT \ln c_{OH^-,m} - FE_m \quad (2)$$

Since electroneutrality requires that  $c_{B^+,s} = c_{OH^-,s}$  and  $c_{B^+,m} = c_{OH^-,m}$  when  $c_{H^+} \ll c_{OH^-}$ , the relation for  $E_s - E_m = \Delta E$  will become on subtracting eqn. (2) from eqn. (1):

$$2 F \Delta E = \Delta \mu_{0,OH^-} - \Delta \mu_{0,B^+} \quad (3)$$

where  $\Delta$  represents the difference of the quantity involved between the stationary phase and the mobile phase.

The values of the thermodynamic standard potentials of the base added to the solvent will therefore influence the partition of the acid between the two phases. Consequently, alteration of a buffer or base in a solvent system will influence the  $R_F$  values, even if no change of the pH in the stationary phase has occurred.

In addition, there is the possibility of ion association. This is most likely when the dielectric constant of the solvent is rather low and when the concentration of the complexing ion is large. An effect of the electrolytes added to the solvent system may also be expected.

In the present publication two models are discussed. In the first case, total dissociation of the acids to be separated is assumed to occur in both phases. In the second, ion association is assumed to occur to some extent in the mobile phase, while the acids are almost completely dissociated in the stationary phase.

## THEORY

### Model 1

A theory is developed first for the case in which a polybasic acid  $H_kA$  is completely dissociated in both phases into  $kH^+$  and  $A^{-k}$ . The thermodynamic equilibrium equation describing the partition of the ion  $A^{-k}$  between the two phases is given by eqn. (4), neglecting activity coefficients:

$$\mu_{0,A^{-k},s} - kFE_s + RT \ln c_{A^{-k},s} = \mu_{0,A^{-k},m} - kFE_m + RT \ln c_{A^{-k},m} \quad (4)$$

The  $R_F$  value of the acid is a function of the partition coefficient ( $\alpha$ ) of the acid between the two phases<sup>3</sup>. Since the amounts of the undissociated acid and of the other ions are assumed to be negligible relative to the concentration of the ion  $A^{-k}$ ,  $\alpha$  will by approximation be equal to the partition coefficient of that ion:

$$\alpha_k = \frac{q_m}{q_s} \left( \frac{1}{R_{F,k}} - 1 \right) = \frac{c_{A^{-k},s}}{c_{A^{-k},m}} = e^{(-\Delta \mu_{0,A^{-k}} + kF\Delta E)/RT} \quad (5)$$

The index  $k$  means that an acid with  $k$  acidic groups is considered;  $q_s$  and  $q_m$  are the cross sections of the two phases. The symbol  $\Delta$  is explained in the introduction.

Making use of the  $R_M$  value as defined by BATE-SMITH AND WESTALL<sup>4</sup>, we are able to eliminate the  $e$  powers from eqn. (5):

$$R_{M,k} = \log \left( \frac{I}{R_{F,k}} - I \right) = \log \frac{q_s}{q_m} \alpha_k = \log \frac{q_s}{q_m} - \frac{\Delta\mu_{0,A^{-k}}}{2.3 RT} + \frac{kF\Delta E}{2.3 RT} \quad (6)$$

Assuming that the separated ions do not influence the electric potential significantly, *i.e.* when  $kc_A^{-k} \ll c_{B^+}$  holds in both phases, we can apply eqn. (3) to eliminate  $\Delta E$  from eqn. (6):

$$R_{M,k} = \log \frac{q_s}{q_m} - \frac{\Delta\mu_{0,A^{-k}}}{2.3 RT} + k \frac{\Delta\mu_{0,OH^-} - \Delta\mu_{0,B^+}}{4.6 RT} \quad (7)$$

The term  $\log q_s/q_m$  can be eliminated by using the  $R_M$  value of the undissociated acid:  $R_{M,k,0}$ . The thermodynamic equilibrium equation for the acid is:

$$\mu_{0,H_kA,s} + RT \ln c_{H_kA,s} = \mu_{0,H_kA,m} + RT \ln c_{H_kA,m} \quad (8)$$

