

Some comparative values of detector current are given in Table I, the last figure of which obtained by BOURKE *et al.*⁶, probably represents the best obtainable by chemical means.

TABLE I
COMPARATIVE VALUES OF DETECTOR CURRENT

Instrument No.	Carrier gas purifier	Radiation source (mC)		Detector	
		³ H	⁹⁰ Sr	Volts	Amps
1	chemical	100		500	1.1 · 10 ⁻⁸
1	diffusion	100		500	4.2 · 10 ⁻⁹
2 ²	chemical	100		750	1 · 10 ⁻⁸
			10	—	1 · 10 ⁻⁸
3 ⁶	chemical		10	1,000	1.8 · 10 ⁻⁹

Several cylinders of helium have now been processed by this method without difficulty. Rapid venting of the high pressure gas in the diffuser when changing the supply appears to be sufficient to prevent excessive accumulation of impurities and there has been no indication that the life of the system will be limited in any way.

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1 J. E. LOVELOCK, *Res. Develop.*, 2 (1962) 36.

2 R. BERRY, in M. VAN SWAAY (Editor), *Gas Chromatography 1962*, Butterworths, London, 1962, p. 231.

3 P. J. BOURKE, M. D. GRAY AND W. H. DENTON, *J. Chromatog.*, 19 (1965) 189.

4 K. B. MCAFEE, *J. Chem. Phys.*, 28 (1958) 218 and 226.

5 N. MELNYK AND H. W. HABGOOD, *Can. Mining Met. Bull.*, (1961) 768.

6 P. J. BOURKE, R. W. DAWSON AND W. H. DENTON, *J. Chromatog.*, 14 (1964) 387.

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R_M values in simplified four-component systems of the type: ternary mixed solvent/pure solvent

Multi-component solvents, which are more versatile for the choice of optimal conditions of separation, are often used in paper and thin-layer chromatography. It is easier to analyse the effect of phase composition on the partition chromatographic behaviour of solutes when the two liquid phases are essentially immiscible, that is, when the stationary phase held by the supporting material is insoluble in the developing solvent (*e.g.*, the system carbon tetrachloride-benzene-chloroform/formamide¹). Nevertheless, even in these cases, the R_F -composition relationships for four-

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component solvent systems have to be represented by space models, or by employing the method of iso-lines². However, the relationships can be simplified if certain rules are applied when choosing the composition of the system; thus, as shown in an earlier work³, quaternary systems of the type binary phase/binary phase (2/2) give simple relationships of the type binary phase/pure solvent (2/1) or *vice versa* (1/2) when the composition of one of the phases is fixed. Similar simple relationships are obtained in systems of the type binary solvent/aqueous buffer solution (2/pH) when the pH of the water phase is kept constant⁴. In the present work the choice of composition of the mixed ternary phase is considered, permitting the simplification of the R_M -composition relationships in systems of the type 3/1 or 1/3 (ternary mixed phase/pure solvent, or *vice versa*); the experimental data are, at the same time, a test of the thesis that (in an idealized case) the R_M value of a solute is additive with respect to the composition of the mixed phase²:

$$R_M = u_1 R_{M1} + u_2 R_{M2} + u_3 R_{M3} \quad (1)$$

In a strictly thermodynamic approach, both the composition (u) of the mixed phase and the concentrations determining the partition ratios K and R_M values should be expressed in mole fractions (*cf.* BUCHOWSKI⁵ for partition coefficients). If, however, the molar volumes of the component solvents do not differ to a greater extent, then the conventional R_M values may be used (in which the concentrations in the extraction coefficient are expressed in the mol/l scale) and the composition of the mixed phase expressed in volume fractions, which is advantageous for practical purposes. Moreover, the use of volume compositions and conventional extraction coefficients may in certain cases compensate for deviations from ideal behaviour of the mixed phase; thus, equations like (1) (u -volume fraction) are useful approximate semi-empirical relationships.

It follows from eqn. (1) that when the composition of the ternary phase is represented on a Gibbs' diagram and the R_M values are plotted above the triangle, then the R_M -composition relationship is given by a plane surface passing through the three points corresponding to R_M values for the three pure component solvents². Therefore, a straight line lying in this plane surface, projected horizontally on to the side walls of the prism, will also be represented by straight lines which are simple plots of an R_M -composition relationship of the type binary solvent/pure solvent. This allows one to choose series of ternary mixtures resulting in simplified R_M -composition plots.

Experimental

(a) A constant proportion of components 1 and 2 is employed, the content of component 3 being varied (Fig. 1a). The mixtures are prepared simply by mixing a standard mixture of 1 and 2 with various proportions of 3. In this case the R_M value should be linearly dependent on the percentage of component 3 in the mixed phase.

