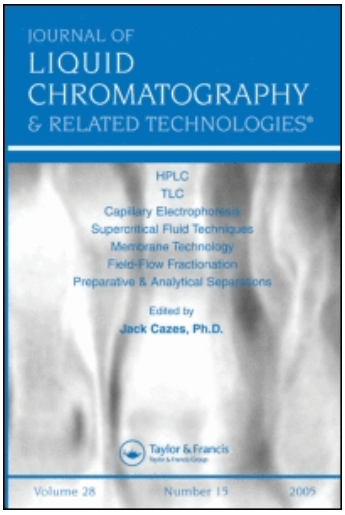

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Quantitative Retention - Eluent Composition Relationships in Liquid Chromatography

E. Soczewinski[a]
[a] Department of Inorganic and Analytical, Chemistry Medical Academy, Lublin, Poland

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QUANTITATIVE RETENTION - ELUENT COMPOSITION RELATIONSHIPS IN LIQUID CHROMATOGRAPHY

E. Soczewiński

Department of Inorganic and Analytical Chemistry

Medical Academy

Staszica 6 St.

20-081 Lublin, Poland

ABSTRACT

Mechanistic molecular models of liquid-liquid and liquid-solid equilibria are discussed for common types of liquid chromatography systems. In spite of the assumed simplifications (e.g., use of concentrations in the definition of equilibrium constants) the approximate formulas for retention-eluent composition relationships are satisfactory for the preliminary optimization of TLC and HPLC systems; the molecular structure of the solute is indirectly expressed by the equilibrium constants and slopes of the plots so that graphical analysis of the relationships may provide information about the chromatographed compounds. It is demonstrated that, depending on the system type, the R_M (log k') values are often a linear function of concentration of the modifier either in linear or in logarithmic scale.

INTRODUCTION

The goal of chromatographic processes, resolution, is described by the well-known Purnell equation:

$$R_S = \frac{\sqrt{n}}{4} \cdot \frac{\alpha-1}{\alpha} \cdot \frac{k'}{1+k'}$$

the three terms of which refer, respectively, to the column efficiency (n - number of theoretical plates), selectivity of the system and the fraction of the more retained analyte in the stationary phase. The third term, which varies from 0 to 1, can be most easily controlled in liquid chromatography by the composition of the eluent; in fact, practically all eluents used are mixed solvents, since even the so-called pure solvents con-

tain water which can strongly influence eluent strength, even at the ppm level for non-polar solvents (1, 2). The range of optimal k' values is rather narrow since, for too low values, the third term also becomes low and, for high k' values, the retention times are too long and the peaks become more diffuse.

The second term, selectivity, is also a function of eluent composition; even low concentrations of certain reagents which influence the selective equilibria of ionization, ion pairing, solvation or other complexation reactions can strongly increase the selectivity of retention.

The first term is less directly related to the eluent composition, whose effect on the column efficiency can, for instance, be analyzed in terms of changes in viscosity and k' values (3, 4).

Therefore, it is essential to formulate, wherever possible, quantitative relationships between the retentions of analytes and the eluent composition.

There are several levels of description of chromatographic systems. In the period of domination of paper chromatography and thin-layer chromatography, many recipes were published for eluents which were frequently mixtures of 3-5 solvents, chosen at random from the eluotropic series. The systems were often not suitable for other kinds of paper or adsorbent and required corrections. Some recipes were found to be suitable also for other analytes of analogous properties and, thus, certain eluents (e.g., the Partridge system, butanol-acetic acid-water; or chloroform-ethanol-diethylamine) were accepted as typical for whole groups of compounds. Some solvent systems found suitable for paper chromatography were adapted to TLC on silica, although they were not optimal ones from the viewpoint of stability, viscosity, toxicity etc.

Further description of eluent is obtained when the solvent systems of a given type are more fully characterized in the form of quantitative relationships between the retention parameters (R_F, V_R, k', log k', etc.) and the eluent composition. This form of characterization (e.g., retention versus concentration of ethyl acetate for series of systems of the type

silica - heptane + ethyl acetate) gives a very good orientation in the properties of the systems and in the optimization of retention and selectivity for varying conditions of chromatographic analysis.

The development of HPLC has demonstrated that the eluent composition can frequently be simplified to binary mixtures (5, 6) (composed of solvents of different polarity, e.g., diluent + polar solvent for silica, or water + methanol for ODS-silica); only subtle control of selectivity may require the addition of a third component (7). For practical reasons it is advisable that retention and eluent composition are expressed in simple, convenient units; on the other hand, it is advantageous to have simple linear relationships which would permit interpolation and even extrapolation of the data.

Examples of early retention-eluent composition relationships can be found in Ref. (8), (R_F of amino acids as function of percent water in eluent) and (9), (R_F vs. pH curves of amino acids). For fundamental processes, such as liquid-liquid partition, such relationships were reported still earlier (10, 11).

It is the purpose of the present review to summarize some quantitative retention versus eluent composition relationships reported for commonly used types of liquid-liquid and liquid-solid chromatography systems. The theoretical models will be limited to the simplest ones (e.g., law of mass action considered in terms of concentrations), bearing in mind the reluctance of practical chromatographers to study more sophisticated and, thus, complex theories as well as the complexity of the chromatographic processes in general which cause the physical parameters to become less definite. The considerations are, thus, largely limited to the first stage of optimization of the chromatographic system.

