

CHROM. 4318

A SIMPLE MOLECULAR MODEL OF ADSORPTION CHROMATOGRAPHY

III. SOLVENT COMPOSITION EFFECTS IN THIN-LAYER
CHROMATOGRAPHY OF ACIDIC SOLUTES IN SYSTEMS OF THE TYPE:
ELECTRON DONOR SOLVENT-POLYAMIDE

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SUMMARY

An equation is discussed relating the R_M value of a proton donor solute with the composition of a binary developing solvent system of the type electron donor solvent + neutral diluting solvent. The equation was derived assuming that adsorption of the solute by polyamide is mainly governed by competitive H-bonding between the solute (proton donor) and the solvent and the polyamide (electron donors), the formation of solvation and adsorption complexes being described by the law of mass action. Experimental results for some solvent systems were found to be in agreement with theoretical predictions.

INTRODUCTION

In the preceding papers of this series^{1,2}, the adsorption of the solute was considered as the reversible formation of molecular complexes between the solute, the solvent and the surface groups of the adsorbent, the law of mass action being applied to the H-bonding equilibria.

These considerations were applied to adsorption by silica; the surface silanol groups were considered as one of the components of a non-aqueous solution whose composition was expressed in mole fractions; the fundamental assumption was that the strongest non-solvated functional group of the solute is adsorbed by a non-solvated silanol group (neglecting non-specific solvation due to dispersion forces as much weaker than H-bonding). In other words, it was assumed that the probability of adsorption of a solute molecule by a silanol group, which is at the time H-bonded by a solvent molecule, is greatly diminished in comparison to adsorption by a free silanol group; the adsorption affinity is thus dependent on the fraction of time which an average silanol group spends in the free (not H-bonded) form. Applying the law of mass action to the competitive H-bonding equilibria and assuming certain simplifications, an equation was derived which postulated a linear relationship between the R_M value

and logarithm of the mole fraction of the active solvent in the binary developing solvent¹ and a linear relationship between the R_M values of related organic bases (adsorbed by single point adsorption) and their pK_A values in aqueous solutions².

Silica belongs to a group of adsorbents with predominately proton donor properties³⁻⁵; it, therefore, seemed of interest to investigate whether the law of mass action could also be applied to adsorbents with different properties, first of all to polyamide which is an adsorbent commonly used in TLC, particularly in the chromatography of proton donor solutes, such as phenols, amino acids etc.⁶.

Polyamide has a structure of linear molecules in which the $-\text{CO}-\text{NH}-$ groups are separated by alkyl chains; the molecules are held together by a three-dimensional network of $=\text{NH} \cdots \text{OC}=\text{}$ hydrogen bonds⁶. In adsorption of proton donor molecules, the carbonyl groups play the role of active sites as a result of their increased basicity due to a mesomeric effect (*cf.* ref. 7, for formamide); however, the $=\text{NH}$ groups can also contribute to adsorption properties, although in a minor degree, according to some reports in the literature⁸. Nitrocompounds and some other types of compounds can be also strongly adsorbed by interaction with free amino groups^{6,9}. Certain strong solvents with small molecules (CHCl_3 , CH_2Cl_2 , $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$) can loosen the structure of polyamide forming a gel which can dissolve the molecules of the solute⁶; other solvents, *e.g.*, formic acid, can dissolve the polyamide completely.

From a theoretical viewpoint we shall consider the adsorption of a proton donor solute (class A or AB in the classification proposed by PIMENTEL AND McCLELLAN¹⁰) from a mixed solvent of the N + B type (*i.e.*, diluting solvent, *e.g.*, cyclohexane, mixed with an electron donor solvent, *e.g.*, cyclohexanone). It is assumed that the adsorption of the solute is caused by H-bonding with the polyamide carbonyl groups and that the variation of the solvent composition does not entail changes in the polyamide structure. Under these conditions the scheme of molecular interactions involved can be represented by the diagram in Fig. 1a (solid lines represent H-bonding, dashed lines—dipole-dipole interactions, dotted lines—dispersion forces). Thus, as opposed to the adsorption by silica where the decisive process is competition of solute and solvent for active sites of the adsorbent surface (Fig. 1b), in the case of adsorption on polyamide the governing process is competition of the solvent and active sites for the solute (*cf.* BARK AND GRAHAM¹¹). Solvation of the less strongly adsorbing part of the solute molecule is similar in the adsorbed and non-adsorbed state and thus is

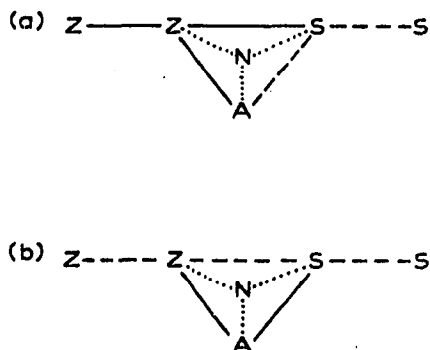


Fig. 1. Diagrammatic representation of interactions involved in adsorption from an electron donor solvent S diluted by an inert solvent N by polyamide (a, proton donor solute) and silica (b, electron donor solute).

largely cancelled (ref. 3 p. 188); association of the solvent S is relatively weak (dipole-dipole interactions) and so is the association of the solute in view of its low concentration and the presence of the electron donor solvent in the solution.

