R_M values and solvent composition in certain cases of paper partition chromatography

R_M values may be considered from two points of view: (1) the effect of the molecular structure of a substance; (2) the effect of the chromatographic system.

The latter approach may provide valuable practical information when looking for suitable solvent systems for analysis of structure or separation of a group of substances. However, only a few papers have been published giving quantitative relationships between R_M values and the composition of solvent systems (a short review of these papers is given in the preceding paper[1]). In this communication, which is a continuation of earlier papers[1-3], some more complex partition systems are considered. For such systems diagrammatical representation of the relationships involved is still more important than for simpler cases, since with geometrical models it is easier to visualize these relationships. Throughout this communication REICHL's definition of R_M is employed[4]. In all solvent systems the two phases are assumed to be practically immiscible.

1. *The system binary organic liquid/aqueous buffer solution*

Systems of this type (for example toluene + amyl alcohol/buffer solution) have been extensively applied by BÜCHI AND SCHUMACHER (e.g.[5]) for the separation of a number of groups of alkaloids. Combining GOLUMBIC AND ORCHIN's[6] and KEMULA AND BUCHOWSKI's[7] equations, and assuming a constant volume coefficient r, the following relation is obtained:

$$\log Kr = u_1\log k_1r + u_2\log k_2r - \log [1 + 10^{\pm (pH - pK_A)}] \tag{1}$$

(the upper sign in the power refers to acids, the lower sign to bases, $pK_A = pK_w - pK_B$); or:

$$R_M = u_1R^\circ_{M1} + u_2R^\circ_{M2} - \log [1 + 10^{pH - pK_A}] \text{ (acids)} \tag{2a}$$

$$R_M = u_1R^\circ_{M1} + u_2R^\circ_{M2} - \log [1 + 10^{- (pH - pK_A)}] \text{ (bases)} \tag{2b}$$

where k is the partition coefficient of unionized electrolyte and indices 1 and 2 refer to the two components of the binary organic phase; R°_{M1} and R°_{M2} denote R_M values of unionized electrolyte.

A space model representing eqn. (2) in the form of a curved surface is given in Fig. 1a. The vertical sides of this model represent simpler systems discussed in earlier papers[1-3]. Below (Fig. 1b) a "map" is shown obtained by projecting horizontal sections of the surface illustrated in Fig. 1a on the base of the model. Each iso-line of the map corresponds to compositions of the binary organic phase and corresponding pH values of the aqueous phase resulting in a constant value of R_M.
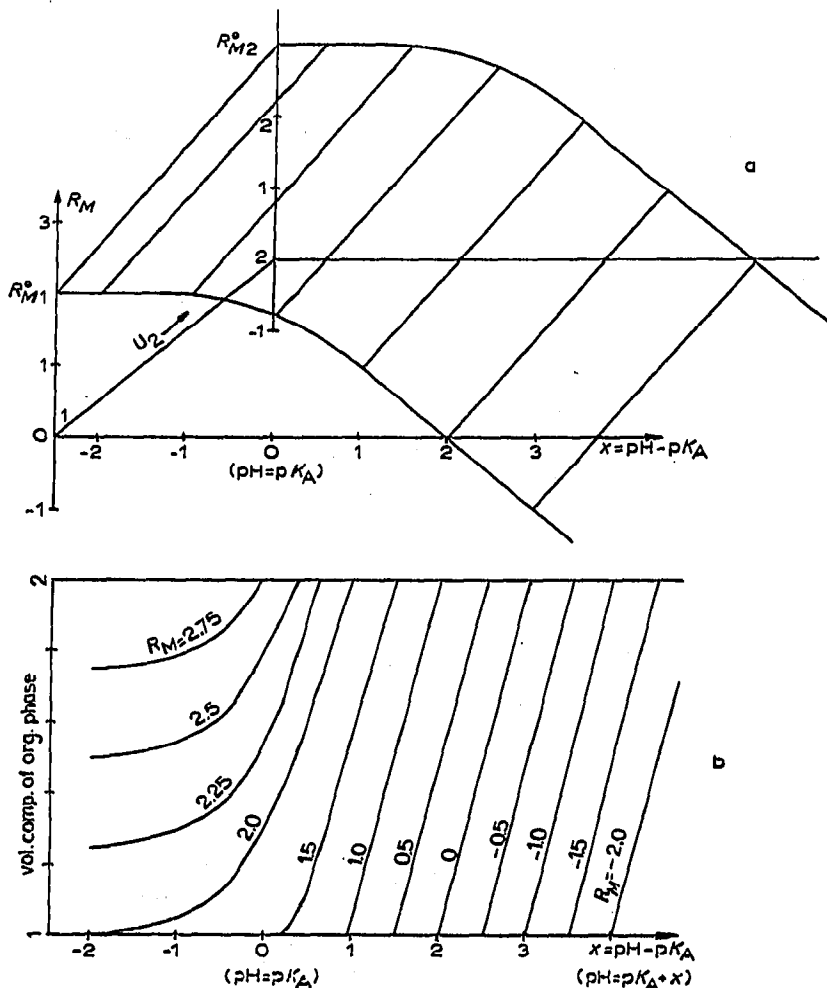
Fig. 1. Diagrams of R_M vs. volume composition for a partition system of the type: binary organic phase/aqueous buffer phase. (a) Space model. (b) Planar diagram.

