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Comparison of Partition Chromatographic Parameters of Lipophilic Organic Electrolytes for Solvents of Various Donor-Acceptor Properties. VI. 4-Pyridyl Alkyl Ketones and 4-Pyridyl Alkyl Alcohols in Aqueous and Formamide Systems

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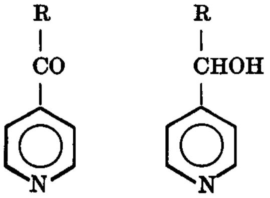
Summary

R_M-solvent spectra have been determined for two homologous series of solutes: 4-pyridyl alkyl ketones and 4-pyridyl alkyl alcohols. The substitution of the carbonyl group by the secondary hydroxyl group had little effect on the extraction strength of the solvents of class N and A; however, for electron donor solvents a marked increase of extraction was observed, the shift of the position of solvents in the spectra being approximately constant for aqueous systems. Scales of extraction strengths for various reference compounds have been compared.

In the preceding paper (*1*) we have shown that two solvent series (arranged to give linear R_M-solvent spectra of quinaldine and 1-naphthol, respectively) characterize the extraction strengths of the solvents relative to numerous electron donor and donor-acceptor solutes. Thus far we have investigated solutes possessing one H-bonding group or two identical H-bonding groups, although a few multifunctional solutes have also been studied (cf. Ref. 1, Figs. 2 and 3), their spectra being more complex than those of the simpler compounds.

To investigate the behavior of more complex solutes possessing two different H-bonding groups, we have chosen two homologous series:



4-pyridyl alkyl ketones and 4-pyridyl alkyl alcohols, the alkyl radical containing one to five carbon atoms. The use of homologous series has the advantage of regular variation of hydrophobic properties with the length of the alkyl chain so that R_F values of at least 2–3 homologues can be obtained within the range of good accuracy (*2*). The first series of solutes can be regarded as a "B + B" type, and the second series as a "B + AB" type (*3*); the comparison of their partition parameters and R_M-solvent spectra permits us to obtain information on the effect of reduction of the ketocarbonyl group to secondary hydroxyl group.

EXPERIMENTAL

For aqueous systems, the "moist paper" technique was used [see Part III of this series (*4*)]. Whatman No. 4 paper strips were impregnated with water, blotted between two sheets of filter paper, and transferred to the tank for descending development after the moisture content dropped to 0.5 ml of water per 1 g of dry paper. For the ketones the R_F values obtained were too high, so that it was necessary to impregnate the strips with 5% aqueous solution of citric acid (thus the aqueous phase during development contained about 10% of citric acid).

The technique for formamide impregnated paper chromatography has been described in the preceding paper (*1*); to reduce too high R_F values of ketones, ca. 20% solution of citric acid in formamide was used for impregnation (diluted with acetone in a 1:4 ratio).

Citric acid has been chosen as a hydrophilic acid which is not likely to be extracted into the organic phase; therefore, it can be expected that the presence of citric acid will shift the whole spectrum in a parallel manner upward, the shift being dependent on the concentration of citric acid and the basicity (pK_a) of the solute.