Since in the model considered the solvents are only weakly adsorbed relative to the solute, the Z-S interactions acquire the decisive role, that is to say, the solvation of solute molecules (or rather their active groups); since the same interactions also determine the solubility of the solute in the solvent, the adsorption of the solute can, in these cases, be expected to correlate with its solubility, contrary to the solvent-adsorbent systems in which solvent-solute interactions are of minor importance (see ref. 3, p. 230). In particular, parallelism of adsorption and solubility in a series of binary solvent mixtures could be anticipated (compare ref. 12 for partition and solubility).

As in the preceding papers^{1,2} we will assume the components of the non-aqueous system to be the surface carbonyl groups of the polyamide (A); the developing solvent (N + S); the solute (Z); the complexes AZ (solute molecules immobilized at a given moment by H-bonding with the polyamide); and the (mobile) solvation complexes ZS and ZS₂ (the latter occur in the case of bifunctional solutes, *e.g.*, dihydroxy compounds). Thus, the composition can be expressed in mole fractions as:

$$X_A + X_S + X_N + X_Z + X_{AZ} + X_{ZS} + X_{ZS_2} = 1$$

As before, we can reasonably assume that

$$X_S + X_N \gg X_A \gg X_{AZ} + X_{ZS} + X_{ZS_2}$$

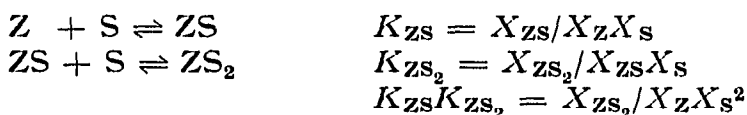
Applying the law of mass action, we have



the adsorption coefficient of solute Z then being

$$k^0 = X_{AZ}/X_Z = K_{AZ} X_A \quad (1)$$

Assuming that the two proton donor groups of the solute are equivalent, we have



The overall distribution coefficient, *i.e.*, the ratio of concentrations of the solute in the stationary phase (AZ) and in the mobile phase (Z, ZS and ZS₂) is

$$\begin{aligned} k &= X_{AZ}/(X_Z + X_{ZS} + X_{ZS_2}) = X_{AZ}/X_Z(1 + K_{ZS}X_S + K_{ZS}K_{ZS_2}X_S^2) \\ k &= k^0/(1 + K_{ZS}X_S + K_{ZS}K_{ZS_2}X_S^2) \end{aligned} \quad (2)$$

$$R_M = \log k = \log k^0 - \log(1 + K_{ZS}X_S + K_{ZS}K_{ZS_2}X_S^2) \quad (3)$$

The terms in the parentheses belong to MICHAELIS' pH-functions for a biprotic electrolyte, and the last equation is analogous to the theoretical R_M vs. pH relationship so that the analysis of the function given in an earlier paper (*cf.* ref. 13 p. 36, 37, eqn. 56) can be applied, assuming that k^0 , K_{ZS} and K_{ZS_2} are constants. Under certain conditions, linear R_M vs. $\log X_S$ relationships are obtained, depending on the relative numerical values of the three terms in the parentheses:

$$\begin{array}{lll} 1 \gg K_{ZS}X_S + K_{ZS}K_{ZS_2}X_S^2 & X_Z \gg X_{ZS} + X_{ZS_2} & \text{slope} = 0 \\ K_{ZS}X_S \gg 1 + K_{ZS}K_{ZS_2}X_S^2 & X_{ZS} \gg X_Z + X_{ZS_2} & \text{slope} = 1^* \end{array}$$

(under these conditions the solute still behaves as a monohydroxy compound)

$$K_{ZS}K_{ZS_2}X_S^2 \gg 1 + K_{ZS}X_S \quad X_{ZS_2} \gg X_Z + X_{ZS} \quad \text{slope} = 2$$

When double solvates cannot be formed ($K_{ZS_2} = 0$), eqn. 3 simplifies to an equation analogous to the R_M vs. pH relationship of a monoprotic electrolyte:

$$R_M = \log k^0 - \log(1 + K_{ZS}X_S) \quad (4)$$

the R_M vs. X_S line then having only two asymptotes: firstly for low X_S values

$$1 \gg K_{ZS}X_S; \quad X_Z \gg X_{ZS}, \quad \text{slope} = 0$$

and secondly at higher concentrations of S:

$$K_{ZS}X_S \gg 1, \quad X_{ZS} \gg X_Z, \quad \text{slope} = 1$$

Theoretical R_M vs. X_S curves are illustrated in Fig. 2 for a monofunctional electrolyte Z' and a bifunctional electrolyte Z'' . The R_M axis is directed downwards so that R_M and R_F both increase.

The above simplified model permits the effect of the molecular structure of the solute, solvent and adsorbent to be expressed as simple physico-chemical parameters, such as the mole fraction of the electron donor solvent, the adsorption coefficient k^0 of the non-solvated (not H-bonded) solute, solvation constants etc.

