

TWO TYPES OF R_M -COMPOSITION RELATIONSHIPS IN LIQUID-LIQUID PARTITION CHROMATOGRAPHY

EDWARD SOCZEWIŃSKI AND GRAŻYNA MATYSIK

Department of Inorganic and Analytical Chemistry, Medical Academy, Lublin (Poland)

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In a review article concerning the prediction and control of liquid-liquid partition parameters¹, SOCZEWIŃSKI briefly discussed two types of relationship between partition coefficients and composition of the binary mixed phase. In the case of weak interactions between the solute and solvent molecules in the mixed phase, the log partition coefficient of the solute ($x_k = x_{\text{org}}/x_w$, equilibrium concentrations expressed in mole fractions) should be linearly dependent on the composition of the mixed phase, expressed in terms of mole fractions^{2,3}. On the other hand, when the interactions in the mixed phase are strong enough to cause stable complexes to be formed reversibly (chemical reaction, H-bonding) so that the law of mass action can be applied, then in the idealized case $\log x_k$ should vary linearly with the logarithm of the mole fraction of the active component in the mixed phase. Relationships of this type are often obtained in the case of complex formation with hydrogen ions or other ligands and with solvents of ion exchange properties⁴.

The two opposite types of $\log x_k$ vs. composition relationships will be called, in the considerations which follow, "physical" and "chemical" for the sake of simplicity; the terms are chosen on account of the explanation of the deviations from the laws of ideal solutions by "physical" theories (*e.g.*, VAN LAAR; HILDEBRAND AND SCATCHARD) and "chemical" theories (DOLEZALEK)⁵.

In the chromatographic literature concerning the R_F -composition relationship, there is still some confusion due to the use of various concentration and composition scales. However, investigation of partition-composition relationships is not only of practical importance (optimization of solvent systems for the separation of mixtures and chromatographic structural analysis⁵) but may also provide information concerning the mechanism of the partition and molecular interactions involved. Therefore, in the present paper the relationships between partition parameters and composition are discussed, and compared for various composition and concentration scales. The considerations are illustrated experimentally; for this purpose, we have investigated the effect of solvent composition in systems of the type oleic acid + diluting solvent/buffer solution on the partition of some organic bases. The organic phase belongs to the class of the so-called liquid cationites; it has been shown elsewhere⁶ that such solvents are very effective extractants in relation to organic bases (*e.g.*, alkaloids). A review of the few applications of liquid ion exchangers to the extraction of organic electrolytes has been recently given by HÄUPKE AND WOLF⁷; further references are given by HECKER⁸, who reviews some papers in which solutions of higher fatty acids (Table 29), or amines (Table 35) were employed for the extraction of antibiotics, sugar phosphates, etc.

Before we proceed with the description of our experimental results, it is necessary to discuss how partition-composition relationships depend on the choice of the concentration and composition scale.

THEORETICAL CONSIDERATIONS

Case for $V_1^0 \doteq V_2^0$

When the two liquid phases (mixed phase 1 + 2 and water) are practically immiscible and the concentrations of the solute in the two phases are low, then the rational partition coefficient xk and the usual coefficient k are related by the equation²:

$$\log {}^xk = \log k + \log \bar{V}_{org}^0 - \log V_w^0 \tag{1}$$

where V_w^0 is the molar volume of water and \bar{V}_{org}^0 is the mean molar volume of the mixed organic phase (assuming that practically no dilatation or contraction is observed on mixing):

$$\bar{V}_{org}^0 = x_1V_{01} + x_2V_{02} \tag{2}$$

the indices 1 and 2 denoting the two components of the mixed phase.

On the other hand:

$$\log \frac{R_F}{1 - R_F} = R_M = \log kv = \log {}^xk - \log \bar{V}_{org}^0 + \log V_w^0 + \log v \tag{3}$$

v denoting the ratio of volumes of the organic and aqueous phase in the chromatographic system (constant for a given degree of impregnation).

Let us assume first, for the sake of simplicity, that the molar volumes of the two solvents forming the mixed phase are very similar; in that case:

$$R_M \doteq \log {}^xk + \text{const.} \tag{4}$$

since \bar{V}_{org}^0 is then practically constant; in other words, R_M vs. composition plots are parallel to $\log {}^xk$ vs. composition relationships. In these cases molar fractions are equal to volume fractions ($x_2 = \varphi_2$).

Ideal physical relationships (linear R_M vs. x and $\log {}^xk$ vs. x relationships)

In Fig. 1 a family of linear physical relationships are illustrated, together with

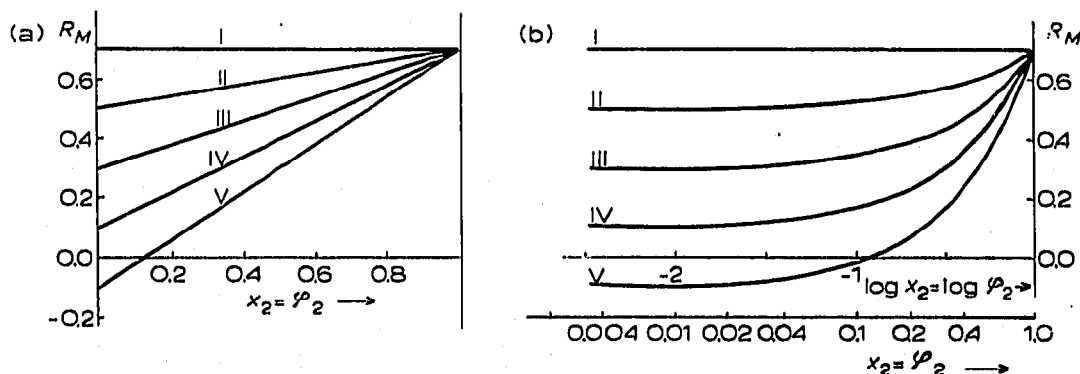


Fig. 1. Ideal "physical" relationships of five solutes (I-V) in (a) R_M vs. x and (b) R_M vs. $\log x$ plots. Equal molar volumes of the component solvents of the mixed phase.

the corresponding relationships on the logarithmic (chemical) scale. As KEMULA AND BUCHOWSKI² have pointed out, such relationships are obtained when the two component solvents form an ideal solution. It can be seen that the use of the "wrong" scale introduces non-linearity even for relationships of the idealized linear type.