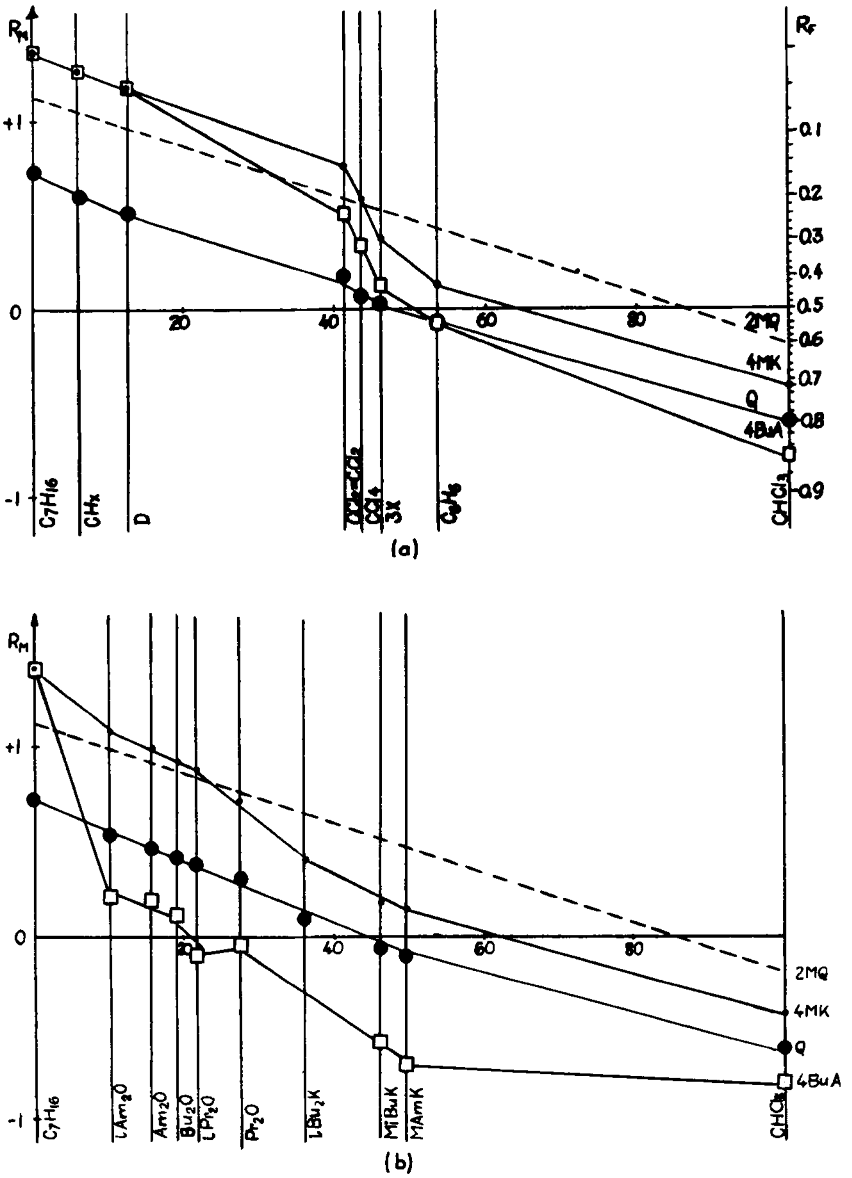


FIG. 1. Comparison of R_M-solvent spectra of 4-pyridyl methyl ketone (fixed phase: 20% citric acid in formamide), 4-pyridyl butyl alcohol (fixed phase: formamide), and two quinoline bases (fixed phase: 4.2% citric acid in formamide) for solvents of class N (a) and B (b). Reference solute: 2-methylquinoline (2MQ).

RESULTS AND DISCUSSION

The experimental data are presented as R_M-solvent spectra, using a modified method (*4*) of Rohrschneider (*5*) and Littlewood (*6*).

In Fig. 1 the positions of the solvents on the abscissa are subordinate to the linear spectrum of quinaldine (in the systems solvent/4.2% citric acid in formamide), the reference solvents being *n*-heptane (0) and chloroform (100). The spectrum of quinoline is also plotted in these diagrams. The spectra of 4-pyridyl methyl ketone and 4-pyridyl butyl alcohol, which give identical R_F values for nonpolar solvents, are presented. It can be seen that the sequence of solvents of class N (Fig. 1a) with respect to their extraction strength based on quinaldine as reference solute applies also for the two pyridine derivatives; however, the spectra are not linear so that the quantitative characterization of the extraction strength differs for some solvents, especially for benzene and *m*-xylene.

For 4-pyridyl methyl ketone, the omission of R_M values obtained for the two aromatic solvents would result in a quite regular linear spectrum for the remaining solvents of class N, the line being steeper due to presence of two electron donor groups (main contributors to ΔR_{Ms} values). For 4-pyridyl butyl alcohol the spectrum is broken in the narrow range CCl_4-*m*-xylene and approximately linear outside this range. The spectra of the ketone and alcohol diverge to the right.

More complex spectra are observed for solvents of class B (Fig. 1b), although the sequence of extraction strength based on quinaldine holds quite well for both solutes. The spectrum of 4-pyridyl butyl alcohol, however, runs much lower than that of the 1-pyridyl methyl ketone (by ca. 0.8 R_M units) and is approximately linear for all solvents of class B; the points of the ketone form two separate correlation lines, for ethers and ketones respectively.

To facilitate comparison of the extraction strength of the solvents, in the following R_M-solvent spectra the solvents are arranged on the abscissa to give linear spectrum for one the homologs investigated. From the five homologs the compound which gives accurate R_M values for heptane and chloroform will be chosen as the reference solute (for aqueous systems, 4-pyridyl propyl ketone and 4-pyridyl propyl alcohol; for formamide systems, 4-pyridyl methyl ketone and 4-pyridyl butyl alcohol). Since $\Delta R_M(CH_2)$ values have been found to be constant for numerous solvents in aqueous as well as in formamide