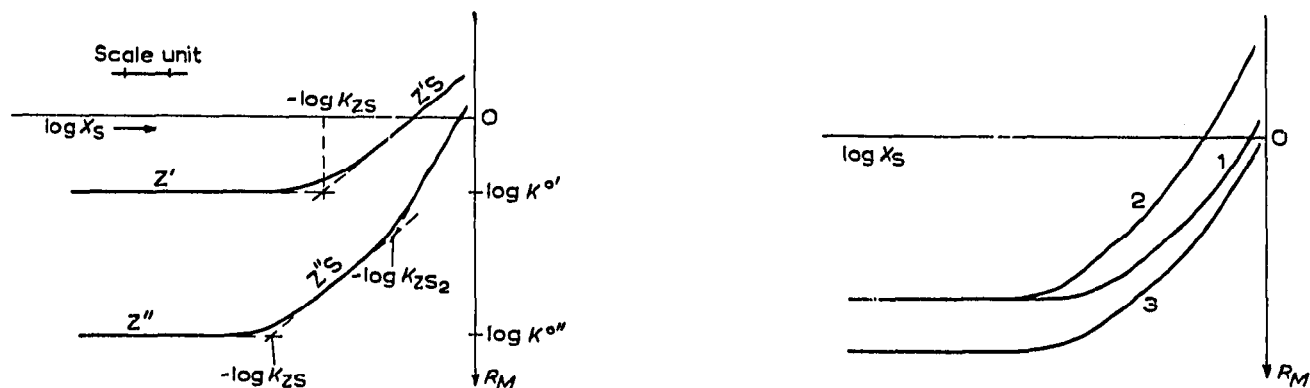


Fig. 2. Idealized R_M vs. $\log X_S$ relationships for a monohydroxyl solute Z' and a dihydroxyl solute Z'' . From TLC data only fragments of the relationships can be obtained (R_M values in the range $-1, +1$).

Fig. 3. Idealized R_M vs. $\log X_S$ relationships of a bifunctional solute adsorbed from three series of binary solvents: N + S (1), N + S' (2) and N' + S (3).

Because the intersection points of the asymptotes are determined by the formation constants of solvation complexes, (Fig. 2), a simple interpretation of the effect of the solvent S is possible: its increased basicity should increase the solvation constants K_{ZS} and K_{ZS_2} , thus shifting the curve to the left so that the $-R_M$ value of the solute increases at lower concentrations of the active solvent. (Fig. 3, compare curves 1 and 2). Substitution of the diluting solvent influences the position and shape of the

* Absolute values of slopes are given.

curve through the values of k^0 , K_{ZS} and K_{ZS_2} . (Fig. 3, compare curves 1 and 3).

However, the simplifying assumptions introduced in the theoretical considerations may cause deviations from anticipated behaviour in real adsorption systems. Among the possible causes of deformation of the theoretical relationship the following should be mentioned:

(1) Formation of composition gradients (demixion) and variation of the ratio of solvent to adsorbent weight along the chromatogram.

(2) Variation of $k^0 = K_{AZ}X_A$ with the composition of the solvent due to:

(a) Changes of the activity coefficients,

(b) Variation of X_A caused by changes in the structure of the adsorbent (*e.g.*, swelling) and by variations of the molar ratio of the solvent and surface adsorbent groups for a series of mixed solvents (see below).

(3) Not only K_{AZ} but also K_{ZS} and K_{ZS_2} may vary with the composition of the solvent.

(4) The =NH groups can also contribute to adsorption, *e.g.*, by H-bonding with the solvent molecules, thus decreasing their concentration in the solution; however, most authors report only a minor contribution due to imido groups (*e.g.*, ref. 8). In addition, some effect due to desorption of the solvent molecules from the polyamide carbonyl groups can be expected; the effect will differ for the diluting solvent N and the electron donor solvent S, since the former interacts by dispersion forces and the second by dipole-dipole interactions (Fig. 1a) and although these two types of interactions are much weaker than H-bonding, the adsorption of the solute Z is, nevertheless, probably weakened at higher X_S values in view of the competition of the solvent S for active sites on the adsorbent surface. Consequently, increase of X_S may cause increased desorption of the solute not only by stronger solvation of its proton donor groups (formation of ZS and ZS₂ complexes) but also by increased competition of the solvent for the active sites. The latter effect results in k^0 , the adsorption coefficient of non-solvated molecules of the solute, possibly being a decreasing function of X_S .

Since the problem of solvent composition effects has been considered from the viewpoint of its application to the theory of thin-layer chromatography, the practical applicability of the theoretical relationships was tested using the TLC technique, although more precise and reliable results could be obtained from column chromatography experiments where at least the evaporation of the solvent and gradient effects can be eliminated³.

Solvent composition effects have great theoretical and practical significance since most developing liquids employed in liquid chromatography are mixed solvents. Before discussion of our experimental results, it is worthwhile discussing this briefly and comparing other approaches to this problem.

SNYDER³ derived the following fundamental equation by applying the law of mass action to the displacement of solvent by solute from the adsorbent surface and assuming two-phase partition:

$$R_M = \log (V_a W / V^0) + \alpha (S^0 - A_S \epsilon^0) \quad (5)$$

where:

V_a = volume of adsorption layer, proportional to the specific surface area of the adsorbent

- W = weight of adsorbent
 V^0 = volume of solvent
 α = adsorbent surface activity function
 S^0 = adsorption energy of solute on adsorbent of unit activity ($\alpha = 1.00$) from pentane solutions ($\varepsilon^0 = 0$)
 A_S = area occupied by adsorbed solute molecules (in 8.5 \AA^2 units)
 ε^0 = solvent strength parameter.

In systems of the type silica–electron donor solvent, anomalously large values of A_S are obtained so that the parameter loses its simple physical sense (ref. 3, p. 202).