(b) A constant percentage of one of the component solvents is maintained (Fig. 1b), while the content of the remaining solvents is varied. In the case illustrated in Fig. 1b, the R_M value should be linearly dependent on the percentage of component 3 (or 1). *Cf.*, for instance, WALDI⁶.

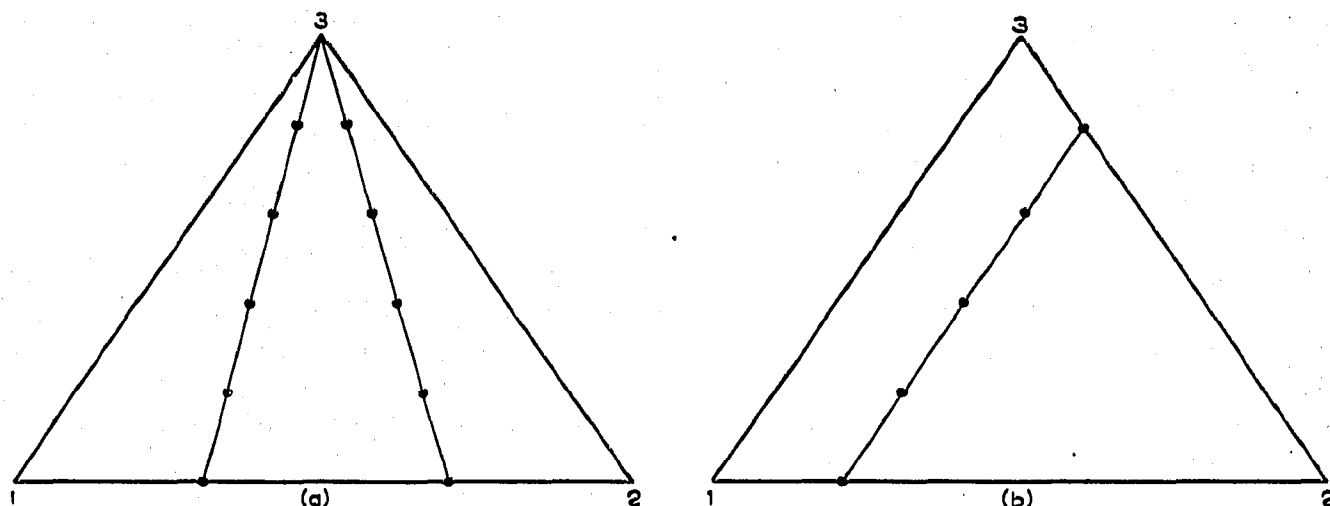


Fig. 1. Linear series of compositions in ternary mixtures. a = constant proportions of components 1 and 2; b = constant content of component 2.

In order to test this hypothesis, R_F and R_M values were determined for a few quinoline bases in solvent systems of the type cyclohexane (1)–carbon tetrachloride (2)–trichloroethylene (3)/aqueous buffer solution. The solvent system was chosen merely as an example in which three component solvents of the mobile phase are practically immiscible with the other phase. The pH of the water phase (3.0) was chosen so that the R_M values of each solute were in the range of optimal accuracy (R_F 0.1–0.7) for any composition of the mixed phase. The “moist buffered paper” technique, described in earlier papers (*cf.*, ref. 4) was employed. The experiments were carried out at $20.0 \pm 0.5^\circ$.