From eqn. (8) the equation for the  $R_{M,k,0}$  value can be derived:

$$R_{M,k,0} = \log \frac{q_s c_{H_kA,s}}{q_m c_{H_kA,m}} = \log \frac{q_s}{q_m} - \frac{\Delta\mu_{0,H_kA}}{2.3 RT} \quad (9)$$

The difference of the  $R_M$  value of the ion  $A^{-k}$  (eqn. 7) and the  $R_M$  value of the undissociated acid (eqn. 9) is given by:

$$R_{M,k} - R_{M,k,0} = \frac{\Delta\mu_{0,H_kA} - \Delta\mu_{0,A^{-k}}}{2.3 RT} + k \frac{\Delta\mu_{0,OH^-} - \Delta\mu_{0,B^+}}{4.6 RT} \quad (10)$$

It is evident that the first term of the right-hand side of eqn. (10) is related to the differences in the  $pK$ 's of the acid involved in the two phases. This relation is expressed by the following equation:

$$\frac{\mu_{0,H_kA} - \mu_{0,A^{-k}} - k\mu_{0,H^+}}{2.3 RT} = - \sum_{i=1}^k pK_i \quad (11)$$

Equation (10) can be converted by means of eqn. (11) into:

$$R_{M,k} - R_{M,k,0} = - \sum_{i=1}^k \Delta pK_i + k \frac{2 \Delta\mu_{0,H^+} + \Delta\mu_{0,OH^-} - \Delta\mu_{0,B^+}}{4.6 RT} \quad (12)$$

It follows from eqn. (12) that, when our model holds, differences of  $R_M - R_{M,0}$  for anions of the same valency can only be due to differences of the sums of the  $\Delta pK_i$  values.  $\Delta pK$  for monobasic acids is related to the reciprocal value of the dielectric constant  $D$ . This relation is expressed by:

$$\Delta pK = a \left( \frac{I}{D} \right) \quad (13)$$

The factor  $\alpha$  depends upon the number, the volume and the position of substituents present in the acid involved. Generally  $\alpha$  increases, when steric inhibition of solvation occurs<sup>5</sup>. Acids having no substituents or substituents that are analogous may be expected to have the same value of  $\alpha$  and also the same value of  $R_M - R_{M,0}$ , if the model developed by us holds.

The effect of a change of the base upon the  $R_M$  values is shown by eqn. (14):

$$R_{M,k,I} - R_{M,k,II} = k \frac{\Delta\mu_{0,B^+,II} - \Delta\mu_{0,B^+,I}}{4.6 RT} \quad (14)$$

I and II denote the two different bases.

It follows from eqn. (14) that in our model the difference between the  $R_M$  values is independent of the acid involved, provided acids containing the same number of acidic groups are considered.

### Model 2

Having considered almost complete dissociation of the acids in the mobile phase, possible ion association in that phase must now be considered. When the ion association is very small in the stationary phase, the  $R_M$  value of the acid is represented by:

$$\begin{aligned} R'_{M,k} &= \log \frac{q_s}{q_m} \alpha^k = \log \frac{q_s}{q_m} \frac{c_{A^{-k},s}}{(c_{A^{-k},m} + c_{B_{k-1}A^{-k+1},m} + c_{B_{k-2}A^{-k+2},m} + \dots + c_{B_k A,m})} \\ &= \log \frac{q_s}{q_m} \frac{c_{A^{-k},s}}{c_{A^{-k},m} \left( 1 + \frac{c_{B^+,m}}{K'_{1,m}} + \frac{c_{B^+,m}^2}{K'_{1,m} K'_{2,m}} + \dots + \frac{c_{B^+,m}^k}{K'_{1,m} K'_{2,m} \dots K'_{k,m}} \right)} \end{aligned} \quad (15)$$