In the case of binary developing solvents composed of an inert diluting liquid and a strong solvent B ($\varepsilon_b^0 \gg \varepsilon_a^0$), and moderately large mole fractions of B, the solvent strength of the mixed solvent is given by the approximate equation (ref. 3, eqn. 8–10a):

$$\varepsilon_{ab}^0 = \varepsilon_b^0 + \frac{\log X_b}{\alpha n_b} \quad (6)$$

where X_b denotes mole fraction of the strong solvent and n_b the area occupied by a single solvent molecule (in 8.5 \AA^2 units equal to $1/6$ of the area of benzene molecule). Combining the last two equations, we have

$$R_M = \log (V_a W / V^0) + \alpha S^0 - \alpha A_S \varepsilon_b^0 - \frac{A_S}{n_b} \log X_b \quad (7)$$

Assuming that the molecules of the solvent and solute displace each other in a 1:1 ratio, the R_M value should be linearly dependent on $\log X_b$, the slope being 1. The remaining terms express various parameters determining the absolute value of R_M , *i.e.*, adsorption affinity of the solute (S^0) and solvent (ε_b^0) etc. However, the last equations mainly refer to situations where the governing process is the competition between the solute and solvent for the adsorbent surface.

OŚCIK *et al.*^{14,15} applied the thermodynamic theory of conformational solutions to the analysis of solvent composition effects deriving the following equation for the adsorption of solutes from binary solvents:

$$R_M = u_1 R_{M(1)} + u_2 R_{M(2)} + (u_1^s - u_1) (\log k_{1,2}^{\infty} + R_{M(1)} - R_{M(2)}) + Y \quad (8)$$

where the subscript 1 denotes the active solvent (S) and 2—the diluting solvent (N), u denotes volume fraction of the solvent, u_1^s —volume fraction of the solvent in the surface layer and $k_{1,2}^{\infty}$ is the hypothetical partition coefficient of the solute between solvents 1 and 2 (at a first approximation equal to the ratio of the partition coefficients of the solute in two partition systems: 1/water and 2/water, provided that solvents 1 and 2 are immiscible with water). Y is a function of u_1 ; however, for conformational solutions its maximum value does not exceed $0.075 R_M$ units and thus its omission does not introduce any significant error in most cases. The effects determining adsorption are expressed here by different parameters, thus, the adsorption affinity of the solute from pure component solvents is expressed by the values of $R_{M(1)}$ and $R_{M(2)}$; differences in solvation of the solute by the two solvents are reflected by the value of $k_{1,2}^{\infty}$; and the difference $u_1^s - u_1$ reflects the effect of the shape of the adsorption isotherm of the solvent S from solutions in the diluting solvent N. For dilute solutions of the active solvent (*i.e.*, $u_1 \rightarrow 0$) it may be assumed that $u_1^s \gg u_1$ and since the initial

part of the adsorption isotherm is usually linear ($u_1^s = \text{const} \cdot u_1$), it follows that

$$R_M \doteq u_1 R_{M(1)} + u_2 R_{M(2)} + \text{const} \cdot u_1 \quad (9)$$

that is to say, R_M is then a linear function of u_1 . For higher concentrations of the strong solvent the R_M vs. u_1 relationships were found to be parabolic in shape¹⁵ and tend to straighten in R_M vs. $\log u_1$ plots (cf. ref. 16).

EXPERIMENTAL

The phenols and their derivatives were chromatographed on thin layers of polyamide (polyamid-pulver, Merck AG, Darmstadt, G.F.R.). The polyamide was mixed with 45 ml of a 3:2 mixture of CH_3OH and CHCl_3 and spread over 18×19 cm glass plates in layers ca. 0.1 mm thick, excess solvent was evaporated and the plates heated for 15 min at 80° ¹¹. After spotting the samples, the plates were conditioned for 1.5 h in the tanks and developed with binary mixed solvents; the spots were detected

TABLE I

SLOPES OF R_M vs. $\log X_S$ LINES FOR VARIOUS ELECTRON-DONOR SOLVENTS (S) DILUTED WITH CYCLOHEXANE

Solute	Electron-donor solvent						
	Acetone	Methyl ethyl ketone	Dioxane	Cyclohexanone	Tetrahydrofuran	Diethyl ketone	
Phenol	P	2.0	1.6	1.3	1.0	1.0	0.9
<i>o</i> -Cresol	2MP	2.0	1.6	1.4	1.0	0.8	—
<i>m</i> -Cresol	3MP	2.0	1.6	1.4	1.0	0.8	—
<i>p</i> -Cresol	4MP	2.0	1.6	1.7	1.0	0.9	—
2,3-Xylenol	23MP	2.0	1.6	1.2	1.0	0.8	0.8
2,4-Xylenol	24MP	2.0	1.6	1.2	1.0	0.8	0.8
2,5-Xylenol	25MP	2.0	1.6	1.2	1.0	0.8	0.9
2,6-Xylenol	26MP	—	—	—	—	0.8	—
3,4-Xylenol	34MP	2.0	1.6	1.2	1.0	0.8	0.9
3,5-Xylenol	35MP	2.0	1.6	1.2	1.0	0.8	0.9
Pyrocatechol	12HB	3.1	2.0	—	1.8	—	1.3
Resorcinol	13HB	3.8	2.0	—	2.0	—	—
Hydroquinone	14HB	3.8	2.0	—	—	—	1.4
Phloroglucinol	135HB	5.4	—	—	2.7	—	—
Pyrogallol	123HB	—	—	—	—	2.6	—
<i>p</i> -Methoxyphenol	13MOP	2.0	1.4	—	0.9	—	—
Orcinol	OR	—	2.2	2.0	1.5	2.5	—
(3,5-dihydroxytoluene)							
<i>o</i> -Nitrophenol	2NP	1.8	—	—	—	1.0	—
<i>p</i> -Nitrophenol	4NP	2.1	2.0	2.0	1.0	0.8	—
<i>m</i> -Aminophenol	3AP	2.7	—	—	1.4	—	—
<i>p</i> -Aminophenol	4AP	3.0	—	—	1.6	—	—
<i>o</i> -Chlorophenol	2CP	—	1.3	0.9	0.7	2.4	—
<i>p</i> -Chlorophenol	4CP	—	1.5	0.9	0.7	2.4	—
1-Naphthol	1HN	1.9	1.4	0.9	0.7	2.4	—
2-Naphthol	2HN	1.9	1.4	0.9	0.7	2.4	—
1,6-Hydroxynaphthalene	16HN	3.9	2.1	2.0	2.0	4.0	—
2,7-Hydroxynaphthalene	27HN	3.9	2.1	2.0	2.0	4.0	—