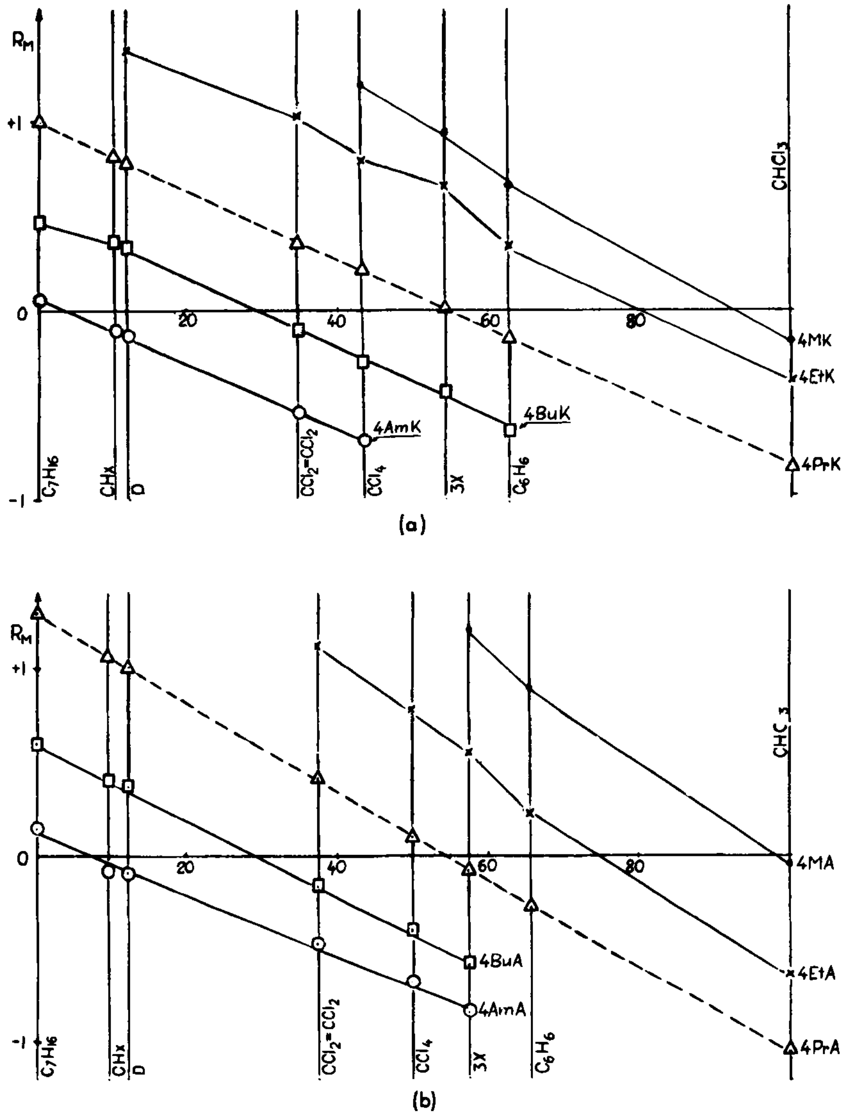


FIG. 2. (a) R_M-solvent spectra for the homologous series of 4-pyridyl alkyl ketones for the system N/H_2O + 5% citric acid (reference solute: 4-pyridyl propyl ketone). (b) Analogous plot for 4-pyridyl alkyl alcohols for the system N/H_2O (reference solute: 4-pyridyl propyl alcohol). The radicals are: ●, Me; ×, Et; △, Pr; □, Bu; ○, Am.

systems (*2*), the spectra of individual homologs should be approximately parallel and regularly spaced.

In Fig. 2a,b the spectra of pyridyl ketones (2a) and pyridyl alcohols (2b) are presented for solvents of class N. It can be seen that the positions of solvents on the abscissa are similar for both series of compounds, in accordance with Fig. 1a, where the two spectra are identical for heptane, cyclohexane, decalin, and approximately parallel for the remaining solvents of class N. In accordance with expectations, the spectra are parallel and regularly spaced, except for the first ketone [due to difference of basicity—or "first homolog" anomaly, e.g., (*7*)]. The slopes of R_M-solvent spectra of pyridyl alkyl alcohols are steeper (greater ΔR_{M_s} values for the systems heptane/water and chloroform/water).

Similar conclusions also follow from inspection of Figs. 3a,b where solvents of class A are represented; the shifts of solvent strengths are insignificant and do not exceed experimental error by much. It seems, therefore, that for solvents of class N and A the arrangement of solvents is common for both homologous series and similar to that obtained for quinaldine as reference solute (see Fig. 8).

The largest differences are observed for solvents of class B in view of specific interaction with the hydroxyl group of the alcohols (Figs. 4a,b). All positions of the solvents are shifted to the right; however, the shift is similar in all cases and equal to ca. 40 ± 5 arbitrary units of extraction strength, the sequence and spacing of solvents being essentially the same, mostly within the experimental error.

Similar conclusions also follow from inspection of Figs. 5–7 where the R_M-solvent spectra for formamide systems are plotted. There are only minor shifts in extraction strength for solvents of class N and A, and a large increase (by ca. 35 units) of extraction strength for solvents of class B as the result of substitution of $>$CO group by $>$CHOH group. The shifts, however, are less regular than for aqueous systems so that the sequence of solvents is occasionally changed for the pyridyl alcohols.