The accent is used to distinguish the quantities involved from those concerned in the first model. Activity coefficients are not considered in this case, either.  $K'_i$  is the dissociation constant of the complex  $B_{k-i+1}A^{-i+1}$  ( $i = 1 \dots k$ ). The quotient of the concentrations of the completely dissociated ions in the two phases is equal to  $\alpha_k$  and can be eliminated from eqn. (15) by means of the relation for  $R_{M,k}$  (see eqn. 6). The quotient  $q_s/q_m$  is then also eliminated:

$$R'_{M,k} = R_{M,k} - \log \left( 1 + \frac{c_{B^+,m}}{K'_{1,m}} + \frac{c_{B^+,m}^2}{K'_{1,m} K'_{2,m}} + \dots + \frac{c_{B^+,m}^k}{K'_{1,m} K'_{2,m} \dots K'_{k,m}} \right)^n \quad (16)$$

It is evident that where the dissociation constants of the complexes greatly exceed the concentration of the base cation, the logarithmic term of eqn. (16) approaches zero. On the other hand when the dissociation constants  $K'_{i,m}$  are much smaller than the concentration of the cation  $c_{B^+,m}$ , eqn. (16) approaches:

$$R'_{M,k} = R_{M,k} - \log \frac{c_{B^+,m}^k}{K'_{1,m} K'_{2,m} \dots K'_{k,m}} = R_{M,k} - \sum_{i=1}^k pK'_{i,m} - k \log c_{B^+,m} \quad (17)$$

\* Making use of the mathematical symbol  $\Pi$  indicating multiplication, eqn. (16) becomes:

$$R'_{M,k} = R_{M,k} - \log \left( 1 + \sum_{i=1}^k \prod_{j=1}^i \frac{c_{B^+,m}}{K'_{j,m}} \right)$$

The difference  $R'_{M,k} - R_{M,k,0}$  is given by the following equation obtained by eliminating  $R_{M,k}$  from eqn. (17) by means of eqn. (12):

$$R'_{M,k} - R_{M,k,0} = - \sum_{i \rightarrow k} \Delta pK_i + k \frac{2 \Delta\mu_{0,H^+} + \Delta\mu_{0,OH^-} - \Delta\mu_{0,B^+}}{4.6 RT} - \sum_{i \rightarrow k} pK'_{i,m} - k \log c_{B^+,m} \quad (18)$$

This is the equation for the  $R_M$  value of an acid, which is almost completely associated in the mobile phase and almost completely dissociated in the stationary phase. The  $R_M$  values for incomplete association in the mobile phase lie in the range defined by eqns. (18) and (12).

It follows from eqn. (16) that, contrary to what is expected in the first model, the concentration of the cation of the bases also influences the  $R_M$  value in the second case considered. This concentration will depend upon the dissociation constant of the base in the solvent and upon the concentration of the base.

The effect of replacing the base by another base is expressed by eqn. (19), which is derived from eqn. (16) and (14):

$$R'_{M,k,I} - R'_{M,k,II} = k \frac{\Delta\mu_{0,B^+,II} - \Delta\mu_{0,B^+,I}}{4.6 RT} + \log \frac{\left( 1 + \frac{c_{B^+,m,II}}{K'_{1,m,II}} + \frac{c^2_{B^+,m,II}}{K'_{1,m,II} K'_{2,m,II}} + \cdots + \frac{c^k_{B^+,m,II}}{K'_{1,m,II} K'_{2,m,II} \cdots K'_{k,m,II}} \right)}{\left( 1 + \frac{c_{B^+,m,I}}{K'_{1,m,I}} + \frac{c^2_{B^+,m,I}}{K'_{1,m,I} K'_{2,m,I}} + \cdots + \frac{c^k_{B^+,m,I}}{K'_{1,m,I} K'_{2,m,I} \cdots K'_{k,m,I}} \right)} \quad (19)$$

It is evident from eqn. (19) that proportionality of  $R'_{M,I} - R'_{M,II}$  to  $k$  may not be generally expected. Deviations from such a proportionality, therefore, may indicate complex formation.