Bases will be represented by a mirror image of Fig. 1a, the plane of symmetry being parallel to R_M — 1 — 2 and passing through pK_A.

2. The system ternary liquid/pure liquid

When one of the phases consists of three liquids that are completely miscible with each other, but immiscible with the other phase at practically any composition (for example, the system hexane + benzene + chloroform/water), then, generalizing the considerations of KEMULA AND BUCHOWSKI[7] (cf.[8]), and assuming a constant volume coefficient r, we can write:

$$\log Kr = u_1 \log K_1 r + u_2 \log K_2 r + u_3 \log K_3 r \qquad (3)$$

or

$$R_M = u_1 R_{M1} + u_2 R_{M2} + u_3 R_{M3} \qquad (4)$$

(the symbols are analogous to those used in refs.[1,3]).

Equation (4) can be represented by a space model (Fig. 2a). The base of the prism, an equilateral triangle (Gibbs' triangle), represents the compositions of the ternary

phase; the R_M values for the respective compositions are recorded vertically above the triangle. Thus the vertical sides of the prism represent three simpler systems (binary solvent/pure solvent), which were discussed in the preceding papers[1,3].

For systems obeying eqn. (4), as can easily be demonstrated, the R_M vs. volume composition relationship will be represented by a plane passing through the three limiting R_M values (R_{M1} — for the system: pure component 1 of the ternary phase/ other phase, etc.).
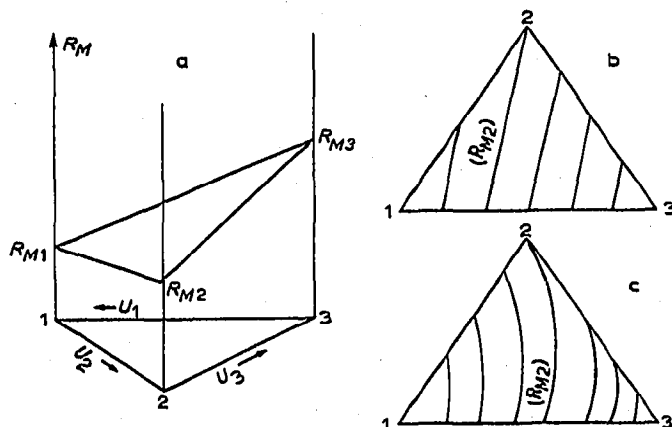

Fig. 2. Diagrams of R_M vs. volume composition for the system: ternary liquid/pure liquid (a) Space model. (b) and (c) "Maps".

By projecting horizontal sections of this plane onto the base of the prism a "map" is obtained, which represents the R_M vs. volume composition relationship on a planar diagram. In the ideal case the iso-lines (connecting compositions of the ternary phase resulting in constant R_M values) will be straight, parallel lines (Fig. 2b). When negative deviations from additivity occur in the whole range of compositions, the iso-lines will be concave with respect to R_{M1} (Fig. 2c), etc.