For R_F values still more complicated relationships are obtained⁹.

Ideal chemical relationships

Very simple relationships of the chemical type can be obtained when the solute is strongly extracted by the active solvent (2), and hardly extracted at all by the diluting solvent (1), *i.e.* when, for the diluting solvent $x_{k_1} \doteq 0$ and $R_{M_1} = -\infty$ (R_M defined according to REICHL, eqn. 3). In the idealized case (activity coefficients constant over the whole composition range and independent of the concentration of the solute) $\log x_k$, and hence R_M as well, should be linear with respect to $\log x_2$ and $\log \varphi_2$, the index 2 denoting the active solvent in the mixed phase; the active solvent is usually in a large excess by comparison with the concentration of the solute. The slope of the straight line indicates the composition of the extractable complex, *e.g.*, a slope equal to 2.0 indicates that there are two molecules of the active solvent per one solute molecule in the complex (*cf.* ref. 10). Relationships of this type are also obtained when extractable complexes are formed with hydrogen ions, complexing ligands or with liquid ion exchangers.

In Fig. 2 a family of straight lines of various slopes is given for the logarithmic relationship and the corresponding R_M vs. x curves on the physical scale.

However, in the case of partition of lipophilic organic electrolytes it is often found that the unionized molecules of the solute can also be extracted to a marked extent by the "inert" diluting solvent. In these cases, the two mechanisms contribute to a varying extent to the overall partition so that relationships of more complex types are then observed. Examples of such relationships are given in the experimental part.

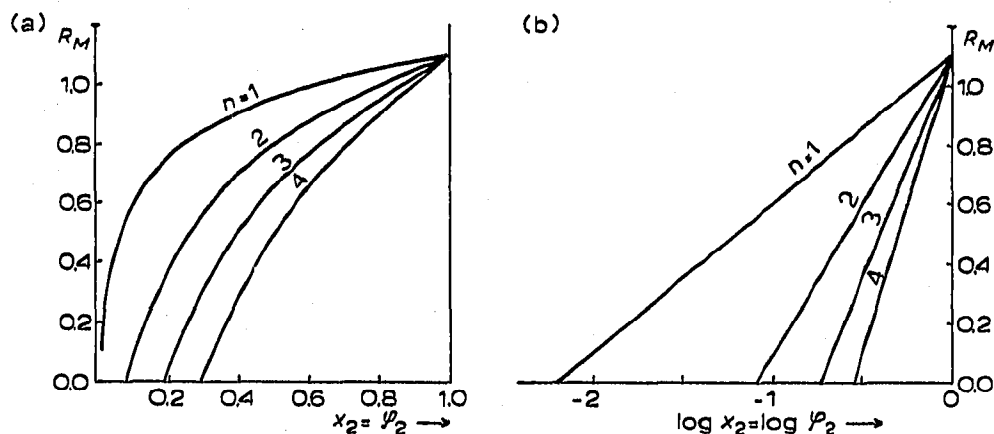


Fig. 2. Ideal "chemical" relationships of four solutes in (a) R_M vs. x and (b) R_M vs. $\log x$ plots. Equal molar volumes of component solvents.

Case for $V_1^0 \neq V_2^0$

In the case when the molar volumes of the component solvents in the mixed phase differ appreciably, the mean molar volume of the mixed phase varies with its composition (eqn. 2); this complicates the R_M -composition relationships (eqn. 3).

Further complication arises from the fact that most chromatographers are, for practical reasons, interested in R_M vs. volume composition relationships, and not R_M vs. molar composition plots.

Therefore, we shall restrict ourselves mostly to R_M vs. φ (or R_M vs. $\log \varphi$) relationships (φ = volume fraction), and will discuss the deviations from the idealized linear relationships (both physical and chemical) caused by the substitution of molar fractions by volume fractions as the abscissa and the use of R_M values instead of $\log x_k$ on the ordinate.

The physical scale (R_M vs. φ)

When the molar volumes of the component solvents 1, 2 do not differ markedly (e.g., by 50%), $\log \bar{V}^0$ is approximately a linear function of x (Fig. 3); this means that the substitution of $\log x_k$ by R_M does not introduce any appreciable deviation from linearity, and may only change the slope of the R_M -composition line. Even for $V_2^0 = 2 V_1^0$ or $V_2^0 = 1/2 V_1^0$ the deviations from linearity due to the substitution of $\log x_k$ by R_M are negligible, amounting maximally to 0.025 R_M units (at $x_2 = 0.5$); only the difference of levels of the limiting points (R_{M1}, R_{M2}) is changed, in comparison to $\log x_{k1}, \log x_{k2}$, by $\log 2 = 0.3$ units (Fig. 4 a, b).

On the other hand, the substitution of molar fractions by volume fractions on the abscissa axis introduces more pronounced deviations from linearity, even for small differences in molar volumes of the component solvents (e.g., for $V_2^0/V_1^0 > 1.2$).

Changes brought about by substitution of $\log x_k$ by R_M and molar composition by volume composition are illustrated in Fig. 4, for the case when $V_2^0 = 2 V_1^0$. The deviation of the R_M vs. φ relationship from linearity is mostly due to the horizontal shifts of the points, caused by alteration of the composition scale (b \rightarrow c). The shifts are smaller at the extremities of the line which causes the new line to deviate (more or