For alcohols the spectra seem to tend to diverge to the left, which would indicate some increase of $\Delta R_M(CH_2)$ values for less polar solvents. The $\Delta R_M(CH_2)$ are lower than for aqueous systems (cf. Ref. *2*). The values of extraction strengths of individual solvents are similar but not identical for aqueous and formamide systems (Fig. 8); this is presumably due to mutual solubility of the two phases in partition

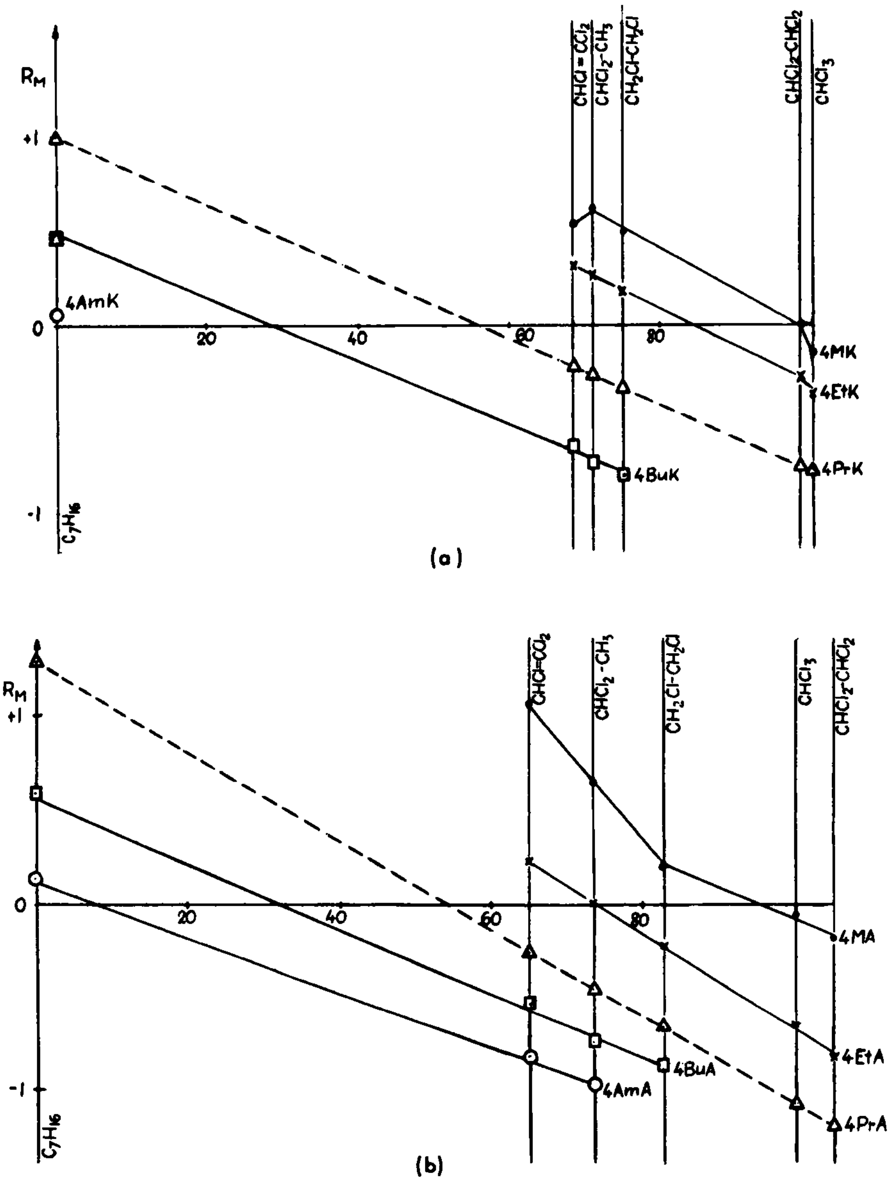


FIG. 3. As in Fig. 2, proton donor solvents (class A). See Fig. 2 caption for key to symbols.