The fundamental theory of retention is common for TLC and HPLC; however, in the former technique the specific phenomena such as solvent demixing and preadsorption of solvent vapours introduce specific distortion of the process (5, 12-14). Retention versus eluent composition relationships are frequently expressed by one of two equations (15, 16):

$$\log k' = a + b \log c \quad \text{(Type I)} \quad (1)$$

$$\log k' = a + b\, c \quad \text{(Type II)} \quad (2)$$

where c is concentration of the modifier in the eluent (polar solvent, ion-pairing reagent, hydrogen ions, counter ions etc.). Equation of Type I is typical for systems in which the additive (modifier) interacts with the analyte in a reversible reaction obeying the law of mass action or the analyte and modifier compete for active sites in an adsorbent or ion exchanger.

LIQUID-LIQUID PARTITION SYSTEMS

Although mixed retention mechanisms are the rule (even adsorption + partition + ion exchange + size exclusion!), under certain conditions one predominates; it is thus permissible to discuss, separately, liquid-liquid and liquid-solid systems.

Liquid-liquid systems can be formed in-situ by preferential sorption of one of the eluent components which fills the pores of the active solid or forms a gel stationary phase (polyamide, cellulose); or by impregnation of the support with the stationary, non-volatile liquid diluted with a volatile solvent.

Relationships of Type II were reported for numerous systems of the type paraffin oil - water + methanol (Fig. 1) (17) and the linearity of the plots was utilized to determine R_M values beyond the optimal range by extrapolation (18). Actually, the relationship, derived originally for ideal mixtures of solvents (10, 19), was found to describe well such strongly non-ideal mixed phases as water + dimethyl sulphoxide (Fig. 2)(20), water + acetone, water + methanol, water + acetonitrile (also for liquid-solid systems, see below) (16).

Relationships of Type I are also popular, especially in cases where the overall partition equilibrium involves secondary equilibria which can be described by the law of mass action. The following types of systems can be given as examples:

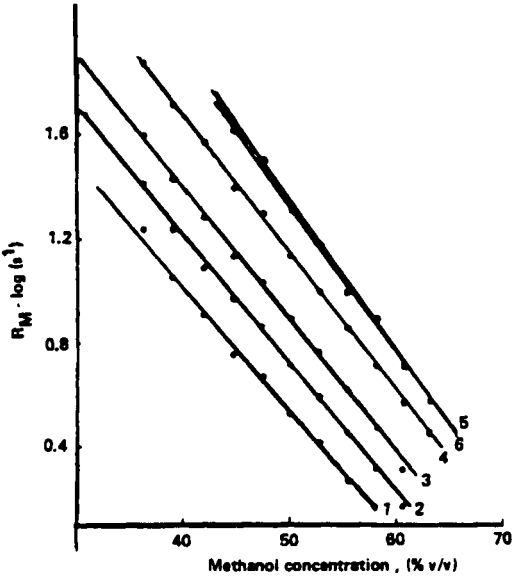

Figure 1. R_M vs. % MeOH plots of promazines. Stationary phase: oleyl alcohol (17). For experimental details for this and following figures, see original papers.

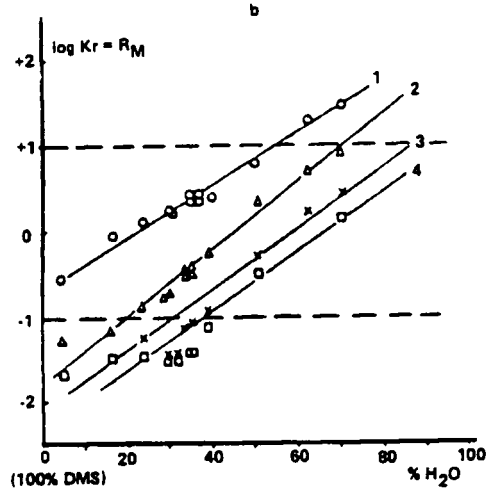

Figure 2. Analogous plots of dihydroxydibenzofurans. Partition system: H_2O + Me_2SO (stationary phase) - Bu_2O (eluent) (20).

a. *Buffered aqeuous phase as eluent (RP system)*

The partition equilibrium can be represented as follows:

$$\begin{array}{l} HA_{org} \rightleftharpoons HA_{w} \xrightleftharpoons{K_A} H^+ + A^- \ w \ (mob.) \\ \qquad\qquad\qquad\qquad org \ (stat) \end{array} \qquad K_A = \frac{[H^+]\,[A^-]}{[HA]} \qquad k_d = \frac{[HA]_{org}}{[HA]_w}$$

the overall equilibrium is represented by the reaction

$$A^-_w + H^+_w \rightleftharpoons HA_{org}$$

with extraction constant

$$E = [HA]_{org}\,[A^-]^{-1}_w [H^+]^{-1}_w \qquad (3)$$

Thus, the distribution coefficient (for $[HA]_{org} \gg [HA]_w$*)*

$$D = [HA]_{org}\,[A^-]^{-1}_w = E\,[H^+] \qquad (4)$$

$$k' = DV_{org}\,V_w^{-1} = const.\,[H^+] \qquad (V_{org}\,V_w^{-1} = \text{phase ratio})$$

$$R_M = \log k' = const + \log [H^+] = const - pH \qquad (5a)$$

The constant in equation 5a includes the partition coefficient of the unionized electrolyte (k_d) *and its ionization constant* K_A *so that any differences in these parameters determine the selectivty of separation (21, 22).*

