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Solubility and Partition Chromatographic Parameters in Systems of the Type Binary Solvent–Pure Solvent

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Summary

In accordance with theoretical anticipations, parallelity was found between R_M vs. composition and log c_s vs. composition lines for two naphtols chromatographed in three series of partition chromatographic systems (c_s = solubility).

The results indicate that in certain cases the solubility of substances may be approximately estimated from chromatographic data, especially when a partition mechanism is obtained, e.g., by impregnating the paper with a nonvolatile liquid and developing with a solvent practically immiscible with the fixed phase.

In the theoretical treatment of chromatographic processes it has been attempted to relate the chromatographic parameters with various physicochemical properties of the solutes and solvents, such as the dielectric constants, dipole moments, solubility parameters, etc. A long time ago it was observed (*1*) that there exists a clear relation between the R_F value of the solute and its solubility; by changing the solubility of the chromatographed solutes in one of the phases it is possible to control the R_F values and to choose optimal separation conditions, i.e., to improve the selectivity and to secure a suitable distribution of the spots along the chromatogram. As an example, the use of cyclohexane-chloroform mixtures of varying composition for the development of formamide-impregnated papers may be cited; also the use of paper strips impregnated with buffer solutions is based on the increased solubility of lipophilic organic electrolytes in the aqueous phase due to their controlled ionization.

The relation between the chromatographic behavior of solutes and their solubilities has been discussed so far in a qualitative manner; in this note we shall consider whether a quantitative approach is possible and if any quantitative parallelity of the two phenomena can be demonstrated. In the considerations we shall assume an idealized partition model of the chromatographic process; we shall also assume that one of the phases is a mixture of two solvents miscible with each other but immiscible, at any proportion, with the second liquid phase.

The first problem is the choice of the chromatographic parameter and concentration units. As a starting point, it should be pointed out that in the ideal case there exists a close analogy between the partition of a solute in such a system and its solubility (x_s) in the mixed phase. Moreover, the parallelity extends also on the vapor pressure and partition chromatographic behavior. In all four cases linear relationships are obtained against mole-fraction composition of the mixed solvent for log ^{x}k (*2,3*), log x_s (*4*), $^{x}R_M$, and p, respectively [in the first three cases the concentrations are expressed in mole fractions (x)]. The analogies between the property-composition relationships are also often maintained when the mixture of solvents is not ideal; thus, according to Disselkamp's rule (*5,6*), the solubility curve of a third component resembles generally the vapor-pressure curve of the mixed binary solvent. For parallelity of partition and solubility in mixed solvents forming a regular solution, see (*2,3,5,* and *7*).

For practical reasons, it would be more convenient to employ the usual R_M values [$R_M = \log [R_F/(1 - R_F)] = \log Kr$, concentrations expressed in moles per volume] and the composition of the mixed solvent in volume fractions. These changed concentration scales may contribute to deviations from linear relationships; however, in many cases these deviations may compensate for the nonideality of the solvent mixture, so that the equations

$$\begin{aligned} \log k &= \varphi_1 \log k_1 + \varphi_2 \log k_2 \\ R_M &= \varphi_1 R_{M1} + \varphi_2 R_{M2} \end{aligned} \tag{1}$$

(φ is the volume fraction) are useful semiempirical relationships (*3,8*).

The simplest relationship between the chromatographic parameter and solubility in the convenient concentration scales is obtained when it is assumed that the partition coefficient of a solute is equal to the ratio of its solubilities in the two phases; then

$$K = \frac{c_s^{\mathrm{org}}}{c_s^w} \qquad \log K = \log c_s^{\mathrm{org}} - \log c_s^w$$

On the other hand,

$$R_M = \log Kr = \log K + p$$

(p is a "paper constant"). If the composition of one of the phases is fixed so that the solubility of the solute in that phase is constant, then

$$R_M = \log c_s^{\mathrm{org}} + \text{constant}$$

or

$$R_M = -\log c_s^w + \text{constant}' \qquad (2)$$

Thus there should be a parallel between the variation of R_M value and the solubility of the solute in the mixed phase of varying composition. The use of different concentration scales (e.g., x_s and the usual R_M value) may cause the two relationships to be not directly comparable, especially in the case of large differences of molar volumes of the solutes and solvents.