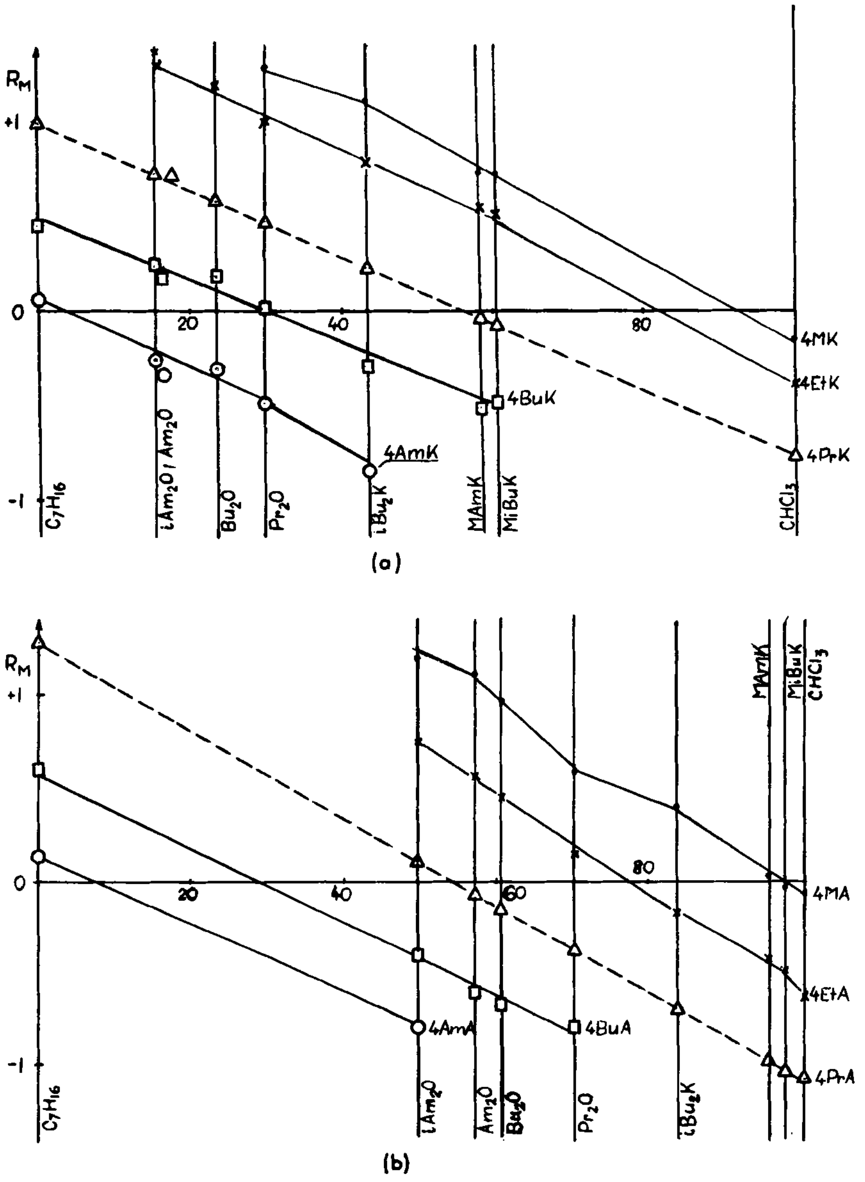


FIG. 4. As in Fig. 2; electron donor solvents (class B). See Fig. 2 caption for key to symbols.