For bases, a symmetrical equation is obtained

$$R_M = \log k' = const + pH \qquad (5b)$$

Analogous relationships were also reported for straight-phase systems, the signs before pH being then reversed (21-23). For pH values in the proximity of pK_A*, the straight line deviates to a horizontal asymptote owing to suppression of ionization of the electrolyte. An example of relationship of this type is given in Figure 3. For a detailed discussion of systems with buffered aqueous phase, see Ref. (22).*

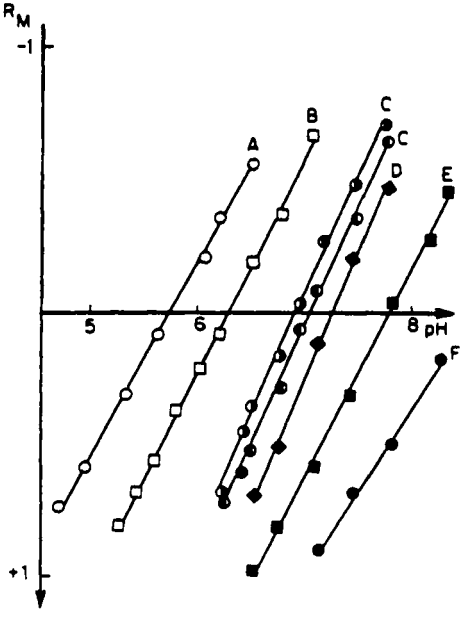

Figure 3. R_M vs. pH plots of Sedum acre L. alkaloids. Partition system: benzene (eluent) - aqueous buffer solution (23).

b. *Solvation systems (e.g., non-polar diluent + polar solvent - formamide)*

By impregnation of cellulose or silica with formamide and elution with binary solvents composed of a non-polar diluent N (heptane) and a solvent capable of H-bonding, S (e.g., chloroform) a series of systems with a broad range of partitioning properties is obtained. The molecular mechanism for a solute Z can be represented as follows:

$$\begin{array}{ccc} Z + nS & \overset{\beta_{ZS_n}}{\rightleftharpoons} & ZS_n \qquad N + S \text{ (mob.)} \\ \updownarrow\, k_d & & \\ Z & & FA \quad \text{(stat.)} \end{array}$$

By analogous consideration we have

$$Z_{FA} + nS_{(mob.)} \rightleftharpoons ZS_{n\ (mob.)}$$

$$E = [ZS_n]_{mob}.[Z]_{FA}^{-1}[S]_{mob}^{-n} \quad (6)$$

$$D = [ZS_n]_{mob}[Z]_{FA}^{-1} = E\,[S]_{mob}^{+n} \quad (7)$$

$$k' = D^{-1}V_{FA}V_{mob}^{-1} = const\,[S]^{-n} \quad (8)$$

$$R_M = \log k' = const - n \log [S] \quad (9)$$

Equation 9 is illustrated in Figures 4 (24) and 5 (25), in which the R_M axis is directed downward so that the plots have positive slopes. The slopes depend on the ability of the solutes to form lower or higher solvates, i.e., on the presence of polar groups and their mutual positions (e.g., intramolecular H-bond between two polar groups prevents them from forming a double solvate). Further examples can be found in Refs. 26, 27.

Actually, gradual shifts of solvation equilibria should be taken into account (e.g., 16, 24), with the slope increasing from zero (low concentrations of solvent S) to the highest value (high concentrations). However, for the

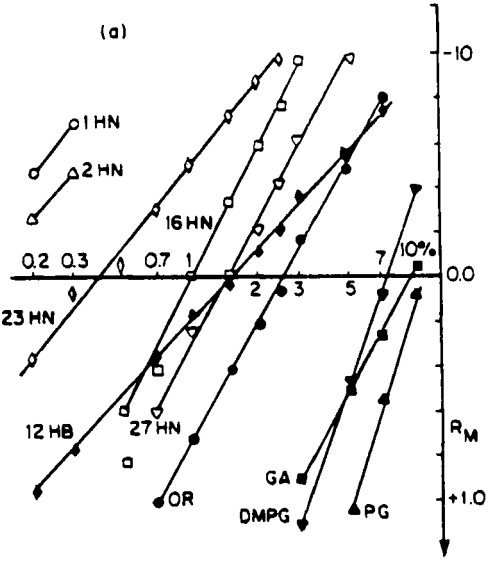

Figure 4. R_M vs. log % TBP plot of phenols. Partition system: cyclohexane + tri-n-butyl phosphate (eluent) - water (24).

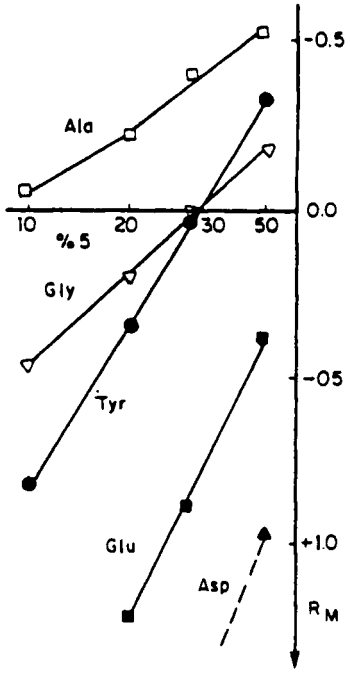

Figure 5. R_M vs. log log % Et_2CO plot of PTH-amino acids. Partition system: toluene + diethyl ketone (eluent) - formamide (25).

narrow range of log k' values essential for optimization, straight log k' vs. log C_S fragments of the general relationship are frequently obtained, owing to the predominance of a single solvate in the narrow concentration range considered. Since the model does not take into account changes of activity coefficients, varying mutual solubility of the two liquid phases and other factors, the slopes of the lines usually do not correspond strictly to the molecular solvation mechanism.

