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NOTE

Extraction of Organic Acids with Solutions of Tributylphosphate in Various Diluents

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Abstract

The extraction of 10 phenolic acids from aqueous solutions was investigated by liquid–liquid partition chromatography using four diluents of various polarities: cyclohexane, benzene, di-*n*-butyl ether and diisobutyl ketone. Apparent solvation numbers were estimated from log D vs log % TBP plots. It is demonstrated that even low concentrations of TBP cause a significant increase of extraction of organic acids.

Tributyl phosphate belongs to the very effective extractants of inorganic compounds and has been extensively applied in preparative and industrial scale separation processes (*1–3*).

In the extraction of organic electrolytes its strong electron donor properties are exhibited especially in the presence of acidic groups: thus for aliphatic hydroxy acids the composition of the solvates is determined by the number of carboxylic groups (*4–6*); for instance, HA·2TBP solvates are formed both by malonic acid (*6*) and by trihydroxyglutaric acid (*5*). It has also been demonstrated that TBP is a strong extractant of phenols (*7*).

In the present study the extraction of phenolic acids and the derivatives of cinnamic and benzoic acids were investigated by the dilution method.

EXPERIMENTAL

The secure liquid–liquid partition mechanism, controlled impregnation of paper strips with water was employed ("moist buffered paper" technique; 0.5 cm^3 of water per gram of dry paper). For experimental details see, for instance, Refs. 7 and 8. In the technique used, $V_{org} \approx 2V_w$ so that $\log D \approx -R_M - 0.3$ (see parallel ordinate in Fig. 1).

As developing solvents, 1 to 30% v/v solutions of TBP in cyclohexane or 1 to 10% v/v solutions in other diluents were used. The spots were detected with bis-diazotized benzidine. The results (averages from 5 runs) are represented as R_M vs log % TBP plots which are equivalent to the usual log D vs log C plots (*1*).

RESULTS AND DISCUSSION

Although the slopes of log D vs log C plots give only indirect information about the molecular mechanism of liquid–liquid partitions (*1*, *2*), they nevertheless reflect the analogies and differences in the molecular interactions involved (see, for instance, Refs. *7–12*). Furthermore, quantitative descriptions of R_M (log k') vs solvent composition relationships form a necessary starting point for the rational design of solvent programming in gradient elution (*13*), which may be necessary for solutes which differ strongly in hydrophobic properties (wide range of k' values).

As expected, the increase of extraction ability with the concentration of TBP is strongest for solutions in cyclohexane which extracts in significant amounts only the most hydrophobic compounds. Straight R_M vs log % TBP lines were obtained (Fig. 1), the slopes ranging from 1.5 for compounds with two polar groups, one of which can form an intramolecular H-bond, to 2.0 for solutes with an unhindered hydroxyl group (or two vicinal hydroxyl groups) and still higher slopes for gallic acid (three vicinal phenol groups) and especially for chlorogenic acid (one carboxyl group, two vicinal phenol groups, three hydroxyl groups in the cyclohexane ring). Ten percent solutions of TBP extract most of the compounds investigated ($D > 1$), and 30% solutions extract even the most hydrophilic chlorogenic acid.

Solutions of TBP in benzene have somewhat greater extraction ability (Fig. 2); moreover, the slopes of R_M vs log % TBP lines are differentiated, which is presumably caused by a more active role of the diluent in the

