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Edward Soczewiński[a]; Wiesława Maciejewicz[a]
[a] DEPARTMENT OF INORGANIC AND ANALYTICAL CHEMISTRY MEDICAL ACADEMY, LUBLIN, POLAND

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Comparison of Partition Chromatographic Parameters of Lipophilic Organic Electrolytes for Solvents of Various Donor-Acceptor Properties. V. Phenols in Systems of the Type Organic Solvent/Formamide

EDWARD SOCZEWIŃSKI and WIESŁAWA MACIEJEWICZ
DEPARTMENT OF INORGANIC AND ANALYTICAL CHEMISTRY
MEDICAL ACADEMY
LUBLIN, POLAND

Summary

R_M values of a number of phenols (cresols, xylenols, chlorophenols, hydroxynaphthalenes) have been determined for numerous solvent systems of the type, weakly polar solvent/formamide. To determine a quantitative scale of extraction strengths, R_M-solvent spectra have been plotted using a modified method of Rohrschneider and Littlewood. 2-Methylquinoline, used in previous investigations as a reference solute for nitrogen bases, has been found unsuitable for phenols, and much more regular spectra have been obtained with 1-naphthol as the reference compound. The experimental results indicate that the extraction strengths of solvents cannot be characterized by a single series. Much more satisfactory results are obtained when two series are determined, based on the partition chromatographic parameters of two solutes of opposite H-bonding properties, e.g., 2-methylquinoline and 1-naphthol. For many of the phenols, linear R_M-solvent spectra are obtained when the solvents on the abscissa are arranged to give a linear spectrum for 1-naphthol, so that the spectra can be used to predict chromatographic parameters of related solutes.

Numerous solvents and their mixtures have been employed in partition and adsorption chromatography; therefore, attempts have been made to construct a classification of pure and mixed solvents. The simplest qualitative approach consists in the determination of eluotropic series (adsorption) or mixotropic series (liquid–liquid partition).

The task is simpler in adsorption chromatography, where the eluent strength frequently depends solely on the adsorbent-solvent interactions, so that an universal eluotropic series can be determined for a given adsorbent, irrespective of the molecular structure of the chromatographed solute [Trappe (*1*), Strain (*2*); for mixed solvents with quantitative comparison of solvent strength, see Neher (*3*)], although solvation effects and other phenomena can occasionally introduce irregularities in the eluotropic sequence (*4*). Snyder (*5*) determined the eluent strength of numerous solvents quantitatively, in relation to his equation of adsorption equilibrium.

The situation in liquid–liquid partition is much more complicated, where the extraction power of solvents is determined by solvation of the solute molecules in both phases and by "squeezing" of the molecules from the more polar, associated phase. These parameters are strongly dependent on the molecular structure of the solute, and the "mixotropic series" arranged by Hecker (*6*) is at best a qualitative rule as regards the extraction power of solvents [see, for instance, Buchowski (*7*) and Bush (*8*)]. Attempts to relate the extraction strength of solvents with their physicochemical properties, such as dielectric constant, solubility parameter, and solubility of water, had only limited success (*7*, *9*, *10*). The arrangement of solvents on the abscissa according to their parameters, such as dielectric constant, resembles a line spectrum; when the partition coefficients plotted in such diagram form straight lines, then the physicochemical parameter can be considered as a quantitative measure of the extraction strength of solvents. However, such regular relationships have so far been observed only for certain types of solvents (*7*) or solutes (*11*), and they show frequent discrepancies; for instance, areas of immiscibility for systems of the type dimethyl sulfoxide-water-organic solvent plotted against the dielectric constants of the organic solvents have been found to give individual correlation lines for alcohols, ketones, ethers, etc. (Fig. 1) (*11*).

The failure in attempts to find a certain physicochemical parameter which would be directly related to the extraction strength of solvents resulted in more formal attempts to arrange the extraction power of solvents according to the partition coefficients of one or two solutes chosen as reference compounds. The solvents are arranged on the abscissa so that the partition parameters of solutes follow a straight correlation line; the method was originated by Rohrschneider (*12*, *13*)