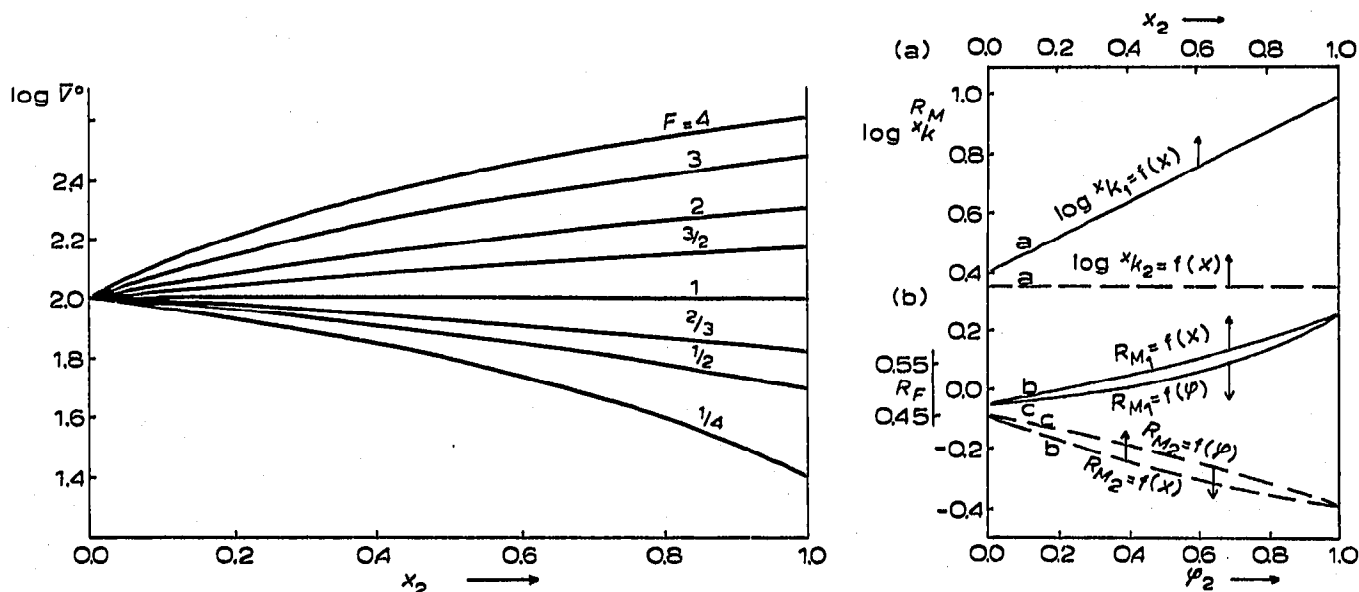


Fig. 3. Variation of $\log \bar{V}^0$ with composition of mixed phase for various ratios of molar volumes of the component solvents forming the mixed phase ($F = V_2^0/V_1^0$).

Fig. 4. Deformations of linear $\log x_k$ vs. x relationships caused by alteration of composition scales. Solid lines: solute 1; dashed lines: solute 2.

less) from linearity. It can be seen that the two contributing deviations sum up when the R_M value is higher for the solvent of higher molar volume (solute 1), and may partly compensate in the opposite case (solute 2). The shift of points on the composition scale depends on the ratio of molar volumes of the component solvents; this is illustrated in Fig. 5, which may be used for the rapid transformation of composition scales¹¹. For $x \rightarrow \varphi$ transformations, $F = V^0_1/V^0_2$; in the opposite case, $F = V^0_2/V^0_1$. The horizontal line passing through a given value of F on the ordinate gives the right positions of the points of the new scale, corresponding to the compositions (t) in the old scale. For example, $t_2 = x_2 = 0.5$, for $F = V^0_1/V^0_2 = 0.5$, corresponds to $\varphi_2 = 0.67$ (point "a" in Fig. 5); and $t_2 = \varphi_2 = 0.5$ for $F = V^0_2/V^0_1 = 2.0$, corresponds to $x_2 = 0.33$ (point "b"). It can be seen that the deformation increases with the difference in molar volumes of the component solvents.

However, as BUCHOWSKI³ has shown, the deformation is often compensated by deviations from ideality of the mixed phase due to differences in shape and size of the component solvents so that even for $V^0_1 \neq V^0_2$ linear R_M vs. φ relationships are often obtained (e.g. ref. 9); this may be considered advantageous from the practical point of view.

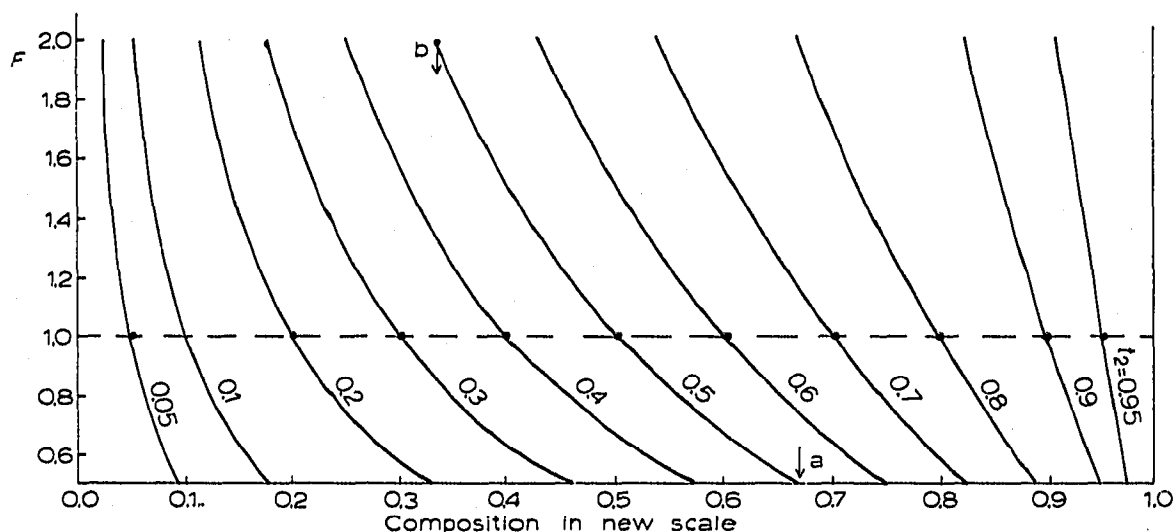


Fig. 5. Deformation of composition scale for increasing values of the molar volume ratio F . The two scales (φ , x) are identical for $F = 1$ (dashed horizontal line).