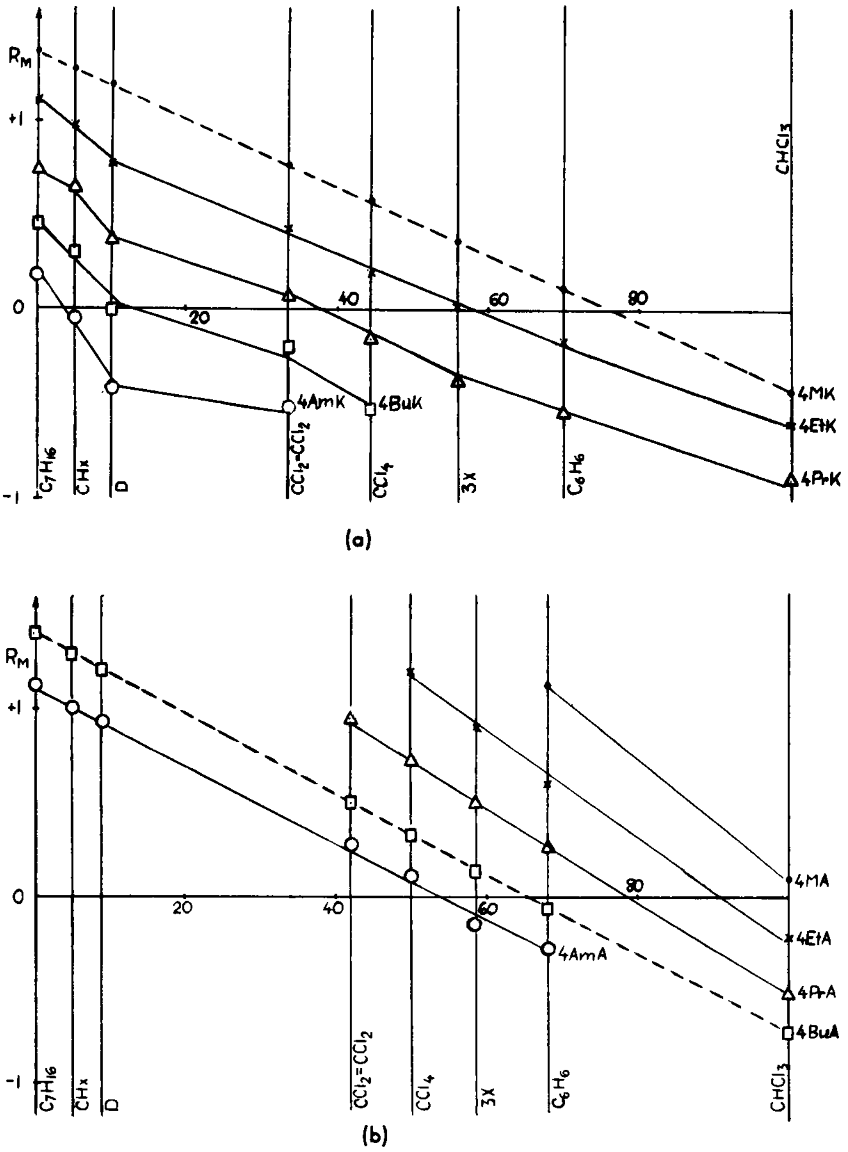


FIG. 5. (a) R_M-solvent spectra of 4-pyridyl alkyl ketones in solvent-systems of the type N/FA + 20% citric acid (reference solute: 4-pyridyl methyl ketone). (b) 4-Pyridyl alkyl alcohols in solvent systems of the type N/FA (reference solute: 4-pyridyl butyl alcohol). See Fig. 2 caption for key to symbols.

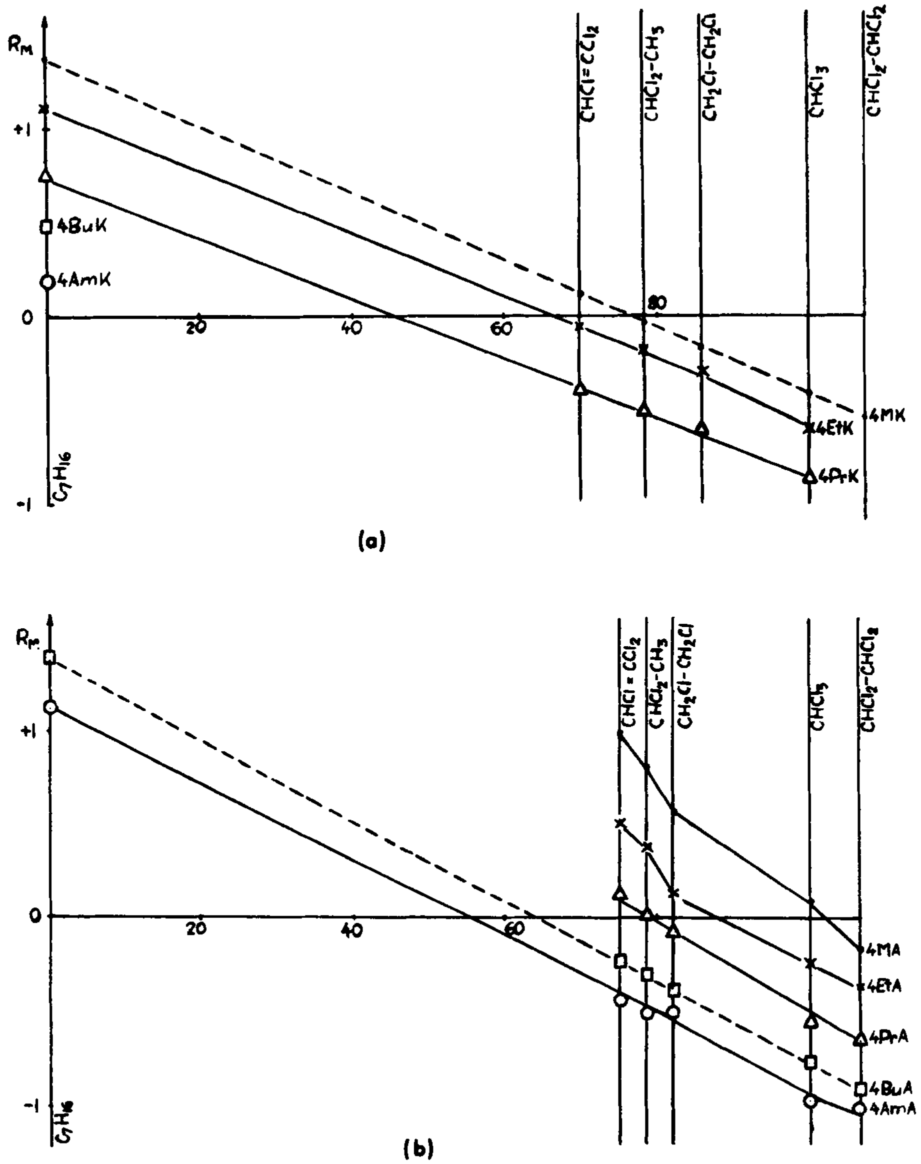


FIG. 6. As in Fig. 5, proton donor solvents (class A). See Fig. 2 caption for key to symbols.