Analogous relationships are obtained for systems in which the stationary phase contains a strongly interacting component, e.g., the R_M values of nitrogen bases are linear function of concentration of formic acid in systems of the type formamide + formic acid (immobilized on cellulose or silica) - weakly polar eluent (28).

c. *Ion association systems*

The partition of organic electrolytes can be varied in wide limits by the addition of ion-pairing and adduct forming reagents (29); for hydrophilic, strongly ionized electrolytes (such as quaternary ammonium salts, sulphonic acids) an ion association mechanism is necessary to secure sufficient extraction by the organic solvent.

The simplest mechanism of partition of analyte ions Q^+ in the presence of counterion X^- can be written as

$$Q^+_w + X^-_w \rightleftharpoons QX_{org}$$

with the extraction constant

$$E = [QX]_{org}[Q^+]_w^{-1}[X^-]_w^{-1} \qquad (10)$$

and the distribution ratio

$$D = [QX]_{org}[Q^+]_w^{-1} = E\,[X^-]_w \qquad (11)$$

As in the former cases, the final conclusion is then

$$R_M = \log k' = \text{const} \pm \log [X^-] \qquad (12)$$

where the sign depends on the system type (straight or reversed phase).

The counterion can be introduced into the system in the eluent or deposited by impregnation as the acid HX or its salt; since the reagent distributes between the two phases according to its partition coefficient, eq. 12 for cases when the reagent is introduced with the less polar phase can be written in analogous form

$$R_M = \log k' = \text{const} \pm \log [HX]_{org} \qquad (13)$$

For a similar case of an anionic (acidic) analyte, quaternary ammonium salts are added as ion-pairing reagents. Examples of retention-composition relationships for ion pair partition systems are given in Figures 6-8 (30-32).

This discussion refers to the simplest case and, frequently, additional effects such as dissociation of ion pairs in the organic phase, association

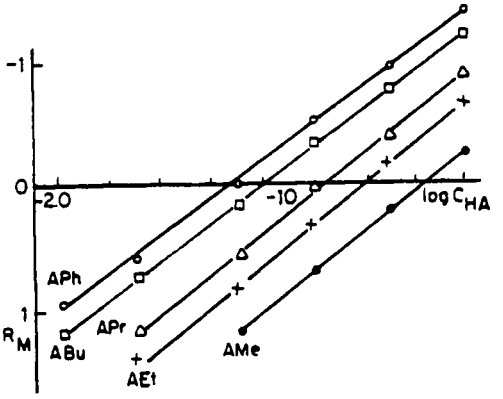

Figure 6. *R_M vs. log [HDEHP] plots of piperidine bases. Partition system: chloroform + di(2-ethyl hexyl) orthophosphoric acid (eluent) - 0.5 M aqueous H_3PO_4(30).*

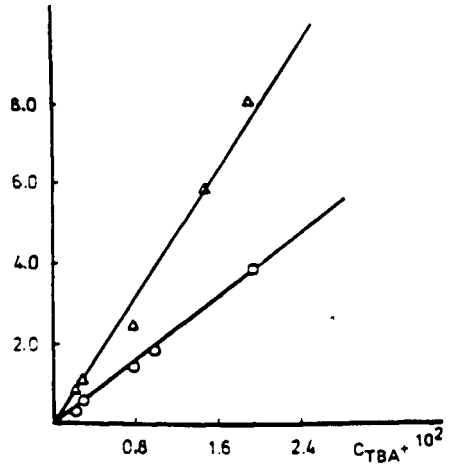

Figure 7. *1/k' values of sulphonic acids plotted against concentration of tetrabutyl-ammonium hydroxide in stationary phase. Eluent: chloroform (31).*

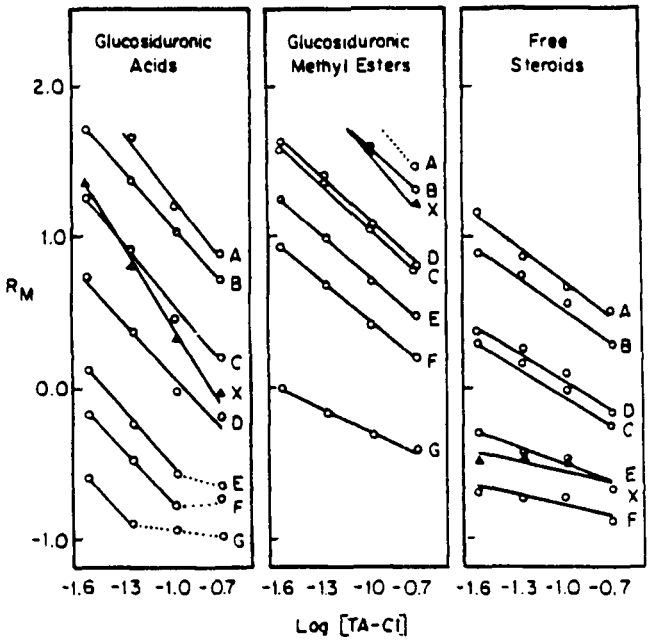

Figure 8. R_M values of glucosiduronic acids, their methyl esters and steroids plotted against concentration of tetraheptylammonium chloride in chloroform (eluent). Stationary phase: formamide (32).

of the ion pair or the ion-pairing reagent, formation of more complex adducts causes deviation from the simple relationships (29, 33).