The chemical scale (R_M vs. $\log \varphi$)

Concerning the substitution of $\log x_k$ by R_M (eqn. 3) it can be shown that $\log V^0$ is practically constant when V^0_1/V^0_2 is in the range 0.8–1.2; the variations do not exceed 0.1 R_M units so that the only result is a vertical, almost parallel shift of the line. In the case of greater differences of the molar volumes of the component solvents, parallel shift is observed only in the range of low concentrations of the active solvent (2, usually of higher molar volume). This is illustrated in Fig. 6 where $\log V^0$ vs. $\log x_2$ lines are plotted for several values of F ; it can be seen that for $F = 2$ (or $F = 1/2$) the relationship is approximately linear up to $x_2 = 0.2$ and in this range substitution of $\log x_k$ by R_M does not introduce any appreciable deformation of the relationship. Even for $F = 4$ the changes do not exceed 0.1 R_M unit for concentrations of x_2 in the range 0.0–0.2, and for $F = 2$ in the range 0.0–0.4. The deformations

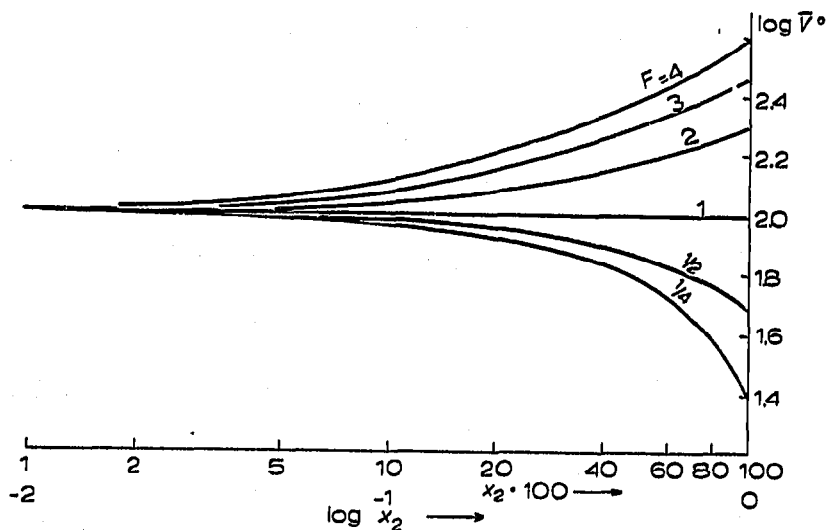


Fig. 6. As Fig. 3, $\log \bar{V}^0$ plotted against $\log x$.

are still less significant if the R_M vs. composition relationship is steep so that variations of R_M in the measurable range ($-1.0, +1.0$) can be observed only in a narrow range of composition.

Deformations of R_M vs. composition relationships caused by the use of $\log \varphi$ scale instead of $\log x$ can be estimated from Fig. 7 where $\log x$ - $\log \varphi$ relationships are plotted for several values of the ratio of molar volumes F . It can be seen that even for $F = 2$ (or $F = 1/2$) the $\log x$ vs. $\log \varphi$ relationship is almost linear (except for high contents of the active solvent 2), which means that the substitution of $\log x$ by $\log \varphi$ only causes a parallel shift of the R_M vs. composition line. Moreover, even for $F = 4$ the relationship is approximately linear up to $\varphi_2 = 0.2$. Thus, it would be expected that the substitution of $\log x_2$ by $\log \varphi_2$ will cause only a parallel shift, without any appreciable deformation, when the molar volumes of the two solvents

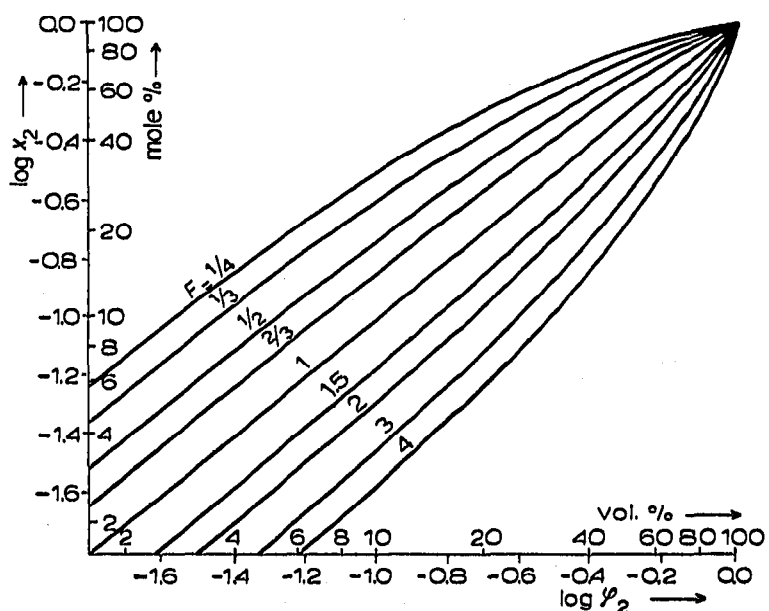


Fig. 7. $\log x$ vs. $\log \varphi$ plots for various values of the molar volume ratio F .

(i.e., active solvent and diluting solvent) are similar, and, in the opposite case, when the content of the active solvent in the mixed phase is not too high.

The above considerations have demonstrated when simple semi-empirical relationships can be expected between R_M values and volume composition of the mixed binary phase. To sum up:

(1) In the case of weak, spherically symmetrical interactions between the molecules of the solute and component solvents, the R_M value is theoretically a linear function of the volume composition ("physical" relationship) when the molar volumes of the component solvents are similar (and often this is true without the last restriction, in view of the counterbalancing of the deviations caused by altered concentration ($xk \rightarrow k, R_M$) and composition scales ($x \rightarrow \varphi$) and the deviations due to non-ideality of the mixed solvent). Then⁹:

$$R_M = \varphi_1 R_{M1} + \varphi_2 R_{M2} \quad (5)$$

(2) In the case of strong, oriented interactions between the solute and one of the component solvents, and no interaction with the other solvent of the mixed phase, it may be expected that R_M is linear with respect to log volume fraction of the active solvent, especially when the molar volumes of the two solvents are similar. If the molar volumes of the active solvent and diluting solvent differ markedly (e.g., oleic acid + decalin), linear relationships can be obtained for composition ranges with a low content of the active solvent (e.g., $\varphi_{act} < 0.20$ for $V_{act}^0/V_{dil}^0 = 4$). This is still more true for cases when R_M depends largely on the content of the active solvent so that R_M varies from -1.0 to $+1.0$ (range of values determinable with sufficient accuracy) within a narrow composition range.

The slopes of $\log xk$ vs. $\log x$ lines and the corresponding R_M vs. $\log \varphi$ lines are similar when the molar volumes of the two solvents (V_1^0, V_2^0) do not differ markedly, or when the mixed phases are dilute solutions of the active solvent (cf. Figs. 6 and 7).