The assumption on which these simple considerations are based is, of course, a far-reaching approximation (9). Nevertheless, it may be expected that the last equations will be approximately valid because of the elimination of effects which cause deviations from Eq. (2). One of these effects is the mutual solubility of the two phases, which entails the possibility of solvation of the solute; thus, in the case of the system organic solvent–water the solute molecules in the organic phase may be hydrated, which is confirmed by the difference of solubilities in "dry" and "wet" solvents. In the case of R_M-composition relationships in systems of the type mentioned, this effect will probably play a less important role, since in all cases the organic phase is saturated with water and the solute molecules are present in hydrated form; probably better parallelity would be obtained for solubilities determined for the corresponding series of "wet" mixed solvents. The second important effect that may cause discrepancies between solubilities and R_M values is due to the difference of concentrations in the case of saturated solutions and in chromatographic partition; it may be expected that this effect will be more important when the solute is well soluble.

As examples of parallelity between R_M values and solubilities, the case of buffered paper chromatography of lipophilic electrolytes may be referred to; thus Rybař et al. (*10*) have found in such a case that the R_M value varies linearly with the pH of the aqueous solution, the slope of the line being ca. 1.0 [for further examples see (*11–13*)]. On the other hand, it is known that the solubility of such solutes also varies in a similar manner with the pH of the aqueous solution (*14*).

To investigate the R_M-solubility relations for the case of mixed nonpolar phases we have chosen three systems of the type binary mobile phase-formamide, using 1-naphtol and 2-naphtol as the chromatographed solutes.

EXPERIMENTAL

Whatman No. 4 paper strips were impregnated by passing them through a 20% v/v solution of formamide in acetone and blotting the excess liquid between two sheets of filter paper. The chroma-

TABLE 1

			% v/v CCl_4 in the mixed phase									
		Solute	0	20	30	40	50	60	70	80	90	100
$C_6H_6 + CCl_4/FA$	R_F	1-naphtol	0.77	0.685		0.64		0.61	0.545	0.53	0.44	0.33
		2-naphtol	0.71	0.63		0.58		0.52	0.45	0.41	0.33	0.25
	c_s, moles/liter	1-naphtol	0.690	0.59				0.393		0.228	0.180	0.1350
		2-naphtol	0.1666	0.178		0.1531		0.1225	0.0872	0.0654		0.0526
$C_2HCl_3 + CCl_4/FA$	R_F	1-naphtol	0.55		0.495		0.47		0.425		0.38	0.33
		2-naphtol	0.48		0.395		0.38		0.33		0.30	0.25
	c_s, moles/liter	1-naphtol	0.336		0.2327		0.2200		0.1626			0.1350
		2-naphtol	0.0848		0.0798		0.0720		0.0611			0.0526
$C_2Cl_4 + CCl_4/FA$	R_F	1-naphtol	0.36		0.38		0.37			0.33		0.33
		2-naphtol	0.26		0.27		0.28			0.235		0.25
	c_s, moles/liter	1-naphtol			0.155					0.1434		0.1350
		2-naphtol			0.0574					0.0586		0.0526