#### DISCUSSION

We are aware of the incompleteness of the proposed models. The approximations are rather rough: activity coefficients are neglected, possible effects of the ions separated upon the partition of charges between the two phases are not considered, nor is the influence of the ions upon the dissociation of the base. When the dielectric constant of the solvent is low and the acids have a large  $pK$ , incomplete dissociation of the acids in the mobile phase should also be taken into account. Furthermore, association of the acids or ions may also be possible. On the other hand, consideration of all these possibilities leads to very complex equations.

We have checked one of the most important consequences of the theory developed, namely that the  $R_M$  values should depend upon the base applied to the solvent. The solvent system is composed of *n*-propanol-2 *N* methylamine (70:30) or of *n*-propanol-2 *N* isopropylamine (70:30). These solvent systems are denoted by I and II respectively. The acids used by us are assumed to be almost completely dissociated in these solvents, since the bases applied are rather strong and the dielectric constant of the medium is not very low. Addition of a solution of a "Merck" universal indi-

cator showed that acids with a  $pK_{\text{water}}$  of about 9 are about 50% dissociated in the solvent. Most of the acids used by us for checking the effect of the base have no higher  $pK$  values than about 6. It seems rather improbable that the dissociation of these acids in the moving phase should not be nearly complete. Even acids having a  $pK$  of about 7, such as the second  $pK$  of maleic acid or the third  $pK$  of mellitic acid may be dissociated to a large extent, unless the increase of the  $pK$  values of these acids on changing from water to the propanol-water mixture is much larger than for the acids present in the universal indicator.

On the other hand extensive formation of ion complexes between the cations of the base and the anions is uncertain. The results obtained must therefore always be considered from two points of view, the presence of single ions in the mobile phase and the occurrence of ion complexes in addition to these ions.

The experiments were carried out as follows:

The acids are spotted once on a sheet of Whatman No. 541 paper within a circle of about 30 mm<sup>2</sup> as 0.1 *N* solutions in 2 *N* methylamine or in 2 *N* isopropylamine respectively. The chromatograms are then equilibrated for 90 min at 25° and are developed in the horizontal direction. The solvent level is held 4.5 cm from the start-

TABLE I

MEAN  $R_F$  VALUES,  $R_M$  VALUES AND DIFFERENCES IN  $R_M$  VALUES FOUND WITH THE SOLVENTS PROPANOL-2 *N* METHYLAMINE (70:30) (I) AND PROPANOL-2 *N* ISOPROPYLAMINE (70:30) (II) RESPECTIVELY

The mean  $R_F$  values have been calculated from the mean  $R_M$  values. The chromatograms are made on Whatman No. 541 paper at 25° by the horizontal technique.  $\sigma$  = standard deviation.

Compounds	$R_{F,I}$	$R_{F,II}$	$R_{M,I}$	$\sigma_I$	$R_{M,II}$	$\sigma_{II}$	$R_{M,I}-R_{M,II}$
<i>Neutral compounds</i>							
Glycerol	0.55	0.56	-0.09	0.05	-0.10	0.02	0.01
Sorbitol	0.35	0.36	0.26	0.05	0.25	0.05	0.01
Average				0.05		0.04	0.01
<i>Monobasic acids</i>							
Nitric acid	0.51	0.64	-0.02	0.02	-0.25	0.02	0.23
Hydrochloric acid	0.41	0.54	0.15	0.03	-0.07	0.02	0.22
Perchloric acid	0.63	0.76	-0.23	0.04	-0.50	0.04	0.27
Formic acid	0.45	0.55	0.09	0.05	-0.09	0.04	0.18
Acetic acid	0.47	0.57	0.06	0.05	-0.12	0.05	0.18
Propionic acid	0.57	0.68	-0.12	0.06	-0.33	0.07	0.21
Butyric acid	0.66	0.75	-0.28	0.03	-0.48	0.07	0.20
Palmitic acid	0.86	0.91	-0.79	0.12	-1.01	0.14	0.22
Isobutyric acid	0.64	0.76	-0.25	0.07	-0.50	0.04	0.25
Iodoacetic acid	0.57	0.71	-0.13	0.03	-0.38	0.04	0.25
Chloroacetic acid	0.53	0.65	-0.06	0.03	-0.26	0.01	0.20
Dichloroacetic acid	0.68	0.78	-0.33	0.03	-0.55	0.06	0.22
Trichloroacetic acid	0.78	0.85	-0.54	0.04	-0.76	0.10	0.22
Benzoic acid	0.68	0.76	-0.32	0.02	-0.51	0.06	0.19
Picric acid	0.82	0.89	-0.66	0.08	-0.91	0.07	0.25
Nicotinic acid	0.56	0.67	-0.10	0.04	-0.31	0.05	0.21
Indolyacetic acid	0.60	0.68	-0.17	0.04	-0.32	0.03	0.15
Average				0.05		0.05	0.215 ±0.007