Illustrations of the theses summed up in the first paragraph can be found in several papers of KEMULA AND BUCHOWSKI² and of the first author of this paper (for references, cf. ref. 12). In the present work, some examples of relationships of the "chemical" type are given, including some more complex cases.

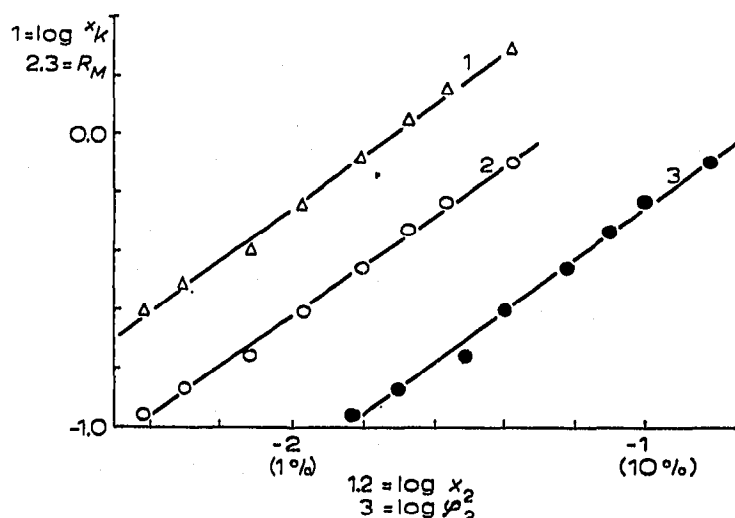


Fig. 8. Effect of composition on $\log xk$ and R_M values of cinchonidine in the system chloroform + oleic acid/pH 2.5: 1 = $\log xk$ vs. $\log x$; 2 = R_M vs. $\log x$; 3 = R_M vs. $\log \varphi$.

EXPERIMENTAL

To obtain a constant and reproducible cross-sectional area ratio, the "moist buffered paper" technique¹² was employed with a humidity coefficient of 1.5 (0.5 ml of buffer solution per 1 g of dry paper). Whatman No. 4 paper was impregnated with McIlvaine's buffer mixtures. The chromatograms were developed by the descending method for a distance of 16 cm (+ 4 cm of solvent-start line distance), in tanks $5 \times 8 \times 22$ cm, at room temperature ($20 \pm 1^\circ$). The spots were detected with Dragendorff's reagent.

Care was taken during experiments to avoid changes in the composition of the mixed solvent, which could be caused by evaporation of the more volatile diluting solvent.

The experimental results illustrating the theoretical considerations are presented in Figs. 8-11.

Fig. 8 illustrates the effect of the composition of the developing solvent on the $\log x/k$ and R_M values of cinchonidine in the system chloroform + oleic acid/pH 2.5, the composition being expressed in terms of mole fractions (the two upper lines) and volume fractions (bottom line). It can be seen that a linear relationship is obtained both for $\log x/k$ vs. $\log x$ and for R_M vs. $\log \varphi$ relationships; this is due to the fact that the partition parameters were determined in a range where the content of the active solvent, oleic acid ($x_2 < 0.1$), is low. The linear relationships are observed because at pH 2.5 the pure diluting solvent, chloroform, extracts cinchonidine to a negligible degree; it was estimated from the extrapolation of the R_M vs. pH line for pure chloroform that under these conditions the extraction coefficient of cinchonidine is of the order 10^{-4} . The slope of the $\log x/k$ vs. $\log x$ line is about 0.9, which in view of the tendency of the oleic acid to dimerize (see below) seems to indicate the formation of a solvation complex in the ratio of 2 molecules of oleic acid per 1 molecule of cinchonidine. The remaining lines (R_M vs. $\log x$ and R_M vs. $\log \varphi$) are almost parallel to the $\log x/k$ vs. $\log x$ line for the reasons discussed above.

In Figs 9a-c the results obtained for a number of alkaloids are illustrated, for systems of the type chloroform + oleic acid/buffer solution, for three systems of coordinates. The pH of the buffer solution was chosen so that the R_M values of individual alkaloids varied within the range of optimal accuracy, *i.e.*, -1.0 to +1.0 (pH 2.5 for brucine, strychnine and cinchonidine, and 4.6 for the remaining alkaloids). In this case also, almost linear $\log x/k$ vs. $\log x$ and corresponding R_M vs. $\log \varphi$ relationships (Fig. 9a and b) were obtained, in view of the narrow range of concentration of oleic acid. Only in the case of brucine and strychnine are distinct positive deviations from linearity observed at low concentrations of oleic acid; these are probably caused by marked extraction of the two alkaloids by pure chloroform at pH 2.5 (see below). The slopes of the R_M vs. $\log \varphi$ lines are often different for the individual alkaloids, which indicates (considering the relationships for constant pH) that the selectivity of the system varies with composition and that it is possible to optimize the system by choosing a suitable composition of the mixed phase. Fig. 9c illustrates that the use of the physical scale (R_M vs. φ) leads to nonlinear and rather complicated relationships (*cf.* Fig. 2).

Fig. 10 illustrates the effect of the diluting solvent on R_M vs. $\log \varphi$ relationships, for brucine (pH 3.8). With the four weakly polar diluting solvents linear relationships