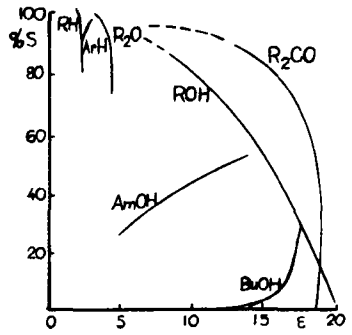


FIG. 1. Immiscibility areas (per cent of Gibbs' triangle) in solvent systems of the type dimethyl sulfoxide-water-organic solvents plotted against the dielectric constants of the third components. R, *n*-alkyl; Ar, aryl; AmOH, isomeric pentanols; BuOH, isomeric butanols (*11*).

and Littlewood (*14*) for gas chromatography and adapted in a modified form by the present authors to liquid–liquid partition chromatography (*15, 16*). In this approach the solvents form line spectra; by analogy, linear relationships R_M-composition, R_M-pH, etc., can be considered as continuous spectra of extraction strength (*9*) since the extraction strength of the mixed phase can be varied continuously.

R_M-solvent spectra plotted in the preceding papers (*15, 16*) in this series were based on 2-methylquinoline as reference compound and gave also linear and parallel R_M-solvent correlation lines for other quinoline bases, which indicated that the solvent power sequence was common for all solutes investigated, with minor deviations only.

Further examples of R_M vs solvent spectra are presented in Fig. 2 for derivatives of aniline. Unfortunately, the R_M values of 2-methylquinoline are unknown for most solvents studied by Kemula and coworkers (*17*) so that the solvents have been arranged on the abscissa to give a linear spectrum for *p*-toluidine. It can be seen that the spectra are approximately parallel for most solutes.

In Fig. 3 the R_M vs solvent spectra of Fumaria alkaloids are plotted from data reported by Wawrzynowicz (*18*). Although the solutes are more complex than quinoline bases, and possess additional H-bonding groups (—OCH_3, —OCH_2O—, —CO—, —OH), the spectra are generally descending to the right, which indicates that the sequence of solvent power determined by 2-methylquinoline as the reference solute (dashed line) is valid also for Fumaria alkaloids. Their spectra

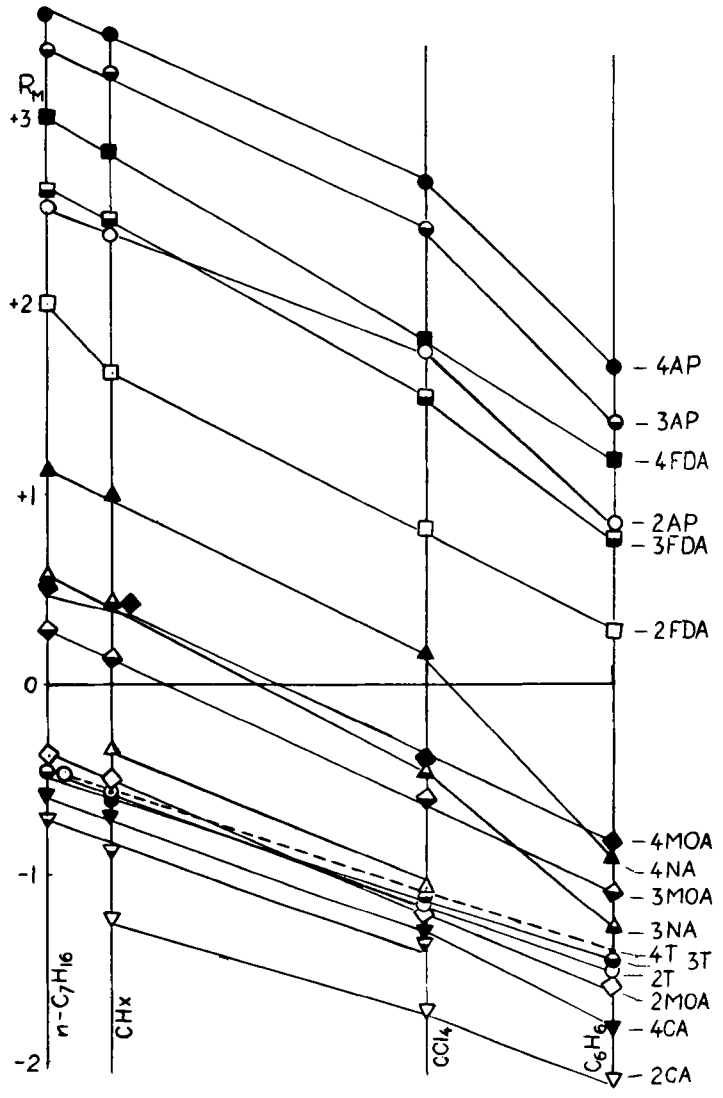


FIG. 2. Logarithms of static partition coefficients (log $k = -R_M = \log c_{org}/c_w$) for four organic solvents arranged on the abscissa to give a linear spectrum of para-toluidine; The solutes are: CA, chloroaniline; T, toluidine; NA, nitroaniline; MOA, anisidine (methoxyaniline); FDA, phenylenediamine; AP, aminophenol. Aminophenols and nitroanilines show regular deviations due to specific interactions with benzene; CHx = cyclohexane (*17*).