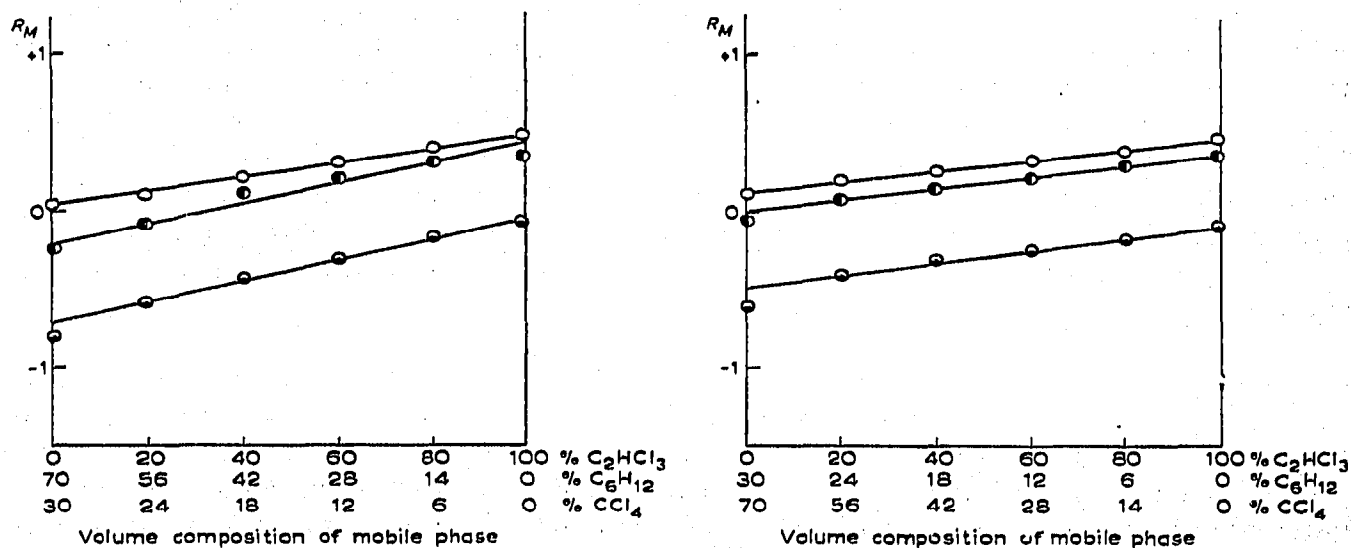


Fig. 2. Simplified R_M vs. volume composition of mobile phase relationship. Choice of compositions of the ternary phase: *cf.* Fig. 1a. ● = quinoline; ◐ = iso-quinoline; ○ = 8-hydroxyquinoline. C₆H₁₂:CCl₄ = 7:3.

Fig. 3. Simplified R_M vs. volume composition of mobile phase relationship. Data as in Fig. 2. C₆H₁₂:CCl₄ = 3:7.

Results

The experimental results are represented in Figs. 2 and 3 (case (a), constant proportion of cyclohexane and carbon tetrachloride, cf. Fig. 1a) and Fig. 4 (case (b), constant content of carbon tetrachloride, cf. Fig. 1b). The compositions of the mobile phase are given under the abscissa axes. R_M is defined here according to REICHL:

$$R_M = \log \frac{R_F}{1 - R_F}$$

It can be seen that, in accordance with theoretical anticipations, the R_M values vary linearly with the concentration of trichloroethylene in the mixed phase. Only the extreme points tend to lie below the straight lines. Thus, in spite of a number of

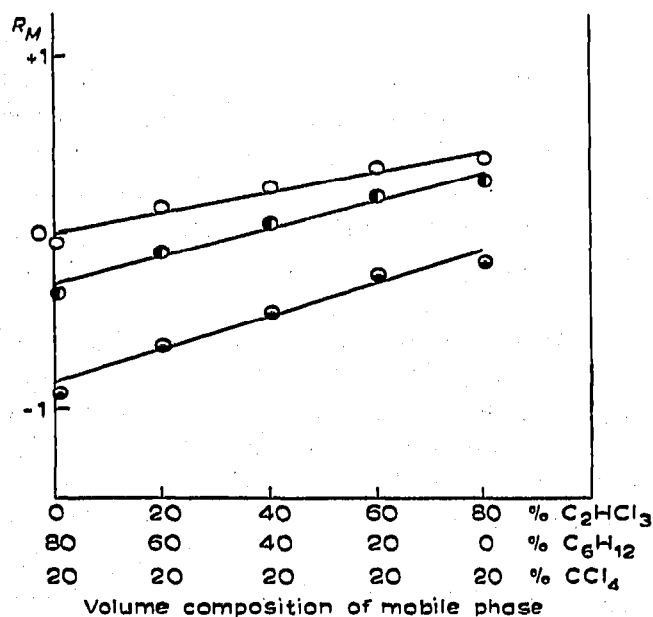


Fig. 4. Simplified R_M vs. volume composition of mobile phase relationship. Choice of composition of the ternary phase: cf. Fig. 1b. $u_{CCl_4} = 0.20$.

simplifications assumed in the theoretical treatment, the experimental results confirm both the additivity of R_M values with respect to the composition of the mixed phase, and the possibility of choosing series of mixed phases which result in simplified relationships, analogous to simple systems of the type: binary phase/pure solvent.

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1 M. PÖHM AND L. FUCHS, *Naturwiss.*, 41 (1954) 63.

2 E. SOCZEWIŃSKI, *J. Chromatog.*, 8 (1962) 119; *Chem. Anal. (Warsaw)*, 8 (1963) 337.

3 E. SOCZEWIŃSKI, *J. Chromatog.*, 11 (1963) 275.

4 E. SOCZEWIŃSKI AND W. MACIEJEWICZ, *J. Chromatog.*, 17 (1965) 333.

5 H. BUCHOWSKI, *Bull. Acad. Polon. Sci., Ser. Chim.*, 10 (1962) 195; *The Effect of the Properties of Solvents on Partition Coefficients of Nonelectrolytes between Water and Organic Solvents* (in Polish), Dissertation Univ. Varsoviensis (Poland) No. 4, PWN, Warsaw, 1963.

6 D. WALDI, in *Some General Problems of Paper Chromatography, Liblice Symposium 1961, 1st*, CSAV, Prague, 1962, p. 139.

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