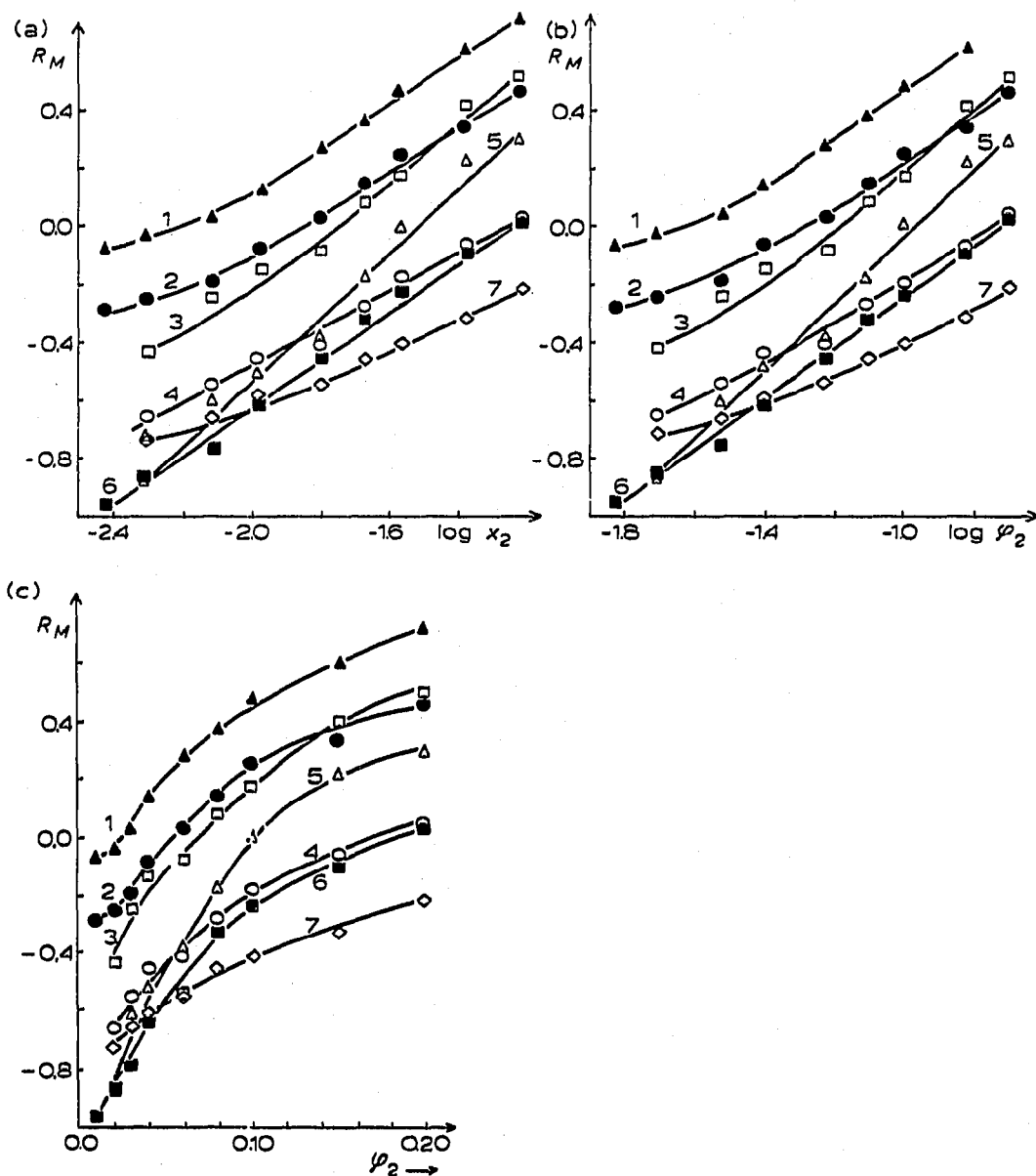


Fig. 9. R_M vs. composition plots of several alkaloids in the system chloroform + oleic acid/buffer solution. R_M is plotted against: (a) $\log x$; (b) $\log \varphi$; (c) φ . The solutes are: 1 = brucine; 2 = strychnine; 3 = atropine; 4 = novocaine; 5 = sparteine; 6 = cinchonidine; 7 = scopolamine.

are observed; only in the case of iso-amyl alcohol is non-linearity observed, due to marked extraction of brucine by the iso-amyl alcohol at the pH used. Fig. 10 indicates which diluting solvent is the most suitable for the extraction of brucine with oleic acid (benzene > trichloroethylene > toluene > xylene). However, the highest extraction power was found for solutions of oleic acid in chloroform; the latter, even in pure form, markedly extracts brucine from aqueous solutions at pH 3.8. The slopes of the R_M vs. $\log \varphi$ lines in many cases are greater than unity, which seems to indicate that in weakly polar solvents, besides the two nitrogen atoms, some oxygen electron donor centres can be partly solvated by oleic acid molecules; it is also possible that more complicated solvation complexes could be formed.

Lastly, in Fig. 11 $\log x^k$ vs. $\log x$ and the corresponding R_M vs. $\log \varphi$ relation-

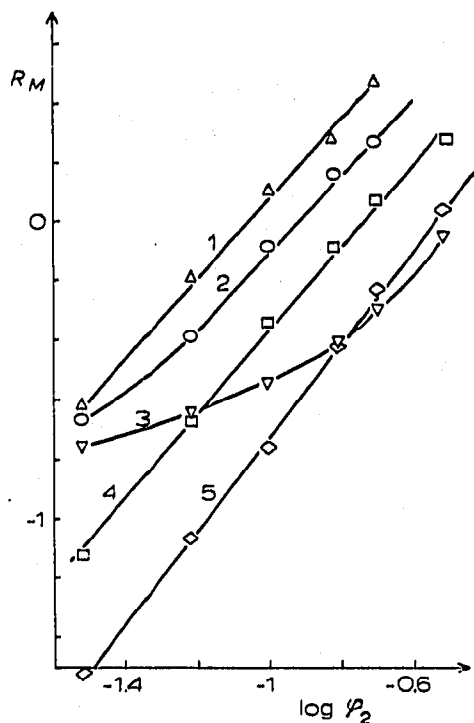


Fig. 10. Effect of diluting solvent on R_M vs. $\log \varphi$ relationships of brucine, in five systems of the type diluting solvent + oleic acid/pH 3.8. 1 = benzene; 2 = trichloroethylene; 3 = iso-amyl alcohol; 4 = toluene; 5 = xylene.