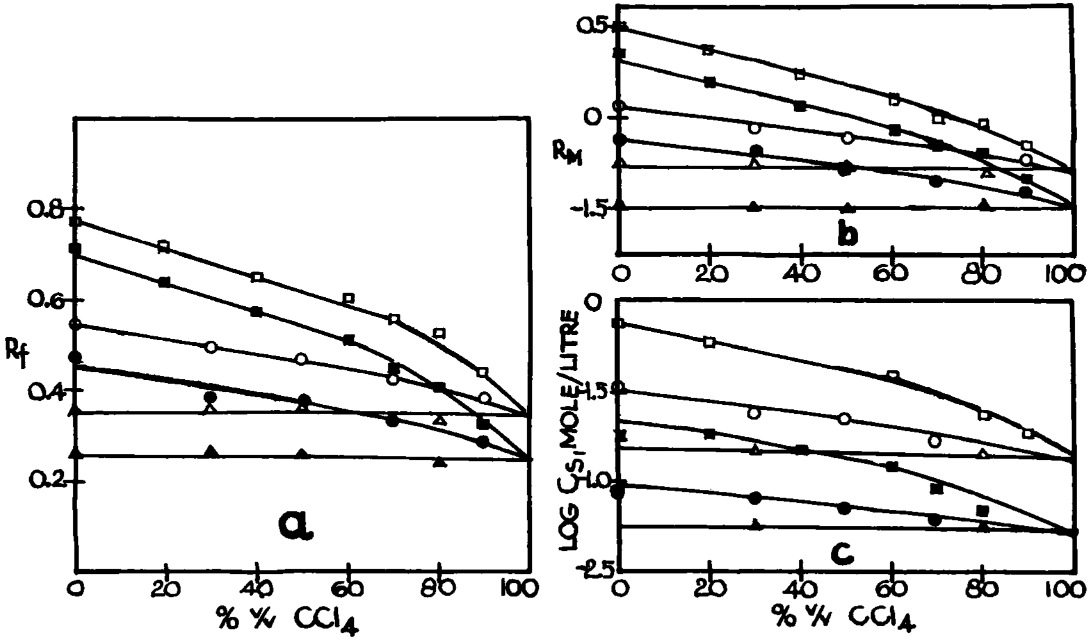

FIG. 1. a and b. R_F vs. volume composition and corresponding R_M vs. composition plots. c. Solubility vs. composition relationships. Mixed (mobile) phase: □ and ■, $C_6H_6 + CCl_4$; ○ and ●, C_2HCl_4; △ and ▲, $C_2Cl_4 + CCl_4$. Hollow squares, circles, and triangles, 1-naphtol; black ones, 2-naphtol.

tograms were developed by the descending technique in chromatographic tanks 5 × 9 × 24 cm on a distance of 16 cm. The spots were detected by coupling with bis-diazotized benzidine.

The solubilities were determined by evaporation at 60°C of saturated solutions of the two naphtols and weighing the dry residues.

The determinations were carried out at 21°C. The experimental results are presented in Table 1 and Fig. 1.

DISCUSSION OF RESULTS

In accordance with Eq. (1), the R_M-volume composition plots are almost linear, with some tendency to positive deviations, especially in the case of benzene–carbon tetrachloride mixtures; incidentally, the R_F-composition plots are almost straight lines, because all R_F values are in the range of an approximately linear R_M–R_F relationship. Pairs of R_M-composition lines of the two naphtols are parallel for a given solvent system, which indicates a constant ratio of partition coefficients of the two solutes, due to their similar molecular structure.

A striking parallelity of R_M-composition and log c_s-composition relationships is seen (Fig. 1, b and c), as expected, from Eq. (2); the corresponding lines have nearly the same shape and slope. Thus in all three series of experiments the substitution of carbon tetrachloride by benzene, trichloroethylene, or tetrachloroethylene increases both the solubility and the partition coefficient of the solute by the same factor, i.e.,

$$\begin{aligned} R_{M(\mathrm{C_6H_6})} - R_{M(\mathrm{CCl_4})} &= \log K_{\mathrm{C_6H_6}} - \log K_{\mathrm{CCl_4}} \\ &= \log c_{s(\mathrm{C_6H_6})} - \log c_{s(\mathrm{CCl_4})} \end{aligned}$$

(since $R_M = \log Kr$ and r, the volume ratio of the two phases, is constant in all experiments).

This observation (it can hardly be called a rule in view of the scarce experimental data being reported) holds, however, only for a given solute; in spite of the similar molecular structure, the distance of solubility lines of the two naphtols is different from the distance of R_M lines, although in both cases the lines are almost parallel. That is,

$$R_M^1 - R_M^2 = \text{constant} \neq \log c_s^1 - \log c_s^2 = \text{constant}'$$

where the indices 1 and 2 refer to 1-naphtol and 2-naphtol, respectively. This is not surprising, as the nonparallelity of partition and solubility, even for solutes of similar molecular structure, has already been reported (*15*).

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