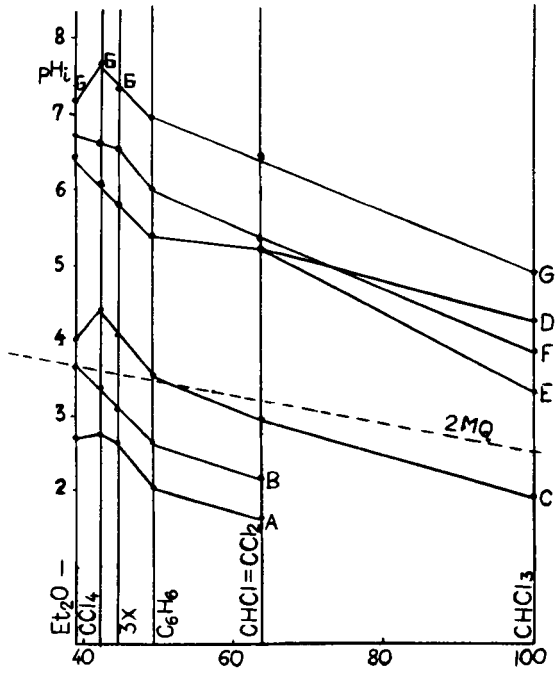


FIG. 3. pH_i-solvent spectra of Fumaria alkaloids (*18*): A, stilopine; B, sinactine; C, aurotensine; D, protopine; F, cryptocavine; E and G, unidentified alkaloids. Reference solute: 2-methylquinoline (broken line). pH_i (pH at which $R_M = 0$) for buffered paper chromatography is equal to $pK_a + R_M^0$ (*9*) so that the diagram is analogous to R_M-solvent spectra. X = xylene.

are more steep than that of 2-methylquinoline, which indicates that the ΔR_{MS} values of the alkaloids are larger due to the presence of several H-bonding groups (main contributors to ΔR_{MS} values) and probably to higher basicity of nitrogen atom. It is significant that the two phenolic alkaloids, C and G, show a clear deviation for the electron donor solvent, diethyl ether. The deviation is apparently due to specific OH . . . O hydrogen bonding so that it could be presumed that solutes with hydroxyl and other donor-acceptor groups may require arrangement of solvents in the spectrum different from that obtained for quinaldine as the reference solute.

Therefore, continuing our earlier research (*15*, *16*) we have investigated the chromatographic behavior of a number of phenols in solvent systems of the type, weakly polar solvent/formamide.