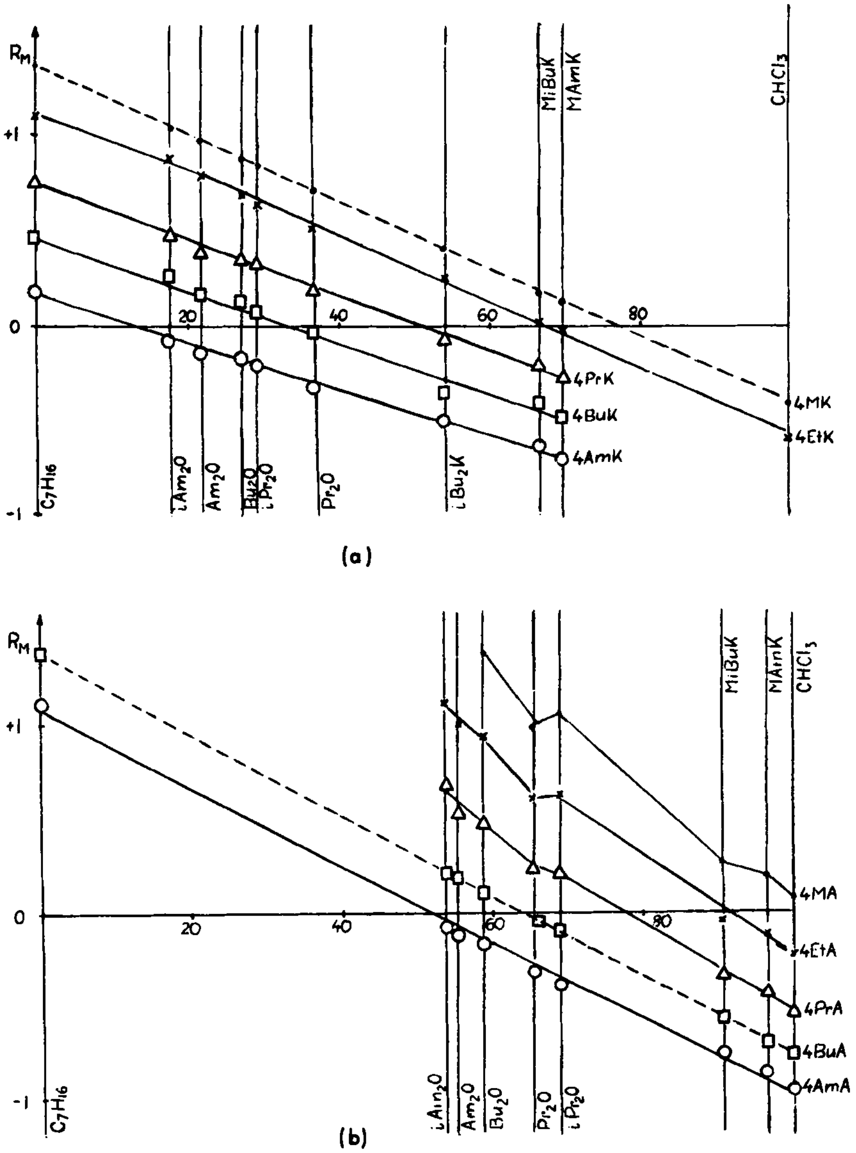


FIG. 7. As in Fig. 5. electron donor solvents (class B). See Fig. 2 caption for key to symbols.

