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INVESTIGATIONS OF THE RELATIONSHIP BETWEEN MOLECULAR STRUCTURE AND CHROMATOGRAPHIC PARAMETERS

VIII. PARTITION OF PHENOLS AND THEIR DERIVATIVES IN SYSTEMS OF THE TYPE (CYCLOHEXANE + POLAR SOLVENT)-WATER

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SUMMARY

The solvation of mono- and polyhydroxyphenols, aminophenols and phenolic acids was investigated by the dilution method. The probable compositions of solvation complexes were determined from the slopes of R_M versus solvent composition relationships using polar solvents (ethers, esters, ketones and alcohols) diluted with cyclohexane as the developing solvent. In most instances, the slopes were correlated with the number of proton-donor groups ($-\text{OH}$, $-\text{NH}_2$, $-\text{COOH}$) in the solute molecule.

INTRODUCTION

The molecular mechanism of partition can be investigated by interpreting the variation of the chromatographic parameters caused by an increasing concentration of a complex-forming additive in a series of analogous partition systems. The method is especially effective if the additive can form discrete solvation or ion-association complexes in a rapid reversible reaction. The method, employed widely in the liquid-liquid extraction of inorganic compounds^{1,2} and less frequently with organic solutes³, is greatly simplified by the application of chromatographic techniques, which so far have been mainly employed with gas-liquid partition systems however⁴.

In this paper, further results on the liquid-liquid partition of organic solutes are reported. As in previous papers in this series⁵⁻⁸, the interpretation of R_M -solvent composition relationships is based on the application of the law of mass action to the formation of discrete solvates. In a simplified way, the partition of a solute, Z, between a polar phase with constant properties (*e.g.*, water) and a series of developing solvents consisting of a neutral diluent (*e.g.*, cyclohexane) and a polar solvent, S, can be described as^{2,3}



with an extraction constant

$$E = \frac{[ZS_n]_{\text{org}}}{[Z]_{\text{aq}} [S]_{\text{org}}^n} \quad (1)$$

so that the distribution ratio

$$D = \frac{[ZS_n]_{\text{org}}}{[Z]_{\text{aq}}} = E [S]_{\text{org}}^n \quad (2)$$

and

$$\begin{aligned} -R_M &= \log \left(\frac{R_F}{1 - R_F} \right) = \log D + \log \left(\frac{V_{\text{org}}}{V_{\text{aq}}} \right) \\ &= \text{constant} + n \log [S]_{\text{org}} \end{aligned} \quad (3)$$

For a simple distribution mechanism, the $-R_M$ versus $\log[S]_{\text{org}}$ line thus gives the "solvation number", n , or the composition of the solvate, ZS_n . The formation of solvation complexes is obviously gradual and, for comparable concentrations of various solvates, intermediate values of n can be obtained. It should also be borne in mind that accompanying phenomena may distort the simple idealized picture^{2,3,9,10}, leading to erroneous or meaningless values of n . Nevertheless, the solvent dilution method, when applied to simple systems, can provide valuable information on the molecular interactions involved, and indirectly also on the molecular structure of the solute, and parallelism of the R_M versus $\log [S]$ lines is sometimes striking^{6,8}. In addition to optimization of the composition of solvent systems and interpretation of chromatographic data, the information thus obtained may also have wider significance, as analogous solvent effects are also present in other phenomena such as adsorption and solubility.

EXPERIMENTAL

As in the previous papers⁵⁻⁷, the "moist paper" technique was used, the controlled amount of water in the paper (0.5 g per gram of dry paper) permitting solvents that are virtually immiscible with water to be used and thus typical aqueous extraction systems could be investigated. The diluent was cyclohexane and the polar components (S) were chosen by taking into account their proton-donor and proton-acceptor properties, that is to say, according to Pimentel and McClellan's classification¹¹.

The solutes chromatographed were dichlorophenols, polyhydroxyphenols, aminophenols and phenolic acids, so that the experimental results provide information on the solvation equilibria of $-\text{OH}$, $-\text{NH}_2$ and $-\text{COOH}$ groups.