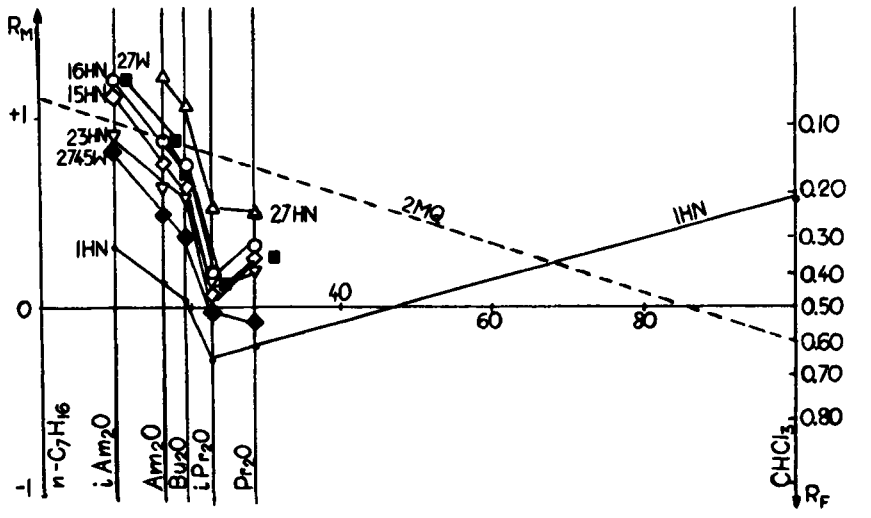
EXPERIMENTAL

Whatman No. 4 paper strips, 7×23.5 cm, were impregnated with 1:4 solution of formamide in acetone. To secure suitable and uniform impregnation, the strips were immersed in the solution, blotted between two sheets of filter paper, and allowed to dry in air for several minutes. The impregnation was repeated once more, this time passing the strip in the opposite direction. The strip contained ca. 0.55 g formamide (ca. 0.5 ml)/1 g dry paper. The phenols were spotted in amounts to give spots 0.5 to 1.5 cm in diameter after development. The chromatograms were developed in all-glass tanks for descending development, $5 \times 7 \times 22$ cm. The spots were detected by coupling with bis-diazotized benzidine (freshly prepared 1:1 mixture of solutions A and B; A: 5 g benzidine + 15 ml concd HCl + 1000 ml water; B: 10% $NaNO_2$ in water), after spraying with saturated solution of $NaHCO_3$.

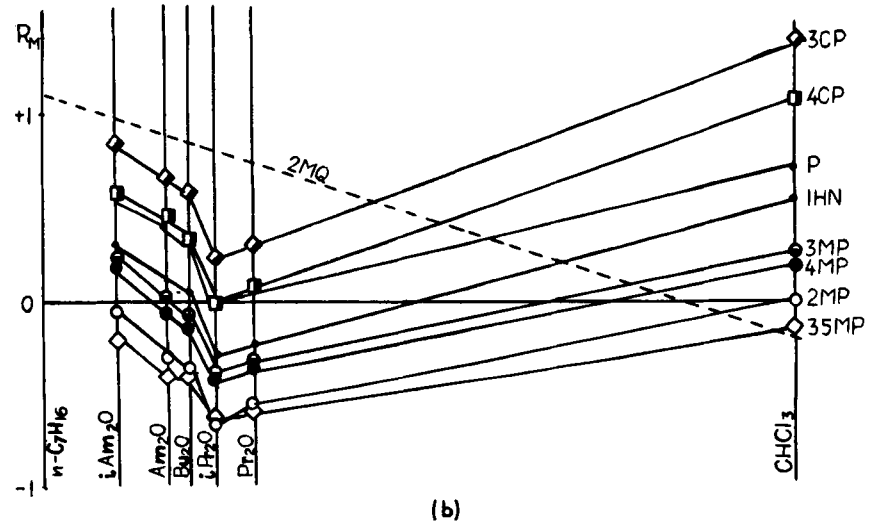
Since some phenols are strongly extracted by electron donor solvents, in some experiments the paper strips were impregnated with Na_2CO_3 to reduce the R_F coefficients to intermediate values (0.05 to 0.80). The paper was impregnated twice with 0.5 M aqueous solution of Na_2CO_3, drying the strips each time in a stream of warm air. The strips contained ca. 0.15 g Na_2CO_3/1 g dry paper and were subsequently impregnated with formamide as described above. Theoretically, ionization in the polar phase should shift the spectrum of the solute parallel without change of shape, the shift being dependent on the concentration of Na_2CO_3 and on the pK_a of the solute.

RESULTS AND DISCUSSION

The experimental results are presented as in earlier papers, as R_M vs solvent spectra, the solvents being arranged on the abscissa to give a linear correlation line for a chosen reference solute. It had been expected that 2-methylquinoline would not be suitable as a reference compound for phenols [see also Littlewood's paper (*14*), Fig. 8, where alcohols give very irregular spectra]. These anticipations were confirmed by experiment, irregular spectra being observed for most electron-donor solvents which can form H-bonds with phenols but cannot H-bond with 2-methylquinoline (Fig. 4a,b). Aromatic solvents were found to be good extractants of phenols, giving R_M values comparable to chloroform, which was chosen as the reference solvent with a solvent strength equal to 100, as in the preceding papers. Electron



(a)



(b)

FIG. 4. R_M-solvent spectra of phenols for solvents of class B. Reference solute (broken linear spectrum): 2-methylquinoline (2MQ). Stationary phase: FA + Na_2CO_3 except for dihydroxynaphthalenes: 16HN, 27HN, and 15HN which gave suitable R_F values without pretreatment with Na_2CO_3, and for 2MQ (FA + 4.2% citric acid).

donor solvents [class B in the classification proposed by Pimentel and McClellan (*19*, *20*)] were found to be much stronger extractants than chloroform, especially ketones which gave high R_F values beyond the range of accuracy. It should be noted, however, that the spectra of phenols, although irregular, are approximately parallel.