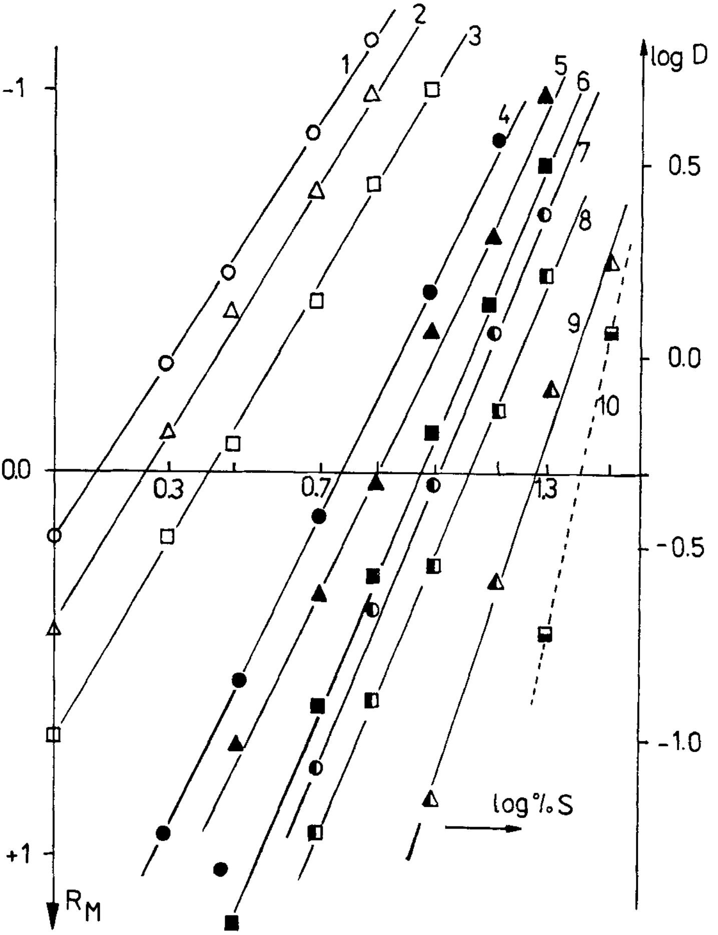

FIG. 1. R_M vs log % TBP plots of phenolic acids: (1) o-coumaric, (2) gentisic, (3) *trans*-hydroxycinnamic, (4) pherulic, (5) vanillic, (6) syringic, (7) caffeic, (8) protocatechuic, (9) gallic, (10) chlorogenic acid. Diluent: cyclohexane.

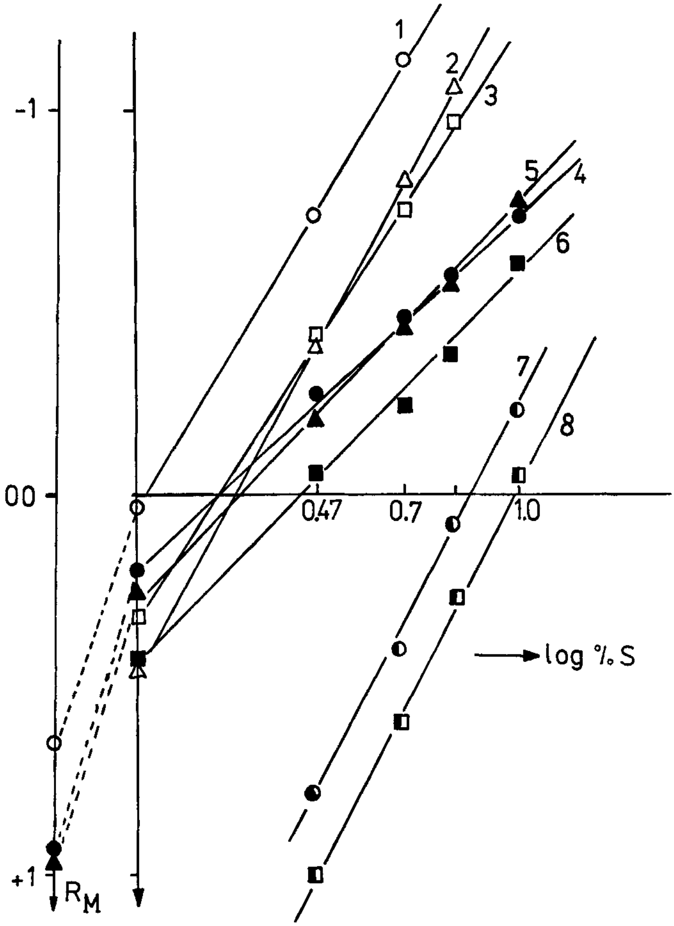

FIG. 2. As in Fig. 1. Diluent: benzene. The R_M values obtained for pure diluent are plotted on the left-hand ordinate.