(continued on p. 367)

TABLE I (continued)

Compounds	$R_{F,I}$	$R_{F,II}$	$R_{M,I}$	$\sigma_I$	$R_{M,II}$	$\sigma_{II}$	$R_{M,I} - R_{M,II}$
<i>Dibasic acids</i>							
Sulphuric acid	0.14	0.30	0.78	0.05	0.37	0.01	0.41
Oxalic acid	0.15	0.32	0.75	0.04	0.33	0.01	0.42
Malonic acid	0.17	0.30	0.68	0.05	0.36	0.05	0.32
Succinic acid	0.19	0.34	0.62	0.04	0.28	0.03	0.34
Fumaric acid	0.20	0.34	0.60	0.09	0.29	0.06	0.31
Maleic acid	0.21	0.38	0.58	0.07	0.22	0.03	0.36
Malic acid	0.17	0.32	0.69	0.02	0.33	0.03	0.36
Tartaric acid	0.15	0.29	0.75	0.04	0.38	0.03	0.37
Phthalic acid	0.33	0.51	0.30	0.10	—0.02	0.04	0.32
Glucose-6-phosphoric acid	0.11	0.20	0.92	0.09	0.61	0.07	0.31
Fructose-6-phosphoric acid	0.12	0.19	0.88	0.07	0.63	0.06	0.25
Phenyl phosphoric acid	0.31	0.49	0.35	0.01	0.01	0.02	0.34
Average				0.06		0.04	0.343 ±0.015
<i>Tribasic acids</i>							
Citric acid	0.10	0.27	0.95	0.02	0.44	0.05	0.51
Aconitic acid	0.10	0.26	0.95	0.03	0.45	0.02	0.50
Tricarballic acid	0.11	0.24	0.93	0.05	0.49	0.02	0.44
Trimethylcarballic acid	0.13	0.30	0.83	0.03	0.37	0.02	0.46
Average				0.03		0.03	0.478 ±0.017
<i>Tetrabasic acids</i>							
Pentametetracarboxylic acid	0.04	0.16	1.33	0.03	0.71	0.02	0.62
Ethylenediaminetetraacetic acid	0.10	0.23	0.94	0.03	0.53	0.14	0.41
Fructose-1,6-diphosphoric acid	0.03	0.09	1.49	0.13	1.01	0.11	0.48
Phenolphthalein diphosphoric acid	0.09	0.26	1.00	0.14	0.46	0.06	0.54
Average				0.08		0.08	0.513 ±0.048
<i>Hexabasic acid</i>							
Mellitic acid	0.02	0.22	1.66	0.09	0.54	0.03	1.12

ing line. The duration of development is 7 h; after that time the front is at a distance of about 30 cm from the starting line. The acids were detected according to HOWE<sup>6</sup>. The neutral compounds are oxidized to acids by spraying the chromatograms with a 1% solution of NaIO<sub>3</sub>. All determinations of the  $R_F$  values are repeated 3–7 times. Table I gives the mean  $R_F$  values and the mean  $R_M$  values for the acids, and also the differences  $R_{M,I} - R_{M,II}$ .