The arrangement of solvents suitable for quinoline bases was thus found to be useless for phenols. Therefore, in the following plots the solvents are arranged on the abscissa so that a linear spectrum is obtained for 1-naphthol, whose R_F values were found to be in the range of accuracy for numerous solvents. For purposes of comparison, in these same spectra heptane and chloroform have been chosen as reference solvents. Twenty-six phenols have been investigated, including cresols, xylenols, chlorophenols, nitrophenols, dihydroxynaphthalenes, and 4,5-dihydroxydibenzofuran (4,5W); the simpler phenols are denoted by mnemonic symbols, e.g., 3MP = metacresol; 26MP = 2,6-xylenol; 26CP = 2,6-dichlorophenol; 27HN = 2,7-dihydroxynaphthalene.

Chromatographic spectra for solvents of class N are presented in Fig. 5a,b; it can be seen that cycloaliphatic solvents and carbon tetrachloride remained in the range of low extraction strength (below 50 units), whereas the two aromatic solvents, benzene and *m*-xylene have extraction power similar to that of chloroform (formation of weak H-bonds between hydroxyl group and π-bonds). The R_M values of quinaldine plotted in this diagram form a broken correlation line which deviates most for the two aromatic solvents (much weaker extraction in comparison to 1-naphthol).

The sequence of monohydroxy compounds is largely determined by the proton-donor properties (acidity) of the hydroxyl group, the molecular size, steric effects, and formation of internal H-bonds; thus, the xylenols are extracted more strongly than the cresols, and for methyl groups in the ortho position the R_F is increased due to steric hindrance of H-bonding with the polar solvent, the effect being especially pronounced for 2,6-xylenol which had highest R_F values in all solvent systems studied. It should be pointed out that 4,5-dihydroxydibenzofuran gives a quite regular spectrum whose slope is somewhat higher than the reference line of 1-naphthol; this similarity of the dihydroxy compound is caused by the formation of a stable internal H-bond which leads 4,5-dihydroxydibenzofuran to behave like a monohydroxy compound. Several other dihydroxy compounds gave such low R_F values that their accurate R_M values could not be determined for solvents of class N.