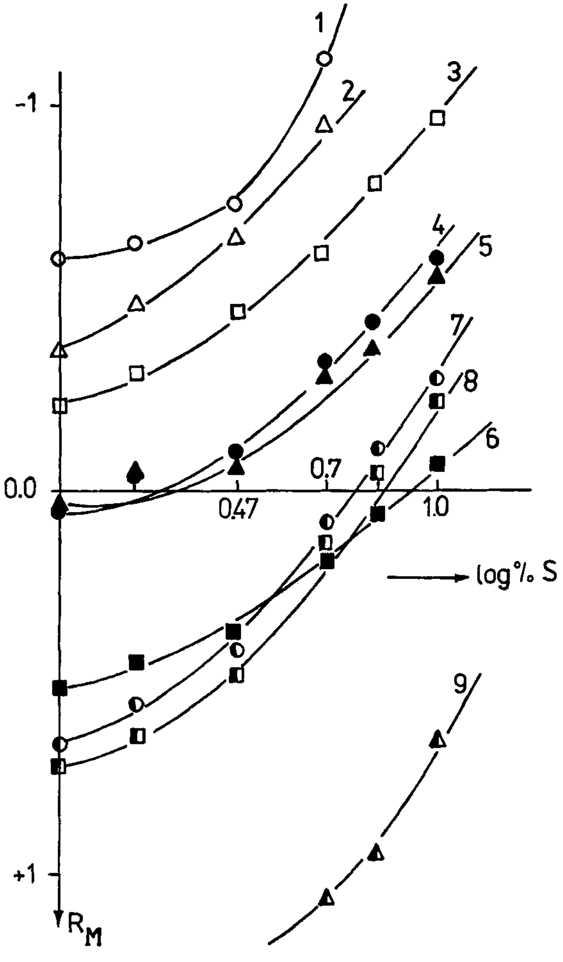

FIG. 3. As in Fig. 1. Diluent: di-*n*-butyl ether.

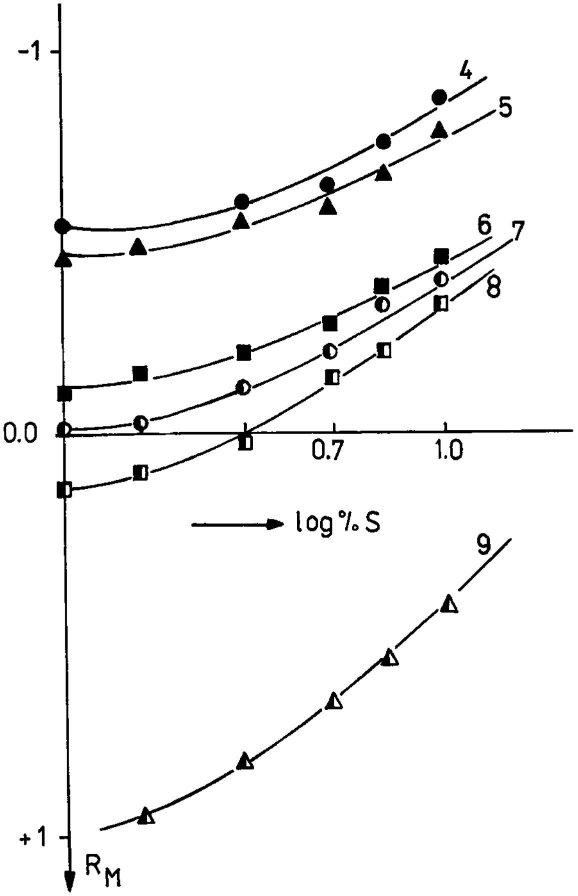

FIG. 4. As in Fig. 1. Diluent: di-*n*-butyl ketone.