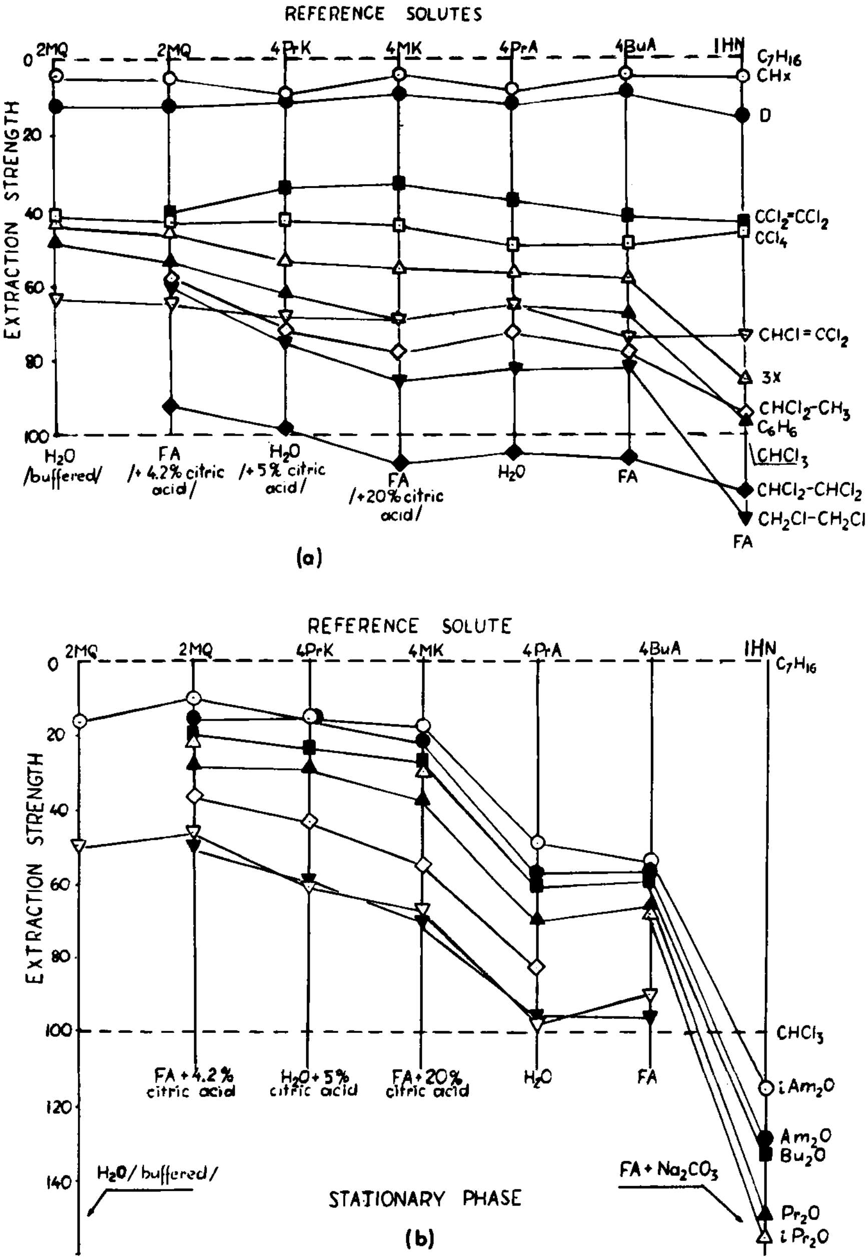


FIG. 8. Comparison of scales of extraction strength of neutral and proton donor solvents (a) and electron donor solvents (b) for various reference solutes.

systems, the presence of the polar liquid in the less-polar phase increasing generally with its polarity and contributing to its extraction strength. There are apparently individual differences between these effects in aqueous and formamide systems. Further contribution can result from adsorption of solutes on the liquid–liquid interface (*8*), which tends to decrease the R_F values. The effect of adsorption is difficult to evaluate, and is probably different for solvent–water and solvent–formamide interface. The contribution of adsorption effects can be expected to be more pronounced for nonpolar solvents and for multifunctional solutes which are strongly adsorbed by solid adsorbents of the silica gel type.

For solvents of class N and A (Fig. 8a) the quantitative characterization of extraction strength is similar for most solvents and reference solutes; the lines connecting the points of individual solvents cross only in several cases, especially for 1-naphthol, which can interact more strongly with the two aromatic solvents (OH—π bonds) and with solvents of class A. The quantitative characterization of extraction strength depends to some extent on the polar phase and the reference solute.

More marked shifts in the quantitative characterization of extraction strength are observed for solvents of class B (Fig. 8b) although the sequence of solvents is practically independent of the reference solute chosen. However, the scales are shifted in the direction of higher extraction strengths when reference solutes of class B are substituted by pyridyl alcohols and the shift is still more pronounced for 1-naphthol as reference solute; for the latter solute a greater differentiation of solvent strength is also observed, both effects being presumably caused by the stronger proton-donor properties of 1-naphthol. The shifts of extraction strengths are obviously related with the ΔR_{Ms} values of the reference solutes, which are determined by the difference of interaction forces between the solute and the individual solvents.

Figure 8 clearly shows the advantages and limitations of characterization of the extraction strength by Rohrschneider's and Littlewood's methods on the basis of two types of reference solutes (B and AB). The results seem to be promising and the relationships are especially simple for solvents of class A and N; however, aromatic solvents, in view of their weak electron-donor properties, should rather be grouped with solvents of class B for reference solutes with strong proton-donor properties (e.g., 1-naphthol). It can be presumed that the method of R_M vs solvent spectra, in combination with the concept of additivity of R_M values, may permit formulation of a more or less general systematization of extraction strength of organic solvents in relation to solutes of various molecular structure.

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