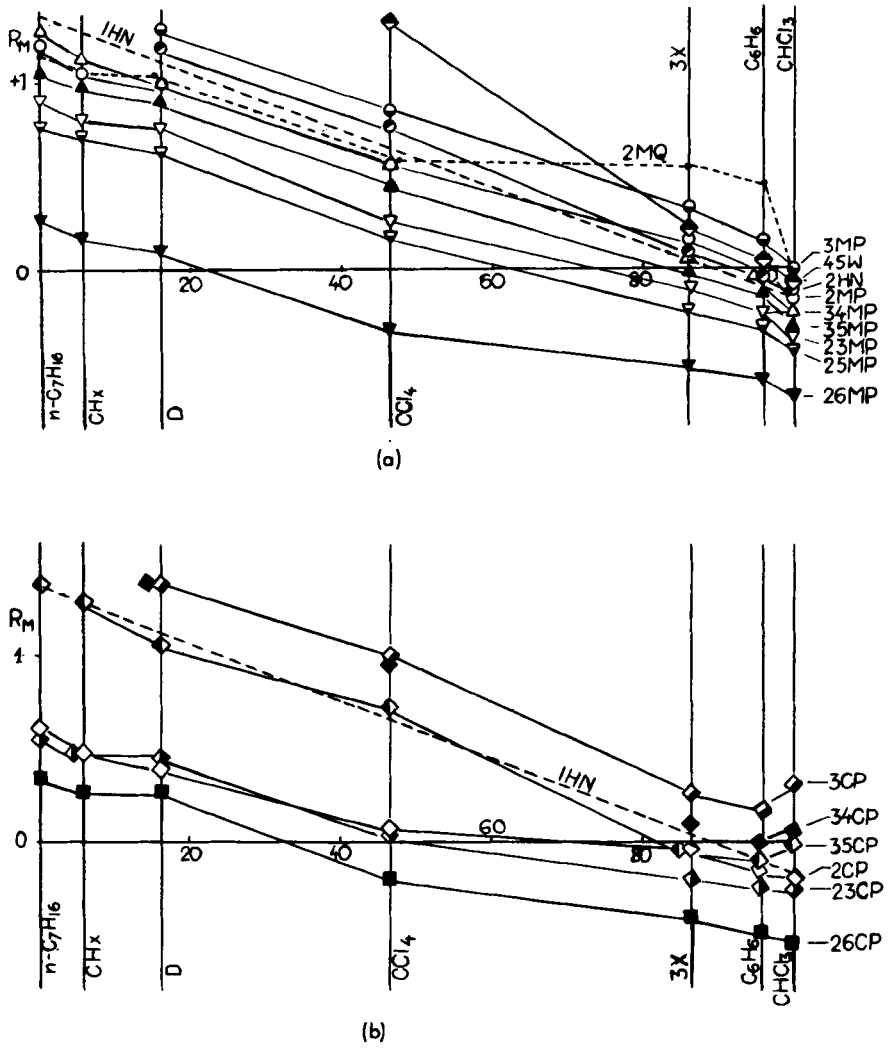
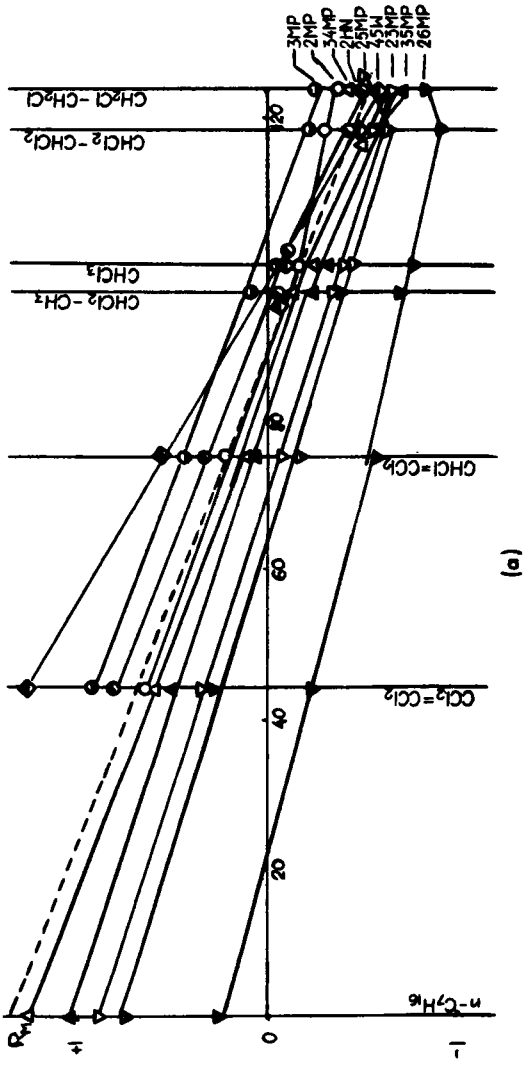


FIG. 5. R_M-solvent spectra for solvent systems of the type N/FA. Reference solute: 1-Naphthol (broken line). D = decalin.

Analogous conclusions can be drawn from Fig. 5b. The spectra of chlorophenols and dichlorophenols are quite regular, the ortho derivatives (2CP, 23CP, 26CP) forming less steep spectra due to their tendency to form a weak H-bond (strained five-membered ring).

Thus, arrangement of the solvents of class N to give a linear spectrum for 1-naphthol gives a satisfactory characterization of their