When the stationary phase is formed by preferential adsorption of some components of the eluent, changes in its composition also causes variation of the composition of the stationary phase so that the retention - eluent composition relationships become more complex, for instance, in the case of TLC on polyamide (34) and in HPLC - when ternary eluents are chosen with compositions corresponding to the binodal curve are used (35). Nevertheless, in these cases, regular log k' vs. log % S plots are sometimes obtained (Fig. 9).

LIQUID - SOLID ADSORPTION SYSTEMS

In liquid-solid TLC (and preparative HPLC) silica remains the most frequently employed adsorbent (36), derivatized silica (mostly of the C-8 &

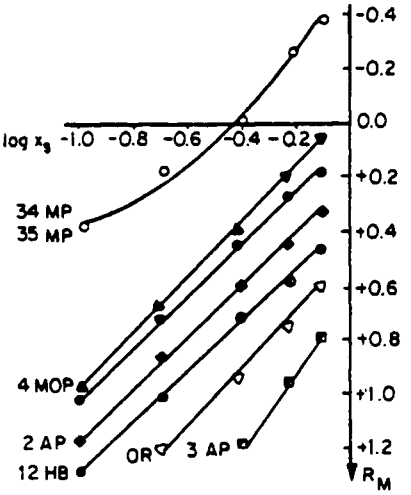

Figure 9. R_M vs. log X_S plots of phenols for the system cyclohexane + diisoamyl ether (S) - polyamide (34).

C-18 type) gaining gradually in importance. In analytical HPLC, the latter types of adsorbents are now predominant (37, 38).

For silica as the adsorbent, the eluent strength can be varied over wide limits using binary mixtures of a non-polar diluent and a polar solvent (e.g., ketone, ester, alcohol etc.); the retention vs. eluent composition relationship is then usually of the first type. On the other hand, non-polar adsorbents (octadecylsilyl silica, Amberlite XAD, carbosils) are usually eluted with aquo-organic solvents, i.e., mixtures of water or aqueous buffer solutions with methanol, acetonitrile and other modifiers. Linear relationships of the second type are then typical. In the case of electrolytes, especially strongly ionized ones, ion pairing reagents are frequently employed, the retention being then controlled by the pH of eluent, concentration of modifier and concentration of ion pairing reagent.

a. *Systems of the type silica - diluent + polar solvent(s)*

It is generally accepted (5, 39, 40) that, for these liquid-solid systems, adsorption of a solute molecule Z is accompanied by displacement of one or more molecules of the polar solvents S from

the surface into the bulk phase. The process can thus be described for the simplest situation, by the reaction

$$\underset{\text{(adsorbent)}}{A\text{-}S} + \underset{\text{(solution)}}{Z} \rightleftharpoons \underset{\text{(adsorbent)}}{A\text{-}Z} + \underset{\text{(solution)}}{S}$$

where A denotes an adsorption site (silanol group for silica). The application of the law of mass action to this reaction results in

$$K = \frac{[AZ]\,[S]}{[AS]\,[Z]} \qquad (14)$$

Thus, for [AS] = const. (i.e., for not too low concentrations of S, e.g., higher than 5%)

$$k' = [AZ]\,[Z]^{-1} = K\,[AS]\,[S]^{-1} \qquad (15)$$

$$R_M = \log k' = \text{const.} - \log [S] \qquad (16)$$

The molecular mechanism of adsorption forms the basic assumption of displacement models proposed by Snyder (6, 40, 41) and Soczewiński (14, 42-44); the latter model differs in several points, e.g., definition of concentration units and formation of discrete silanol-solute and silanol-solvent complexes. For n-point attachment, the equation following from the Snyder-Soczewinski model becomes

$$R_M = \log k' = \text{const.} - n \log [S] \qquad (17)$$

In strict approach, the concentration of polar solvent S in the mobile phase should be expressed in mole fractions. Then

$$R_M = R_{M(S)} - n \log X_S \qquad (18)$$

where the constant, $R_{M(S)}$, corresponds to the extreme right-hand side of the plot (R_M value for pure solvent S, i.e., $X_S = 1.0$). However, only slight deformations are obtained when the more convenient volume composition scale is used (15).

Equation (18) has been confirmed for numerous solute-solvent-adsorbent systems, also including associating (donor-acceptor) polar solvents such as alcohols and polar adsorbents other than silica (florisil, alumina), in spite

of more complex molecular mechanisms. A tabulated survey of linear log k' vs. log % S plots reported by various authors (ca. 40 references, TLC and HPLC) is given in Ref. (14); two plots are illustrated in Figures 10 (43) and 11 (45).

It follows, also, from eq. (15) that

$$(k')^{-1} = R_F (1 - R_F)^{-1} = \text{const. } [S] \qquad (19)$$

which is a simplified form of a relationship reported by Scott and Kucera (46), also convenient for graphical analysis.