It is clearly seen from our results that a significant decrease of the  $R_M$  values occurs on changing the base from methylamine to isopropylamine. This can be explained by the fact that the isopropylamine has a larger "affinity" for the mobile phase than the methylamine. On the other hand the more polar methylamine will have a lower thermodynamic standard potential in the stationary phase than isopropylamine. The difference in electric potential between the two phases  $\Delta E$  will therefore be different for the two solvents. The effect of the change of the bases increases with increasing number of acidic groups as expected from eqns. (14) and (19). This increase is mathematically significant for the differences between monobasic,

dibasic and tribasic acids. The relation of  $R_{M,k,I} - R_{M,k,II}$  and  $k$ , however, is not strictly linear. The results can be expressed by one of the following two relations, in which  $A$ ,  $B$ ,  $C$  and  $D$  are constants:

$$R_{M,k,I} - R_{M,k,II} = A + kB \quad (20)$$

$$R_{M,k,I} - R_{M,k,II} = kC - k^2D \quad (21)$$

This is illustrated in Fig. 1 and Fig. 2 respectively. The point for mellitic acid has been omitted in these figures, since only one observation was made for the hexabasic acids.

Possibly the additional term in eqn. (19) accounting for complex formation in the mobile phase gives rise to the deviations from linearity. The last term of eqn. (19)

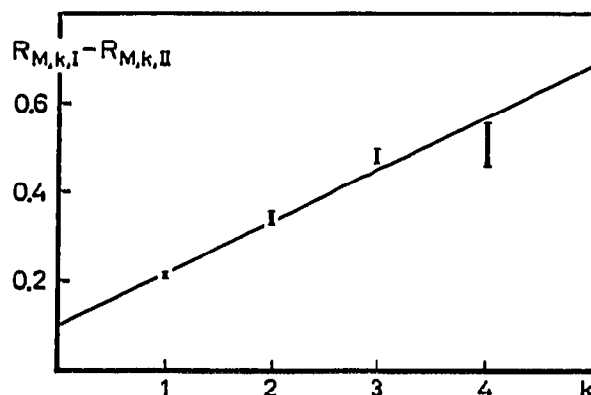


Fig. 1. The effect of changing the base present in the solvent system propanol-2 *N* base (70:30) from methylamine (I) to isopropylamine (II) upon the  $R_M$  values of acids bearing different numbers of acidic groups ( $k$ ). Average data from Table I. The point for mellitic acid has been omitted. The lengths of the vertical stripes indicate the standard deviations of the values concerned.

is not, however, expected to be very great. The concentrations of the cation in the mobile phase will be equal to the concentrations of the ions in the solvent system before contact with the stationary phase, since the papers are equilibrated before chromatography. The amines have approximately the same  $pK$  values, thus the concentration of the methylamine cation will be nearly equal to the concentration of the isopropylamine cation. Furthermore the dissociation constants  $K'_{1,m} \cdots K'_{k,m}$

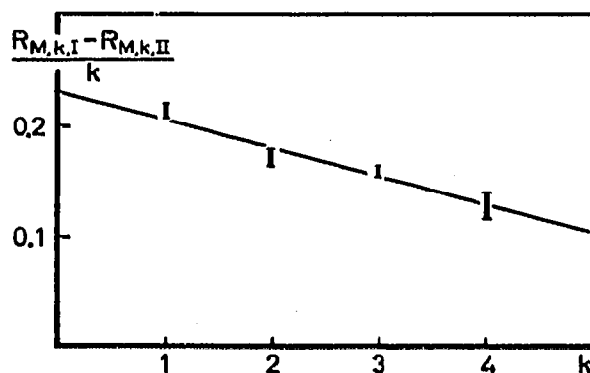


Fig. 2. A plot of  $(R_{M,k,I} - R_{M,k,II})/k$  for the same data as given in Fig. 1.



TABLE II

AVERAGE VALUES OF  $R_M - R_{M,0}$  FOR UNSUBSTITUTED UNBRANCHED ALIPHATIC ACIDS (A) AND FOR AROMATIC ACIDS (B) AS FOUND BY HOWE<sup>6</sup>

Solvent system propanol-2 *N* NH<sub>4</sub>OH (70:30) at 20° on Whatman No. 1 paper by the ascending technique.