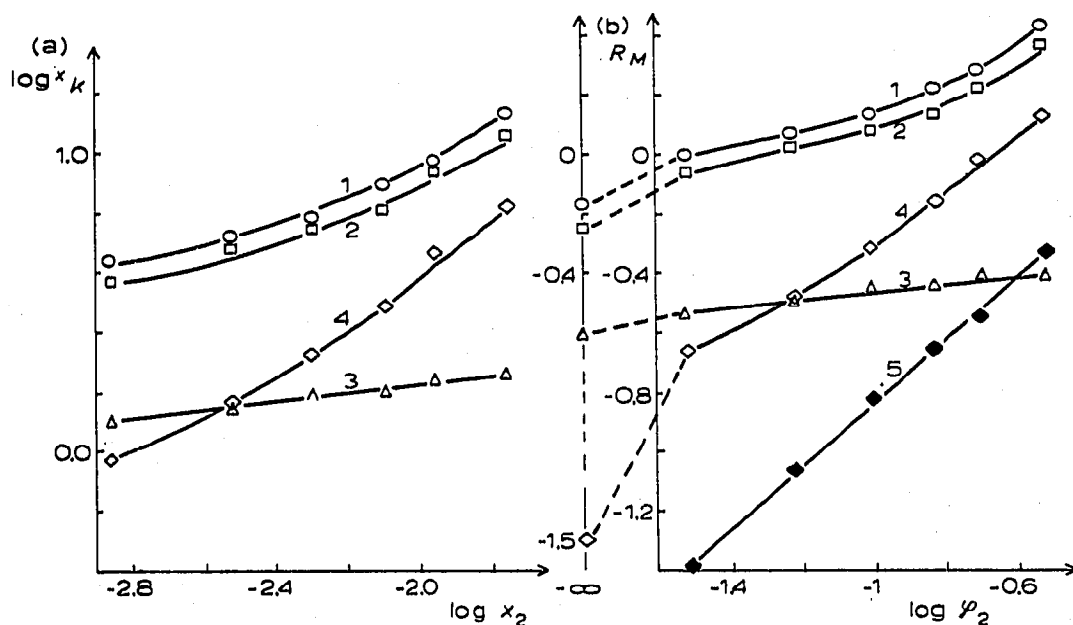


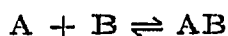
Fig. 11. $\log^x k$ vs. $\log x$ (a) and R_M vs. $\log \varphi$ plots (b) of some heterocyclic bases in the system oleic acid + decalin/buffer solution. The pH of the aqueous phase was chosen to secure the highest accuracy of chromatographic data (pH 3.6 for iso-quinoline (2) and quinaldine (1); pH 2.5 for 8-hydroxy quinoline (3); pH 4.6 and 3.6 for 1,10-phenanthroline (4 and 5, respectively)). On the additional ordinate in Fig. 11 b, R_M values obtained for pure decalin are plotted ($\varphi_2 = 0$, *i.e.* $\log \varphi_2 = -\infty$).

ships of some quinoline bases are presented, for the system decalin + oleic acid/pH 3.6 (except in the case of 1,10-phenanthroline, with pH 4.6). Under these conditions, most of the solutes are extracted to a marked degree by pure decalin (*cf.* the parallel R_M axis in Fig. 11b), so that the simplifications assumed in the theoretical treatment would introduce a significant error; and consequently, the experimental relationships are clearly non-linear.

Therefore, for cases of the last type it is necessary to give a more precise consideration to the effect of the composition of the mixed phase on partition equilibria. The more important simpler cases of complexing equilibria in the organic phase will be considered on the basis of the law of mass action which can be applied here in view of strong H-bonding interactions involved. Considerations of this type have so far been applied mostly to the extraction of metals and partition of organic electrolytes^{1, 13-15}. The index "w" in the discussion which follows denotes the aqueous phase; no index denotes the concentration in the organic phase.

Active solvent (A) not associated (e.g. chloroform)

1:1 complex formed between solute B and solvent A:



$$\text{Solvation constant, } K_{S1} = \frac{x_{AB}}{x_A \cdot x_B}$$

$$\text{Partition coefficient } x_k = \frac{x_B + x_{AB}}{x_{B(w)}} \quad (6)$$

$$= \frac{x_B + K_{S1} \cdot x_A \cdot x_B}{x_{B(w)}} = x_{k_0} (1 + K_{S1} \cdot x_A) \quad (7)$$

where $x_{k_0} = x_B/x_{B(w)}$ — partition coefficient for $x_A = 0$, *i.e.*, in the system pure diluting solvent/water, or partition coefficient of uncomplexed molecules of the solute (in the systems studied, x_{k_0} is a function of pH). It follows from the last equation that:

$$x_k = \frac{1}{r} \frac{R_F}{1 - R_F} \frac{V_{org}^0}{V_w^0}$$

should, for a constant value of the volume ratio, depend linearly on x_A , the slope being equal to $K_{S1} \cdot x_{k_0}$. When $K_{S1} \cdot x_A \gg 1$, then the unity can be neglected and:

$$\log x_k = \log x_{k_0} + \log K_{S1} + \log x_A \quad (8)$$

and as discussed in the introduction, $\log x_k$ (and thus R_M as well, under the conditions given there), depends linearly on $\log x$, the slope being equal to unity.

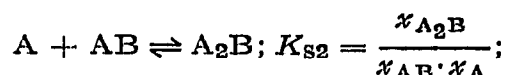
For pure active solvent ($x_A = 1$):

$$\log x_k = \log x_{k_0} + \log K_{S1} \quad (9)$$

(strictly, $\log x_k = \log x_{k_0} + \log (1 + K_{S1})$; *cf.* also BUCHOWSKI¹⁶).

2:1 complex formed

If we assume that there are two active centres in the molecule of the solute, then further complexation can take place:



$$x_2 = K_{S1} \cdot K_{S2} = \frac{x_{A_2B}}{x_B \cdot x_A^2} \quad (10)$$

where K_{S2} is the second (stepwise) formation constant and x is the complexity product.

In this case:

$$x_k = \frac{x_B + x_{AB} + x_{A_2B}}{x_{B(w)}} = \frac{x_B + K_{S1}x_Bx_A + K_{S1}K_{S2}x_Bx_A^2}{x_{B(w)}} \quad (11)$$

$$x_k = x_{k0} (1 + K_{S1}x_A + K_{S1}K_{S2}x_A^2) \quad (12)$$

When:

$$K_{S1}K_{S2}x_A^2 \gg 1 + K_{S1}x_A$$

then:

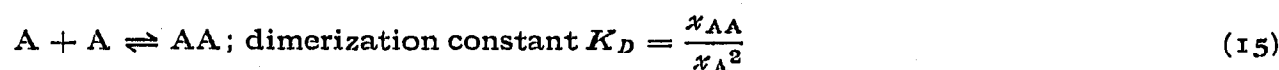
$$x_k \doteq x_{k0} \cdot K_{S1} \cdot K_{S2} x_A^2 = x_{k0} \cdot x_2 \cdot x_A^2 \quad (13)$$

and:

$$\log x_k \doteq \log x_{k0} + \log x_2 + 2 \log x_A \quad (14)$$

Thus, for higher concentrations of the active solvent, when 2:1 complexes are largely formed, $\log x_k$ should be linearly dependent on $\log x_A$, with slope equal to 2; for lower values of x_A the slope gradually decreases to 0 (since $\lim_{x \rightarrow 0} x_k = x_{k0}$). The shape of the curve depends on the ratio of the stepwise formation constants^{1, 13}.