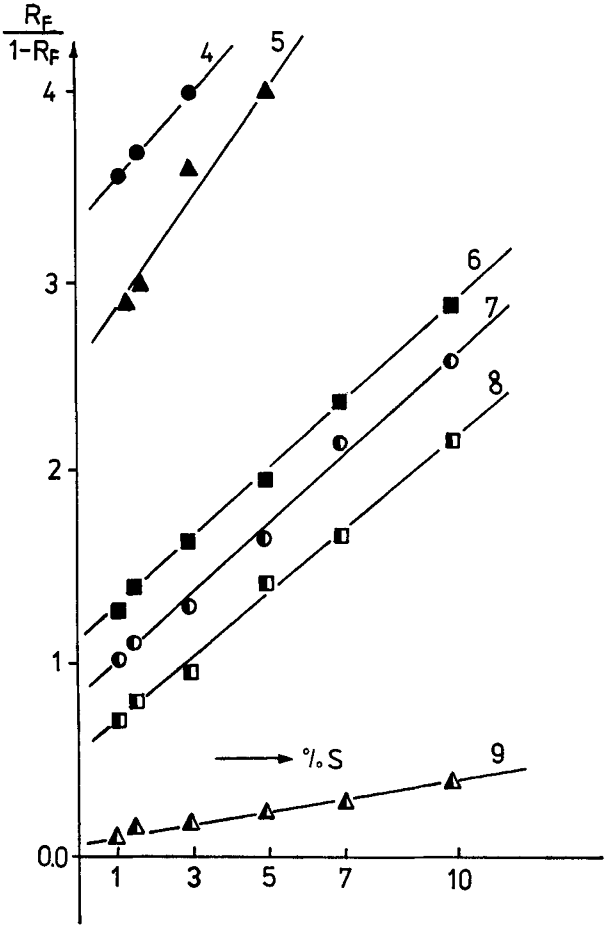

FIG. 5. Data of Fig. 4 plotted in the coordinate system $1/k'$ vs % TBP.

solvation equilibria involved. This effect is especially pronounced for pherulic, vanillic, and syringic acids. Ten percent solutions of TBP in benzene extract most of the acids investigated.

The active role of the diluent is still more pronounced for di-*n*-butyl ether (Fig. 3) for which curved lines of the hockey-stick type are obtained, indicating a significant contribution of solvation by the diluent (*1*), which extracts especially the more hydrophobic acids. Most of the lines have similar slopes with the ascending part of unit slope which presumably indicates the formation of mixed solvates of the $HA \cdot TBP \cdot R_2O$ type in the range of higher concentration of TBP. However, caffeic and protocatechuic acids (and perhaps gallic acid) behave in a different manner which can be explained by the contribution of formation of $HA \cdot 2TBP$ solvates. The addition of 10% of TBP to di-*n*-butyl ether increases the distribution coefficients about 4 to 10 times.

For the relatively polar diisobutyl ketone used as the diluent in the fourth series of experiments (Fig. 4), the increase of extraction due to addition of TBP is relatively insignificant (distribution coefficients being increased 2 to 4 times for a 10% concentration of TBP). Apparently the gradual shift of the solvation equilibria involved

$$HA \cdot R_2CO \rightleftarrows HA \cdot 2R_2CO \rightleftarrows HA \cdot R_2CO \cdot TBP \rightleftarrows HA \cdot 2TBP, \text{etc.}$$

causing only minor variation of the hydrophobic properties of the solvates.

As shown by Bieganowska (*14*), curved R_M vs log % S lines of the hockey-stick type can be replotted in the coordinate system $R_F(1 - R_F)^{-1} = 1/k' = f(\%S)$ (analogous to that used in gas–liquid studies of solvation effects, e.g., Ref. *15*) to form linear relationships. To illustrate this point, the data of Fig. 4 are replotted in the latter coordinate system (Fig. 5).

Systems of the type investigated seem to be promising for liquid–liquid partition HPLC. When a diluent of low viscosity is used (e.g., an aliphatic hydrocarbon) the addition of ~10% TBP will secure a high extraction ability while the viscosity remains reasonably low. The systems seem to be especially suitable for gradient elution of proton donor solutes (phenols, acids, primary amines, etc.) since the log k' vs log % TBP lines are very steep, especially for polyfunctional compounds, and the selectivity is high as is usual for partition systems with very low mutual solubility of the phases.

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