TABLE II

 $R_M \times 100$ VALUES FOR VARIOUS MOLE FRACTIONS OF THE ACTIVE SOLVENT

Solute		Mole fractions of acetone					Mole fractions of methyl ethyl ketone					Mole fractions of diethyl ketone			
		0.2	0.35	0.5	0.65	0.8	0.1	0.2	0.4	0.6	0.8	0.2	0.4	0.6	0.8
phenol	P	13	30	51	62	70	9	23	48	62	—	28	41	50	56
Cresol	2MP	19	38	57	68	76	11	25	52	65	—	31	42	49	58
-Cresol	3MP	18	37	54	65	74	12	28	53	67	—	31	43	49	58
Cresol	4MP	12	29	49	61	70	8	21	47	61	—	30	41	48	57
3-Xylenol	23MP	21	43	61	70	80	14	32	55	71	—	37	48	57	64
4-Xylenol	24MP	21	43	61	70	80	14	32	55	71	—	37	48	57	64
5-Xylenol	25MP	21	43	61	70	80	14	32	55	71	—	37	48	57	64
4-Xylenol	34MP	25	47	67	77	—	15	30	54	70	75	38	54	60	65
5-Xylenol	35MP	25	47	67	77	—	15	30	54	70	75	38	54	60	65
pyrocatechol	12HB	—	13	31	53	68	—	5	18	33	46	8	17	23	33
resorcinol	13HB	—	8	25	45	63	—	5	15	29	43	—	—	—	—
hydroquinone	14HB	—	10	33	56	—	—	5	17	31	43	7	15	24	35
chloroglucinol	135HB	—	—	10	30	52	—	—	—	—	—	—	3	7	14
pyrogallol	123HB	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Methoxyphenol	13MOP	14	33	53	66	—	—	29	48	60	71	—	—	—	—
resorcinol															
2,5-dihydroxytoluene)	OR	—	—	—	—	—	—	5	15	31	47	—	—	—	—
Nitrophenol	2NP	30	53	67	79	—	—	—	—	—	—	—	—	—	—
Nitrophenol	4NP	7	16	30	45	—	—	6	21	38	49	—	—	—	—
-Aminophenol	3AP	5	16	37	57	—	—	—	—	—	—	—	—	—	—
Aminophenol	4AP	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Chlorophenol	2CP	—	—	—	—	—	14	20	38	50	59	—	—	—	—
Chlorophenol	4CP	—	—	—	—	—	12	15	33	49	58	—	—	—	—
Naphthol	1HN	15	33	49	61	70	12	20	39	56	66	—	—	—	—
Naphthol	2HN	13	28	44	56	65	9	18	35	53	63	—	—	—	—
6-Hydroxynaphthalene	16HN	—	6	16	38	58	—	—	10	22	33	—	—	—	—
7-Hydroxynaphthalene	27HN	—	8	21	42	62	—	—	12	25	38	—	—	—	—

by coupling with bis-diazotized benzidine. The experimental results are presented in Figs. 4-9 as R_M vs. $\log X_S$ plots and are averages from three chromatograms.

RESULTS AND DISCUSSION

The solutes are denoted by symbols (P = phenol, N = naphthalene, M = methyl, H = hydroxyl etc.; where 1,6 HN = 1,6-dihydroxynaphthalene, see Table I). The R_M value is defined according to BATE-SMITH AND WESTALL. The experimental results are presented in Tables II, III and in Figs. 4-9.

The results obtained for the system cyclohexane + acetone are plotted in Fig. 4. Although linear R_M vs. $\log X_S$ relationships are observed, the slopes of the lines are not in agreement with theoretical predictions: Thus, for monohydroxyl compounds possessing additional weakly adsorbing groups ($-\text{CH}_3$, $-\text{OCH}_3$, $-\text{NH}_2$, $-\text{NO}_2$) the slopes exceed the expected values by 100% ($n = 2$, cf. Table I). Also in the case of dihydroxy compounds the slopes are higher than expected ($n = 4$ instead of 2), except for pyrocatechol where $n = 3$, i.e., exceeds the expected value by 50%.