Further development of the concepts were reported by Poppe and co-workers who took into account the activity coefficients in the bulk phase (2, 47), Huber et al. (48) and Jaroniec et al. (49), who derived generalized equations for retention - eluent composition relationships. Oscik and Rozylo published

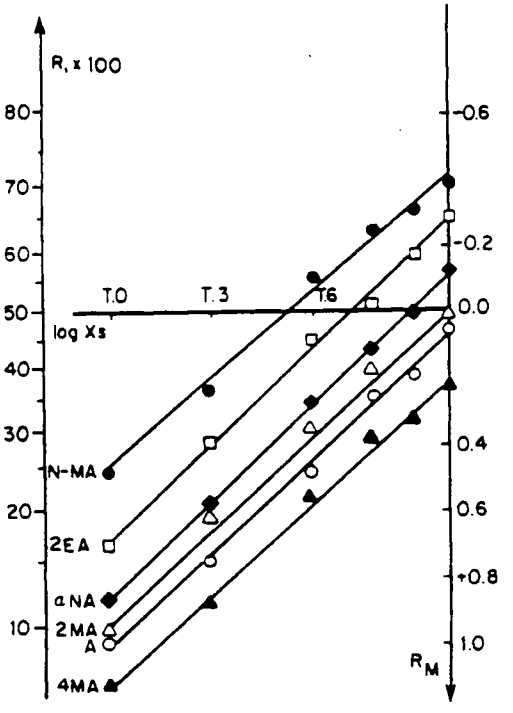

Figure 10. R_M vs. log X_S plots of anilines for the system cyclohexane + di-n-butyl ether (eluent) - silica (43).

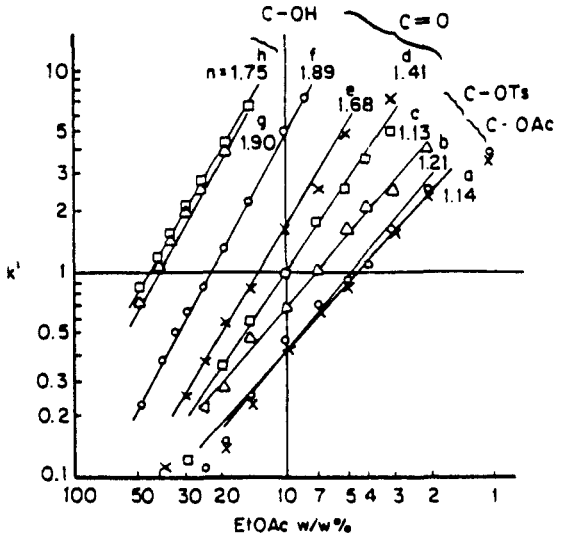

Figure 11. log k' vs. log X_S plots of steroids for the system n-hexane + ethyl acetate (eluent) - silica. HPLC (45).

a series of papers (50, 51 and earlier references cited therein) in which another approach, based on the theory of regular solutions, was used; the conclusions were verified by TLC experiments.

It should be emphasized that, in reality, the solute - diluent - polar solvent - adsorbent systems are very complex (39, 40). The thermodynamic description is difficult owing to the wide ranges of concentrations of the polar solvent and mutual interactions of solute and solvent molecules; the arrangement of silanol groups on the adsorbent surface is irregular and their surface concentration (about 20 nm^2 per one group) is greater than the possible coverage by solute and solvent molecules (40). Especially for donor-acceptor polar solvents, solvation effects in the adsorbent and bulk phase are only partially cancelled. The slopes of the log k' vs. log % S lines are, therefore, only indirectly related to the molecular displacement mechanism and, in wide eluent composition ranges, deviations from linearity are natural.

Equation 17 is not valid for low concentrations of solvent S, when the condition [AS] = const. is not fulfilled (49) (the range of steep adsorp-

tion isotherm of S). The more differentiated log k' vs. log % S relationships in this range are favorable from the viewpoint of selectivity (52).

b. Non-polar adsorbents - aquo-organic eluents

Eluent composition effects are well documented in column chromatography on non-polar adsorbents; RP adsorbents for TLC have only recently became available. Non-polar and weakly-polar solutes are strongly adsorbed from aqueous solutions and are effectively eluted by polar solvents (methanol, acetonitrile) so that retention can be controlled over wide ranges using aqueous solutions of methanol or acetonitrile. As in analogous liquid-liquid RP systems, the retention - eluent composition relationships are frequently described well by the formula of second type, although deviations from linear log k' vs. % H_2O plots have also been reported. Apparently, for water - methanol systems, the plots are more often linear than for water - acetonitrile systems. For instance, Karger et al. (53) reported linear relationships for the whole range of eluent composition for water - methanol mixtures and partly curvilinear plots for the acetonitrile systems, although the deviations from linearity were observed for the range of low k' values. The shape of log k' vs. % H_2O plots depends presumably also on the molecular structure of the solute. Two examples of linear plots are given in Figures 12 (54) and 13 (55). The effect of eluent composition on retention in reversed-phase LC systems and its mechanism has been discussed by Karger et al. (53), Colin and Guiochon (38) and Horvath and Melander (37). The linear relationship has been used by Snyder et al. (56) to formulate a theory of gradient elution in RP systems (see also Ref. 57, 58). An attempt to apply the displacement concept, analogous to that of the Snyder-Soczewiński model, has been reported (59); however, the application of the law of mass action to these systems (aquo-organic eluents) seems to be less justified.