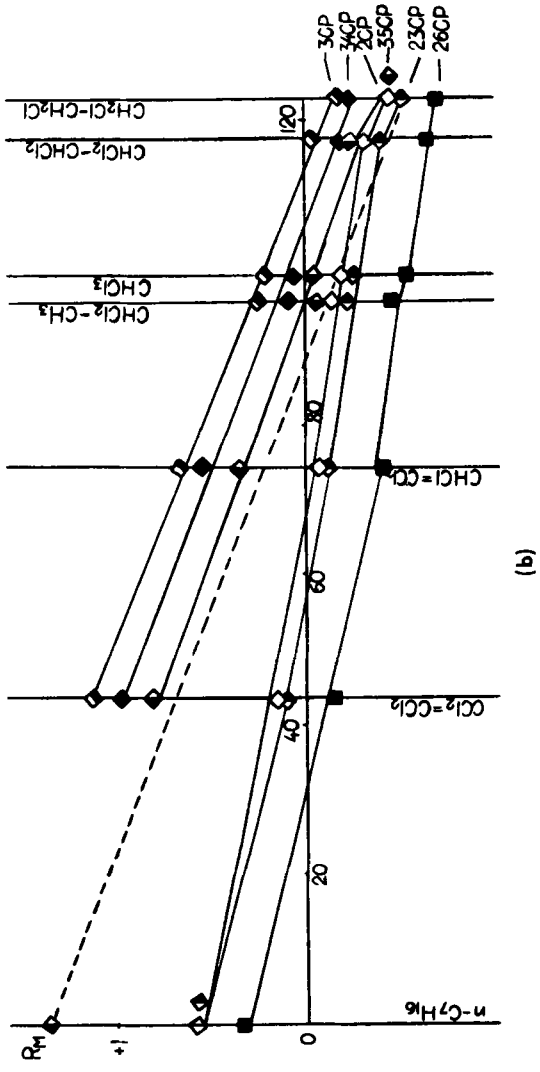


FIG. 6. R_M-solvent spectra of phenols in solvent systems of the type A/FA. Reference solute: 1-Naphthol.

solvent strength relative to a number of phenols (cresols, xylenols, chlorophenols, dichlorophenols). The same conclusion applies also to solvents of class A (Fig. 6a,b); their solvent strength is higher than in the case of quinoline bases so that tetrachlorethane and 1,2-dichloroethane have solvent strengths exceeding that of chloroform. The substitution of the last H-bonding hydrogen atom in trichloroethylene causes a strong decrease of extraction power (tetrachloroethylene, class N, which is included in the diagram for comparison).

Solvents of class B (aliphatic ethers; ketones had too high R_F values) were found to have high extraction strength in relation to phenols, so that dihydroxynaphthalenes (which remained on the base line for solvents of class N and B) had measurable R_M values.

To keep 1-naphthol as the reference solute, it was necessary to reduce its high R_F values by impregnating the paper strips with Na_2CO_3 as described under Experimental. Partial ionization of 1-naphthol in formamide leads to a decrease of its R_F value in the system chloroform/formamide from 0.59 to 0.21.

The R_F values of 1-naphthol were then determined in the same manner for solvents of class B, which were arranged on the abscissa in such a way that the R_M values of 1-naphthol formed a linear spectrum parallel to the straight reference line drawn for 1-naphthol and for pure formamide.

The spectra of naphthol, phenol, cresols, xylenols, and chlorophenols for systems of the type B/FA + Na_2CO_3 are presented in Fig. 7a. As estimated from the R_M values for chloroform, the reference line of 1-naphthol is shifted upward by 0.74 R_M units in relation to the extension of the reference line obtained for pure formamide. It can be seen that the spectra are almost parallel, with some discrepancies for the pair of solvents chloroform-diisoamyl ether. For solvents of class B, dihydroxynaphthalenes gave too low R_M values for paper pretreated with Na_2CO_3; they were therefore chromatographed on paper strips impregnated with formamide only. The experimental results thus obtained are presented in Fig. 7b, the solvents of class B being arranged on the abscissa as in Fig. 7a. The spectra are regular in this case also, which indicates that 1-naphthol is also suitable as a reference compound for the dihydroxynaphthalenes investigated. *m*-Cresol also gives a linear spectrum for these systems, which is shifted downward in Fig. 7b almost parallel for most solvents, with some deviation for diisopropyl ether. The shifts of the spectra of the remaining phenols depend on their pK_a values.