$k$	A	$n$	B	$n$
1	0.49 ± 0.005	7	0.69 ± 0.028	6
2	1.06 ± 0.037	9	1.04 ± 0.06	2
3	1.43	1	1.69	1
4			1.90 ± 0.01	2

are not likely to differ very much for the two bases, unless the ionic volume of the cation plays an important role. At any rate it is evident that the main effect expected theoretically, namely a difference in  $R_M$  on changing the base and an increase of this difference with increasing number of acidic groups, is confirmed.

A check of the equations for  $R_{M,k} - R_{M,k,0}$ , eqns. (12) or (18), has not been carried out by us. HOWE<sup>6</sup>, however, recently published a large number of these values for the solvent system propanol-2 *N* NH<sub>4</sub>OH (70:30). He found an increase in  $R_M - R_{M,0}$  with increasing number of acidic groups (*cf.* Table II). This increase is roughly proportional to  $k$ . It should mean, according to our models, that  $\Sigma \Delta pK_i$  or possibly also  $\Sigma pK'_{i,m}$ , is approximately linearly related to  $k$ .

The differences between monobasic acids belonging to different groups may possibly be explained by differences in  $\Delta pK$  values. These differences may be due to the presence of aromatic substituents in the acids of group B, Table II, with consequent increase in  $a$ . Data for  $a$  (eqn. 13), however, are rather scarce, so that we are not able to check this possibility. Differences in  $pK'_m$  may also play a role when ion association occurs to some extent in the mobile phase. Values of  $pK'_m$ , however, are not available.

It may be concluded, that the observations of HOWE, too, are mainly in accordance with the theories developed. A calculation of  $R_{M,k} - R_{M,k,0}$  or  $R_{M,k,1} - R_{M,k,11}$  based upon values of  $\Delta pK$ ,  $pK'_m$  and thermodynamic standard potentials, however, may give definite evidence for or against the validity of the equations derived.

## LIST OF SYMBOLS EMPLOYED

$\alpha$	= partition coefficient between stationary phase and mobile phase
$\mu$	= chemical potential
$c$	= concentration
$K_i$	= $i^{\text{th}}$ dissociation constant of the acid $H_kA$
$K'_i$	= $i^{\text{th}}$ dissociation constant of the ion complex $B_kA$
$k$	= number of acidic groups
$R$	= gas constant
$T$	= absolute temperature
$q$	= cross section
$D$	= dielectric constant
$F$	= Faraday constant
$E$	= electric potential

- $R_F$  = distance of spot from origin divided by distance of solvent front from origin  
 $R_M$  =  $\log (1/R_F - 1)$   
 $R_{M,k,0}$  =  $R_M$  value of the undissociated acid  $H_kA$   
 $R_{M,k}$  =  $R_M$  value of the acid when partial or complete dissociation occurs  
 $R'_{M,k}$  =  $R_M$  value of the acid when ion association occurs

#### Operator signs

- $\Pi$  = product  
 $\Sigma$  = summation  
 $\ln$  = natural logarithm  
 $\log$  = logarithm to base 10  
 $\Delta$  = difference of the quantity involved between stationary phase and mobile phase

#### Indices

- $s$  = stationary phase  
 $m$  = mobile phase

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#### SUMMARY

An extended theory is given for the  $R_M$  values of acids separated by paper chromatography in alkaline solvents. Two models are developed. One model deals with the case in which the acids are almost completely dissociated in both the stationary phase and the mobile phase. The second model is based on the assumption that the ions associate to some extent in the mobile phase with the cations of the base from the solvent. It can be predicted that replacing the base in the solvent system by another base will lead to a change in the  $R_M$  value and correspondingly to a change in the  $R_F$  value in both cases. This effect is also shown experimentally. In addition the influence on this change of the number of acidic groups in the acids is discussed.

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