c. Non-polar adsorbents - buffered eluents

Ionization of the solute strongly weakens its hydrophobic interactions with non-polar adsorbents so that its retention can be varied across

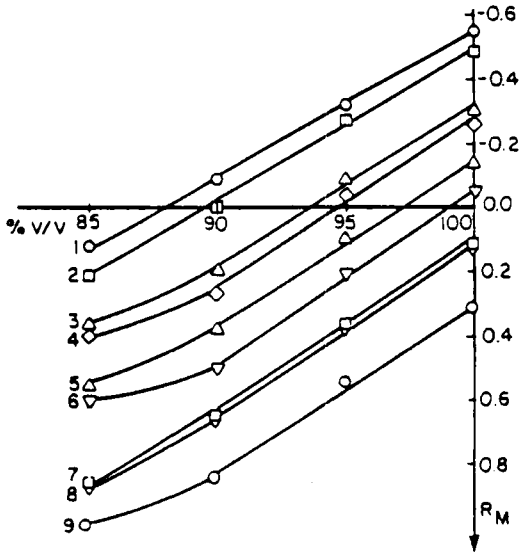

Figure 12. R_M vs. % MeOH plots of aromatic hydrocarbons. Adsorbent - ODS - silica (54).

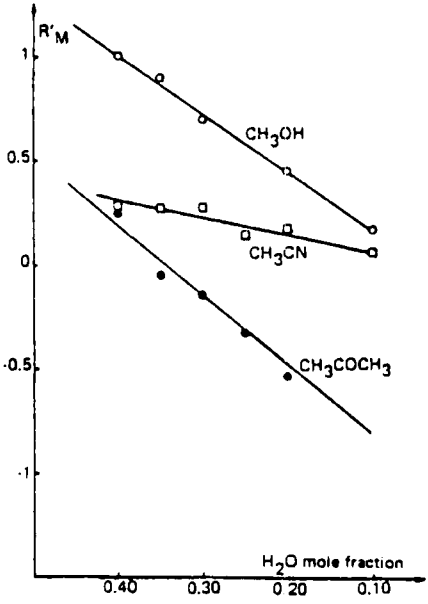

Figure 13. R_M values of pyrene plotted against mole fraction of water for three modifiers: methanol, acetonitrile and acetone. Adsorbent - ODS - silica (55).

broad ranges by using buffered eluents, as in the case of liquid-liquid partition. Thus, relationships analogous to Equation 5a, b should be obtained. Some retention of the ionized form of electrolyte has been reported (60, 61) so that k' > is obtained also for complete ionization. An example is given in Figure 14; since the k' values are plotted in a linear scale, the curves are S-shaped (cf. Ref. 22).

d. Non-polar adsorbents - eluents containing ion-pairing reagents

Ion association systems have become very popular, especially in reversed-phase HPLC; a review of their applications has recently been published by

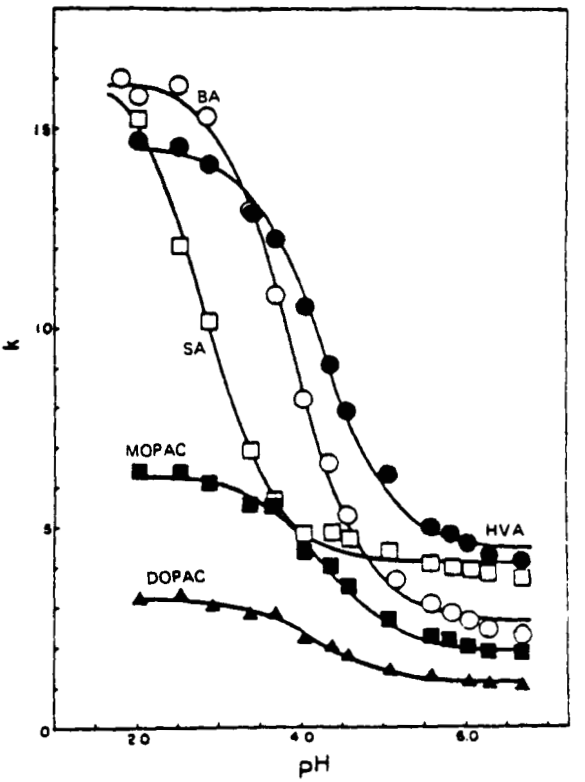

Figure 14. k' vs. pH plots of carboxylic acids for the system aqueous buffer solution (eluent) - ODS silica. HPLC (60).

Tomlinson et al. (33). The adsorption of ionic species is greatly enhanced, especially by formation of ion pairs with hydrophobic counterions such as $C_7H_{15}SO_3^-$, $(C_4H_9)_4N^+$. *The use of ion-pairing reagents of the "liquid ion exchanger" type was first reported for the chromatography of metal ions (62), for some early applications in the chromatography of organic electrolytes cf. Ref. (63) (HPLC) and (64) (paper chromatography). Depending upon the eluent composition, mechanisms ranging from adsorption of ion pairs to liquid-liquid distribution between the mobile phase and stationary phase (formed in the pores of the adsorbent) can be obtained.*

Relationships of the first type, Equation (12), are obtained only for the simplest case of ion-pairing equilibria. As discussed above for liquid-liquid partition systems, additional effects can frequently give more complex relationships, especially in liquid-solid systems (29, 33). Examples of log k' vs. log $[X^-]$ *plots are illustrated in Figure 15 (polar adsorbent) (65), while in Figure 16 (66) other data are represented in a linear coordinate system*