Active solvent dimerized (e.g. carboxylic acids in solvents of class N)



$$\text{concentration of monomers } x_A = \sqrt{\frac{x_{AA}}{K_D}} \quad (16)$$

If the concentration of monomers is small in comparison to dimers, and the diluting solvent is in excess, then it may be assumed that approximately $x_{AA} = 1/2 x'_A$, where x'_A is the apparent (stoichiometric) mole fraction of the active solvent in the mixed phase. Therefore:

$$x_A = \sqrt{\frac{x'_A}{2 K_D}} \quad (17)$$

Complex AB formed

$$x_k = \frac{x_B + x_{AB}}{x_{B(w)}} = \frac{x_B + K_{S1} \cdot x_B \cdot x_A}{x_{B(w)}} \doteq x_{k0} \left(1 + \frac{K_{S1}}{\sqrt{2 K_D}} \cdot \sqrt{x'_A} \right) \quad (18)$$

When the unity in the brackets can be neglected, then:

$$\log x_k = \log x_{k0} + \log \frac{K_{S1}}{\sqrt{2 K_D}} + 1/2 \log x'_A \quad (19)$$

Thus, in certain cases it can be expected that R_M should linearly depend on

$\log x'_A$, the slope being 0.5 (and not unity, as in the case of non-associated active solvent).

Complex A_2B formed

By analogous reasoning it may be demonstrated that in this case:

$$x_k \doteq x_{k0} \left(1 + \frac{K_{S1}}{\sqrt{2} K_D} \sqrt{x'_A} + \frac{K_{S1} \cdot K_{S2}}{2K_D} x'_A \right) \quad (20)$$

When the first two terms in the brackets can be neglected, then:

$$\log x_k = \log x_{k0} + \log \frac{x_2}{2K_D} + \log x'_A \quad (21)$$

so that $\log x_k$ should be linearly dependent on $\log x'_A$, the slope being equal to unity (although a 2:1 complex is formed).

Other cases

Still more complicated relationships are observed when the diluting solvent (*e.g.* chloroform) can also form solvation complexes with the solute or when the active solvent forms multimers (*e.g.* alcohols).

It follows from the theoretical relationships that the gradual increase of the solvation degree with increasing content of the active solvent tends to increase the slope of the $\log x_k$ vs. $\log x$ line. The slopes for the two quinolines and *o*-phenanthroline for higher concentrations of oleic acid are in good agreement with the expected values (*o*-phenanthroline can form A_2B complexes due to the presence of two N atoms in the molecule).

It is remarkable that in the case of 8-hydroxyquinoline the R_M value is almost constant over the composition range studied. Apparently, the ratio $K_{S1}/\sqrt{2} K_D$ is small due to the internal hydrogen bonding in the 8-hydroxyquinoline so that its molecules cannot effectively compete with the strong tendency to dimerization of the oleic acid (at room temperature, the dimerization constants of fatty acids dissolved in non-polar solvents, *e.g.* aliphatic hydrocarbons, are of the order 10^3 – 10^4)¹⁷.

In the case of polyfunctional molecules (*e.g.* many alkaloids), greater slopes of R_M vs. $\log x$ lines are often observed, which seems to indicate the solvation of electron donor centres other than nitrogen atoms (*e.g.* ether oxygens). Since in the case of such substances great differences are often observed between the partition parameters for active and non-active solvents⁵, it is more likely in these cases that linear R_M vs. $\log \varphi$ relationships, such as are illustrated in Figs. 8–10 are obtained. The results can be considered satisfactory in view of the simplifications assumed in the theoretical treatment (neglected activity coefficients, changed composition and concentration scales etc.). The good agreement of experimental data with theoretical considerations seems to indicate that the contribution of ion exchange on the liquid–liquid interface was small, although this possibility cannot be ruled out without separate experiments.

From the viewpoint of theoretical interpretation, the equations derived characterize, quantitatively, the partition equilibria considered; at the same time, the equations illustrate, by means of a few simple parameters, the effect of the molecular structure of the solute, the active solvent and the diluting solvent on the partition

equilibria. Thus, the structure of the solute is reflected by xk_0 , K_{S_1} , and K_{S_2} ; the complex effect of the diluting solvent on the partition is also apparent (through xk_0 , K_{S_1} , K_{S_2} , K_D ; in certain cases, the competitive formation of complexes); etc.

The investigation of such relationships by means of paper chromatography is a relatively simple matter. In this way, information concerning the solvation equilibria in the organic phase can be obtained. Moreover, the effect of solvent composition on the chromatographic behaviour is important in view of the increasing interest in liquid-liquid chromatography (LLC)¹⁸, a technique supplementary to gas-liquid chromatography. In the latter method, the duration of the analysis can be controlled easily by temperature, which can often prove difficult in LLC. Therefore, in LLC the most important method of controlling the retention time is to vary the composition of the system or to control the formation equilibria of extractable species by varying the pH or the concentration of the ligand.

SUMMARY

The effect of the composition of the mixed phase is considered for two idealized extreme cases of solute-solvent interaction. In case of weak interactions, $\log {}^xk$ is frequently approximately linear with respect to the composition of the mixed binary phase expressed in terms of mole fractions (xk , the rational partition coefficient is also defined as the ratio of mole fractions of the solute in the two liquid phases). In the opposite case, $\log {}^xk$ often varies linearly with $\log x$ (x = mole fraction of the active solvent in the mixed phase). Equations taking into account solvation and association equilibria are given. The considerations are illustrated for several solvent systems of the type diluting solvent + oleic acid/buffer solution. Deformations caused by substitution of $\log {}^xk$ by R_M and mole fractions by volume fractions are discussed.

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