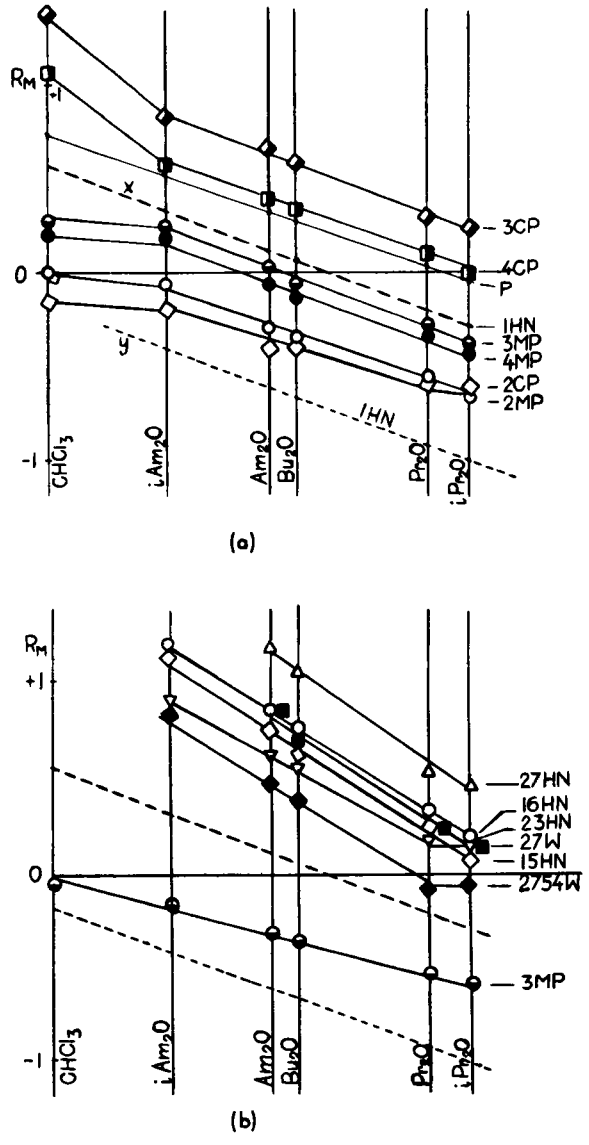


FIG. 7. R_M-solvent spectra of phenols in solvent systems of the type B/FA + Na_2CO_3 (a) and B/FA (b). The solvents are arranged on the abscissa to give for the former system a linear spectrum of 1-naphthol (x) parallel to the extension (y) of its reference line for neutral systems (broken lines), in which 1-naphthol gives too high R_F values.

The slopes of the correlation lines of dihydroxynaphthalenes are almost twice that of 1-naphthol, so that it can be written that ΔR_{MS} (2OH) $= 2\Delta R_{MS}$(OH). The line of 2,3-dihydroxynaphthalene is less steep, its slope approaching that of 1-naphthol; this is presumably due a tendency of formation of an internal H-bond between the two vicinal hydroxyl groups (strained five-membered ring) or hindrance in simultaneous solvation of the two OH groups. The lower slope of the spectrum of *m*-cresol could be caused by its weaker acidic properties.

CONCLUSIONS

Summing up the experimental results, it should be pointed out that in the case of phenols (class AB) the characterization of solvents is frequently quite different from that obtained for solutes of class B (e.g., quinolines), the largest discrepancies being observed for electron donor solvents. Therefore, it is impossible to formulate an universal extraction series of solvents. This conclusion is in accord with Littlewood's data on the retention strength of stationary liquids in gas–liquid chromatography (*14*).

However, our results suggest that it is possible to determine series of solvents for individual groups of related solutes, and especially for solutes possessing certain functional groups capable of forming hydrogen bonds (e.g., heterocyclic nitrogen, hydroxyl group). The experimental data indicate that two extraction series, one based on quinaldine or another electron donor solute, and the other on 1-naphthol or another solute with predominating proton-donor properties, give satisfactory characterization of solvents with respect to their extraction strength for solutes of class B and AB, respectively (i.e., for most organic solutes separated by methods based on liquid–liquid partition). In the ideal case when the spectra of solutes are linear, the characterization of solvents can be regarded as quantitative so that partition parameters can be predicted from R_M-solvent spectra. However, the problem has so far been investigated for few groups of relatively simple solutes; the question is still open for other functional groups, multifunctional solutes (especially with differing functional groups), etc.

In such investigations, paper chromatography experiments can play the role of pilot investigations, the lower accuracy being counterbalanced by simplicity, rapidity, and low cost of the experiments. The experimental data presented in Figs. 4–7 are quite self-consistent, al-

though some divergencies could have been caused by the limited accuracy of paper chromatography. Batch experiments are much more accurate (Fig. 3) and have the additional advantage of eliminating or at least reducing any adsorption effects on the liquid–liquid interface, which is much smaller than in chromatographic experiments.

The problem of "extraction series" can also be more accurately investigated by column liquid–liquid chromatography (*10*). The experiments can then be reasonably planned on the basis of preliminary paper chromatographic data.

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