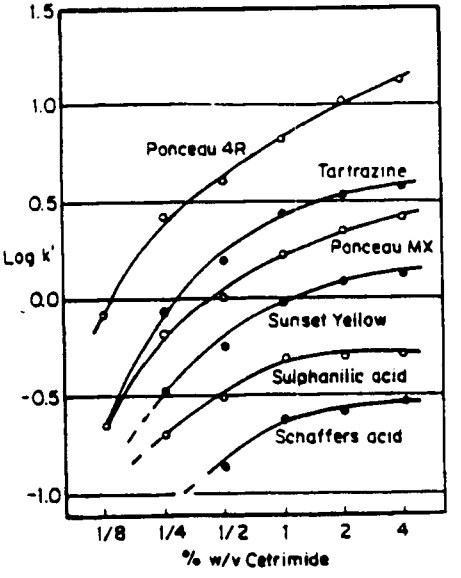

Figure 15. log k' values of dyestuffs and intermediates plotted against log % of cetrimide in 75% aqueous propanol. Adsorbent - silica. HPLC (65).

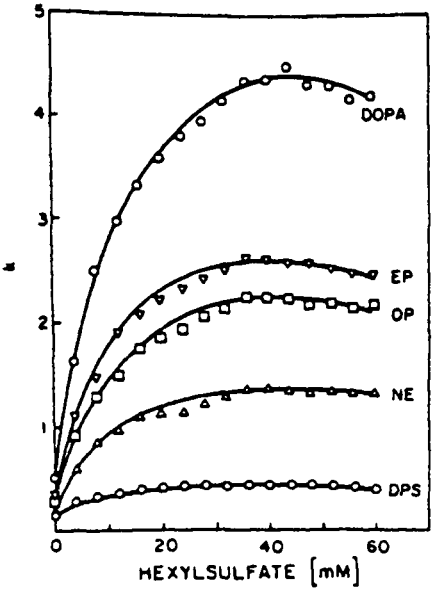

Figure 16. k' values of catecholamine derivatives plotted against concentrations of hexyl sulfate in aqueous eluent. Adsorbent - ODS silica. HPLC (66).

(it follows from Equation 11 that, for the simplest case of reversed-phase systems, k' = const. $[X^-]$).

An analogous association mechanism (however, of the ligand exchange type) has been reported by Karger et al. Solute molecules, e.g., DANS-amino acids, selectively form a complex with 4-dodecyldiethylenetriamine and Zn^{2+} ions, which is strongly adsorbed by the ODS-silica. The exchange and adsorption equilibria are sufficiently rapid and the selectivity of the system is very good, even permitting separation of enantiomers (67).

CONCLUDING REMARKS

The survey of quantitative retention-eluent composition relationships is incomplete owing to the great variety of adsorbent - eluent systems reported so far in the literature (e.g., (68)). Frequently, more complex systems are

employed (for instance, non-polar adsorbent - water + methanol + ion pairing reagent, in which the eluent composition can be varied in two dimensions).

The discussion demonstrated that log k' values (R_M corrected for pre-adsorption effects in TLC) seem to be the most convenient retention parameter in the analysis of quantitative retention-composition relationships, presumably owing to its simple relation to the difference of standard chemical potentials of the solute. The use of the theoretically substantiated plots permits one not only to describe, simply, the properties of the chromatographic system, but also to obtain additional information about the mechanism of retention and, thus, about the molecular structures of the separated compounds. In arbitrary coordinate systems, the analogies and differences of solute behavior are much less obvious (compare Fig. 17 and Fig. 4).

As stated above, the formulas discussed are approximate and linear sections of plots obtained for narrow ranges of determinable k' values and eluent concentrations may, in fact, be parts of curvilinear plots.

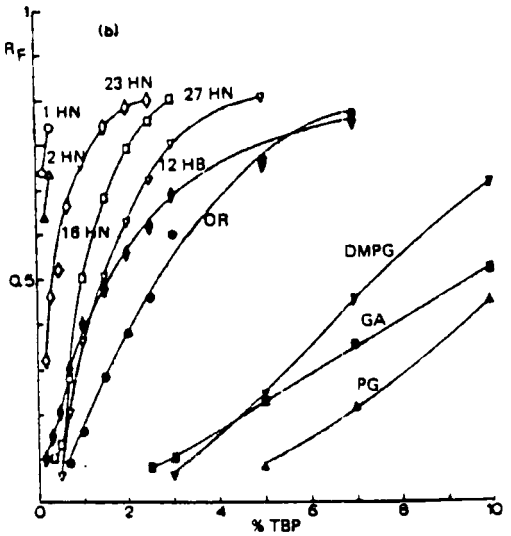

Figure 17. Data of Fig. 4, R_F vs. % TBP plots (24).

For thin-layer chromatography, additional phenomena, which depend upon the technique and experimental conditions, may distort the theoretical relationships; however, under certain conditions, these effects can be limited so that physicochemical conclusions can also be obtained from the less accurate TLC data (14, 49, 69). The effects are less significant for RP adsorbents.

In the author's opinion, the rational use of chromatography requires an understanding of the basic processes, even in simplified form, just as it is necessary to understand acid-base, redox or complexation equilibria to apply titrimetric methods.

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