3. The system binary non-polar phase/binary polar phase

For systems of this type (e.g. hexane + butyl ether/dimethylsulphoxide + water) the following relation can be derived:

$$R_M = u_1 (u_I R_{M1\,I} + u_{II} R_{M1\,II}) + u_2 (u_I R_{M2\,I} + u_{II} R_{M2\,II}) \qquad (5)$$

where arabic numerals denote the two components of the non-polar phase, and Roman numerals those of the polar phase (e.g. u_1 denotes volume fraction of component 1 in the non-polar phase; $R_{M1\,I}$ is the R_M of the substance in the system pure solvent 1/pure solvent I; etc.).

Equation (5) can be represented by a space model with a square base and sides representing the volume compositions of the two phases, as illustrated in Fig. 3a. Each point within the square corresponds to definite compositions of the non-polar and the polar phases; these compositions are found by projecting the point on to the respective sides of the square.

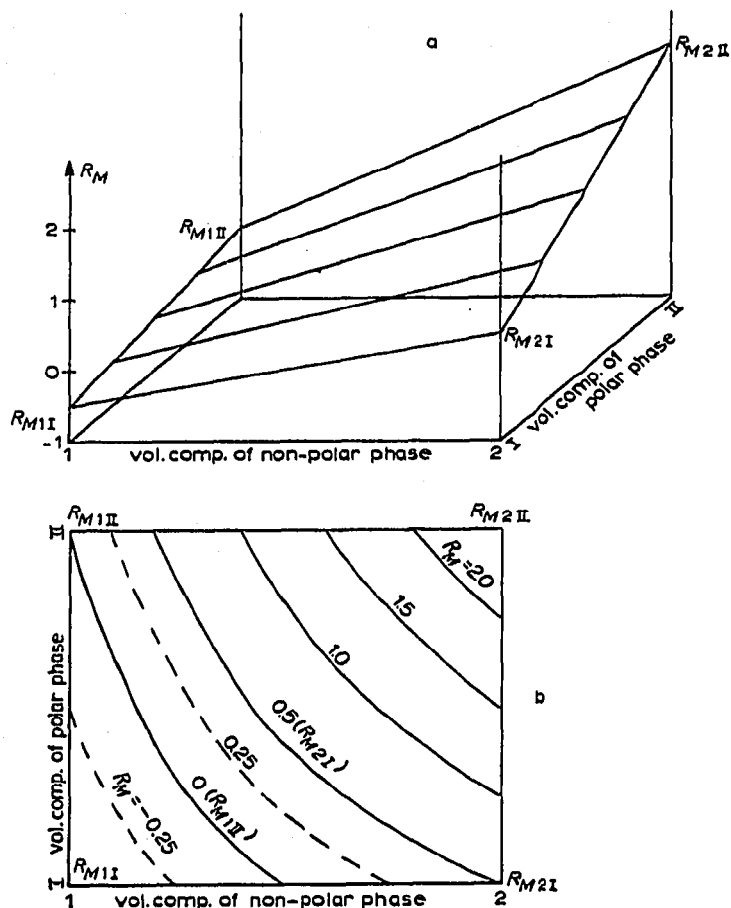Fig. 3b shows a map obtained from Fig. 3a as described above for systems 1 and 2.

Fig. 3. Diagrams of R_M vs. composition for a system: binary non-polar phase/binary polar phase. (a) Space model. (b) "Map".

Substituting $r = 1$ we have: $R_M = \log K$, that is to say, equations (2), (4) and (5) and diagrams 1–3 also apply to partition equilibria in the systems considered, in terms of the partition coefficient K.

If it is desired to express the relationships derived in terms of the more familiar R_F values, it need only be remembered that the R_M values equal to: —2, —1, 0, 1, 2, correspond to the R_F values equal to 0.01, 0.09, 0.50, 0.91 and 0.99, respectively. For more detailed information an R_M vs. R_F diagram can be used.

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