For systems of the type cyclohexane-methyl ethyl ketone (Fig. 5) the slopes

TABLE III

 $R_F \times 100$ VALUES FOR VARIOUS MOLE FRACTIONS OF THE ACTIVE SOLVENT

Solute		Mole fractions of dioxane					Mole fractions of cyclohexanone				Mole fractions of tetrahydrofuran							
		0.1	0.2	0.4	0.6	0.8	0.2	0.4	0.6	0.8	0.1	0.2	0.3	0.4	0.45	0.6	0.7	0.8
Phenol	P	13	27	47	63	—	35	50	60	65	16	27	38	—	42	58	63	78
<i>o</i> -Cresol	2MP	10	26	47	66	—	38	54	62	68	22	32	41	—	44	63	68	83
<i>m</i> -Cresol	3MP	12	26	49	63	—	35	50	60	65	19	26	37	—	43	62	66	82
<i>p</i> -Cresol	4MP	10	24	50	66	—	33	48	56	62	18	24	36	—	42	59	63	78
<i>o</i> , <i>m</i> -Xylenol	23MP	18	35	56	68	—	41	59	67	75	25	34	43	—	52	65	68	85
<i>o</i> , <i>p</i> -Xylenol	24MP	18	35	56	68	—	41	59	67	75	25	34	43	—	52	65	68	85
<i>m</i> , <i>p</i> -Xylenol	25MP	18	35	56	68	—	41	59	67	75	23	31	42	—	51	62	66	84
<i>o</i> , <i>m</i> , <i>p</i> -Xylenol	26MP	—	—	—	—	—	—	—	—	—	42	52	60	—	65	80	80	80
<i>o</i> , <i>p</i> -Xylenol	34MP	23	43	63	72	—	39	55	63	70	23	33	44	—	48	60	68	84
<i>m</i> , <i>p</i> -Xylenol	35MP	23	43	63	72	—	39	55	63	70	23	33	44	—	48	60	68	84
Pyrocatechol	12HB	—	—	—	—	—	8	23	40	51	—	8	—	21	—	59	—	80
Resorcinol	13HB	—	—	—	—	—	6	19	35	50	—	2	—	8	—	42	—	72
Hydroquinone	14HB	—	—	—	—	—	—	—	—	—	—	7	—	16	—	50	—	77
Phloroglucinol	135HB	—	—	—	—	—	2	8	20	35	—	—	—	4	—	20	—	60
Pyrogallol	123HB	—	—	—	—	—	—	—	—	—	—	—	—	5	—	11	25	32
<i>o</i> -Methoxyphenol	13MOP	35	50	60	63	—	40	55	62	68	—	5	—	12	—	29	—	51
Creinol																		
3,5-dihydroxy-toluene)	OR	—	3	15	30	43	9	20	33	42	—	5	8	—	13	30	38	48
<i>o</i> -Nitrophenol	2NP	—	—	—	—	—	—	—	—	—	—	56	—	71	—	76	—	83
<i>m</i> -Nitrophenol	4NP	—	2	12	23	36	14	25	35	40	5	8	11	—	18	35	38	42
<i>p</i> -Aminophenol	3AP	—	—	—	—	—	24	46	61	68	—	5	—	19	—	39	—	65
<i>m</i> -Aminophenol	4AP	—	—	—	—	—	25	53	68	75	—	—	—	—	—	—	—	—
<i>o</i> -Chlorophenol	2CP	19	31	46	55	62	39	50	58	62	—	20	—	51	—	77	—	86
<i>m</i> -Chlorophenol	4CP	18	29	45	54	60	42	55	62	67	—	21	—	53	—	78	—	87
<i>p</i> -Naphthol	1HN	19	31	46	55	62	43	55	62	67	10	25	—	56	—	80	—	87
<i>m</i> -Naphthol	2HN	18	28	45	54	60	42	51	60	64	8	18	—	50	—	78	—	87
<i>o</i> , <i>m</i> -6-Hydroxy-naphthalene	16HN	—	—	13	23	36	4	12	26	40	—	—	—	8	—	31	—	57
<i>o</i> , <i>m</i> , <i>p</i> -7-Hydroxy-naphthalene	27HN	—	6	20	31	46	5	17	33	48	—	3	—	11	—	35	—	61

are lower but still deviate from the expected values. Better results were obtained with diethyl ketone (Fig. 6), and especially with cyclohexanone (Fig. 7) when the monophenols with additional $-\text{CH}_3$ or $-\text{OCH}_3$ groups have unit slopes; for dihydroxy-benzenes the slope is 2 and for the trihydroxy-benzenes 2.7 which approaches the expected value of 3.0. Good agreement with theoretical predictions was obtained with dioxane for dihydroxy-benzenes and some monohydroxy-phenols (Fig. 8). The data are incomplete because some of the dihydroxy compounds gave low R_F values so that their R_M vs. $\log X_S$ relationships could not be determined.

In the case of pyrocatechol (1,2-dihydroxy-benzene) the slope was lower than for the remaining dihydroxy compounds, presumably due to an *ortho*-effect. ENDRES¹⁷ has reported that in an aqueous system pyrocatechol behaves like a monophenol and explained this by the formation of an internal H-bond. In our experiments (non-aqueous systems) pyrocatechol gave slopes intermediate between those of monohydroxy- and dihydroxy-compounds.

For cyclohexane + tetrahydrofuran mixtures linear relationships of unit

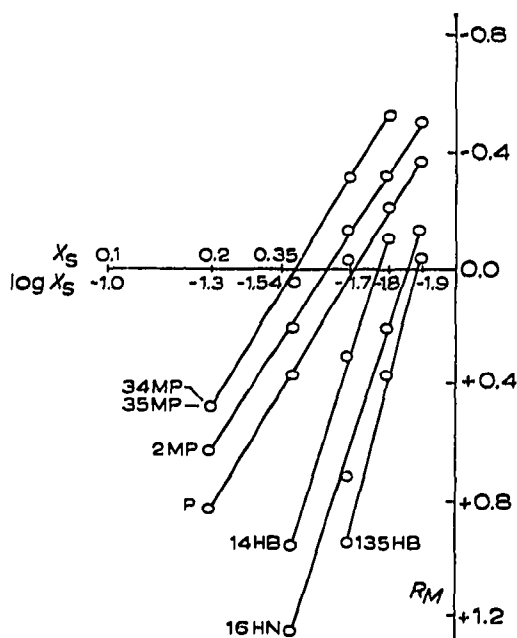


Fig. 4. Experimental R_M vs. $\log X_S$ relationships for developing solvents composed of cyclohexane and acetone. See Table I for notation of solutes.

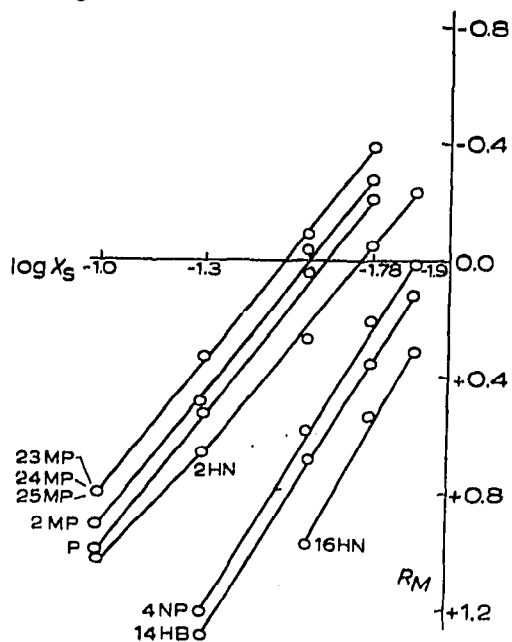


Fig. 5. Experimental R_M vs. $\log X_S$ relationships for developing solvents composed of cyclohexane and methyl ethyl ketone.

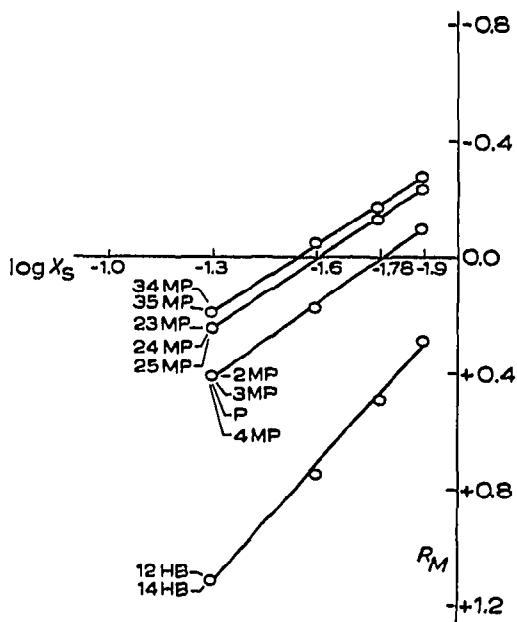


Fig. 6. Experimental R_M vs. $\log X_S$ relationships for developing solvents composed of cyclohexane and diethyl ketone.

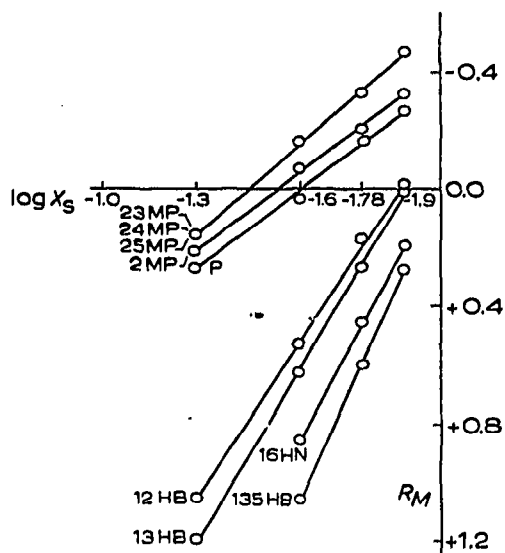


Fig. 7. Experimental R_M vs. $\log X_S$ relationships for developing solvents composed of cyclohexane and cyclohexanone.

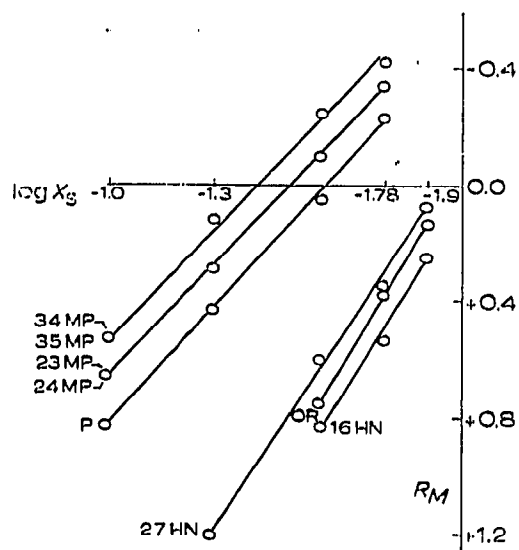


Fig. 8. Experimental R_M vs. $\log X_S$ relationships for developing solvents composed of cyclohexane and dioxane.

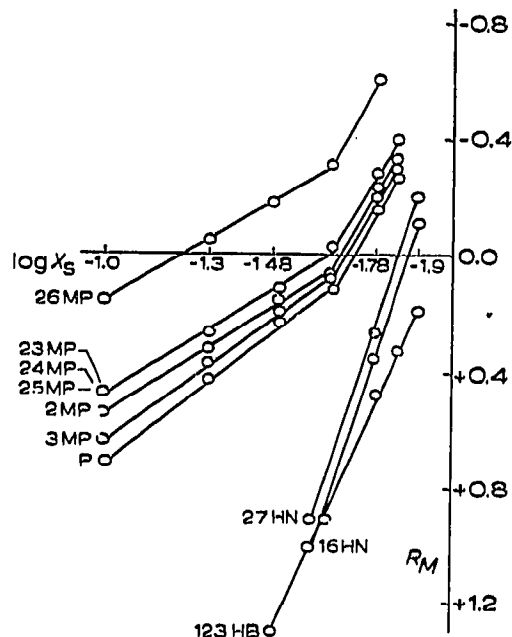


Fig. 9. Experimental R_M vs. $\log X_S$ relationships for developing solvents composed of cyclohexane and tetrahydrofuran.

slopes are observed up to $X_S = 0.5$, the slope increasing to 2.0 in the range of higher concentrations of tetrahydrofuran (Fig. 9). The dihydroxy-benzenes migrated only at higher concentrations of tetrahydrofuran, the slope being twice that of the expected value as in the acetone systems.

In view of complicating effects it was difficult to demonstrate a clear correlation between the basicity of the solvent and its elution power. Apparently the solvation power increases from acetone ($pK_A = -7.2$) through methyl ethyl ketone ($pK_A = -7.2$), to dioxane ($pK_A = -3.22$) and tetrahydrofuran ($pK_A = -2.08$). The strongest solvation effects were observed in the case of cyclohexanone ($pK_A = -6.8$) presumably due to the good accessibility of the carbonyl group. Steric factors can also play an important role in other solvents, and in the case of dioxane the fact that two ether oxygens are present in a single molecule should be taken into account. Moreover, even with solvents where the steric situation of the active group is similar (*e.g.*, a homologous series of ketones), the chromatographic data are not strictly comparable when the molecular level properties are considered, unless the molar volumes of the solvents are taken into account². Even if it is assumed that the volume of the solvent per 1 g of the adsorbent ($V_{\text{solV}}/W_{\text{ads}}$) is constant for various solvents, the difference in the molar volumes of two solvents results in the molar ratio of the active groups of the solvent and of the adsorbent not being identical; for a solvent with a lower molar volume its active groups are in a larger excess, so that the mole fraction X_A of the active groups of the adsorbent surface is lower. The same reasoning also applies to a series of mixed solvents where the molar volume of the active solvent (*e.g.* acetone) differs from that of the diluting solvent (*e.g.*, cyclohexane); X_A (and thus also k^0 , *cf.* eqn. 1) is then a decreasing function of X_S and this effect may contribute to the

abnormally high slopes of the R_M vs. $\log X_S$ relationships (Fig. 4), the second contribution probably being due to competition of acetone molecules for the adsorption sites resulting from dipole-dipole interactions. For higher homologues, whose molar volumes are comparable to that of cyclohexane, both effects are less pronounced and the slopes are approximately equal to the expected values. The better agreement observed for diethyl ketone and cyclohexanone could thus be attributed to the following circumstances:

- (1) Molar volumes comparable to that of the diluting solvent, cyclohexane.
- (2) Lower molar volume concentrations of carbonyl groups even at high values of X_S so that the variation of the formation constants with X_S is reduced and the non-specific solvation of the surface carbonyl groups becomes differentiated less at higher and lower values of X_S .
- (3) Any swelling of the polyamide is reduced in comparison to acetone systems.
- (4) Decreased experimental errors due to changes in composition of the solvent caused by evaporation.

For solvents differing in molar volumes it may be advantageous to substitute mole fractions for molar concentrations; analogous R_M vs. solvent composition relationships would then be obtained. The formation constants would then have other numerical values and would be more strongly dependent on the concentration of the active solvent, in comparison with the constants expressed in mole fractions.

The authors are aware of the fact that in view of the above mentioned complicating effects the relationships derived require further investigation and improvement, and at the present moment can be only regarded as semi-empirical; nevertheless, it is remarkable that in most cases linear R_M vs. $\log X_S$ relationships have been obtained, the slopes being different for monohydroxy-, dihydroxy- and trihydroxy-compounds; this partial agreement with theoretical prediction apparently suggests that in certain types of non-aqueous solvents the decisive mechanism is also solvation of the hydroxyl groups of the solute (*cf.* BARK AND GRAHAM, ref. 11). A further stimulus to present the provisional conclusions and experimental results is the importance of solvent composition effects in the theory of optimization of chromatographic solvent systems; moreover, the theoretical relationships suggest that the realization of the simplified model could allow one to determine the solvation constants (K_{ZS}, K_{ZS_2}) from R_M vs. $\log X_S$ relationships (see Figs. 2, 3), provided that an appropriately modified adsorbent of the polyamide type is employed and the complicating effects can be eliminated or accounted for.

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