RESULTS AND DISCUSSION

The R_F values obtained (means from three runs) are given in Tables I-III. Owing to the very large number of experimental data obtained, only some typical R_M versus $\log [S]$ relationships are presented in the figures. The R_M axis (right-hand

TABLE I

$R_F \times 100$ VALUES OF 1-NAPHTHOL AND DICHLOROPHENOLS FOR VARIOUS CONCENTRATIONS OF CHLOROFORM AND 1,2-DICHLOROETHYLENE IN CYCLOHEXANE

Polar component (S)	Concentration of S (% v/v)	Phenol						
		1HN	23CP	24CP	25CP	26CP	34CP	35CP
Chloroform	1	56	35	42	27	10	19	14
	3	57	37	44	29	11	20	15
	5	58	38	45	30	12	23	17
	10	66	42	48	34	14	28	20
	15	80	46	52	36	16	33	24
	20	88	50	58	40	19	37	30
	30	—	54	63	44	24	48	37
	50	—	63	72	54	37	57	48
Dichloroethylene	1	—	42	50	32	12	20	16
	3	—	43	52	34	14	22	18
	5	—	44	54	36	16	26	20
	10	—	46	56	38	18	30	24
	15	—	48	58	42	20	34	26
	20	—	52	62	44	22	38	30
	30	—	56	66	48	28	42	36
	50	—	66	72	58	38	54	46
70	—	72	80	68	46	72	62	

ordinate) is directed downwards, which is equivalent to using $-R_M$ values on the ordinate. R_F values and the degree of extraction thus increase upwards (see left-hand ordinate in Fig. 1), as is usual in extraction studies^{2,3}. Absolute slopes of the R_M versus log [S] lines are given in Table IV.

The spots of all compounds detected with bis-diazotized benzidine were compact and well defined, except for some of the phenolic acids, which formed elongated spots; in these instances, the R_F values were determined for the maximum colour density. The experimental data are presented as R_M versus log [S] plots (see comment in ref. 7), the solutes being denoted by appropriate symbols. The last letter denotes the following: B, benzene; N, naphthalene; P, phenol; A, acid (C = caffeic, G = gallic, CG = chlorogenic, tHC = *trans*-hydroxycinnamic, PC = protocatechuic, Ph = pterulic, V = vanillic). The first letter and the preceding number denote the following substituents and their positions: C, chloro; A, amino; H, hydroxy; M, methyl. For example, 26CP denotes 2,6-dichlorophenol; 135HB, 1,3,5-trihydroxybenzene; and 4AP, 4-aminophenol. M denotes morin; AZ, alizarin, O, orcinol (3,5-dihydroxytoluene); and DMPG, dimethylphloroglucinol.

Chlorophenols

In Fig. 1, the R_M versus log [S] relationships for several dichlorophenols are presented; the paper strips were impregnated with a 5% solution of sodium hydrogen carbonate in order to decrease the R_F values to the optimum range.

The shapes of the curves are similar and are typical of the gradual shift of the solvation equilibrium of 1:1 solvation complexes (*cf.*, ref. 8, Figs. 5 and 10). As in formamide systems, the lines for *o*-chlorophenols (except 2,6-dichlorophenol) are

TABLE II

$R_F \times 100$ VALUES OF PHENOLS, PHENOLIC ACIDS AND AMINO PHENOLS FOR VARIOUS CONCENTRATIONS OF CLASS B SOLVENTS IN CYCLOHEXANE

Polar component (S)	Concentration of S (% v/v)	Phenol									
		1HN	2HN	16HN	23HN	27HN	13HN	15HN	13HB	12HB	O
Diisopropyl ether (iPr ₂ O)	1	68	54	0	4	0	0	0	0	0	0
	3	82	68	0	9	0	-1	0	0	0	0
	5	86	74	0	16	0	3	2	0	4	0
	10	90	82	6	26	0	8	5	0	8	0
	15	—	86	12	36	6	18	15	0	14	3
	20	—	92	20	44	9	28	22	2	20	8
	30	—	—	37	56	19	50	41	8	32	14
	50	—	—	66	78	51	72	70	24	53	32
70	—	—	80	86	72	84	80	42	68	56	
Di-n-butyl ether (Bu ₂ O)	1	66	54	0	2	0	0	0	0	0	0
	3	76	65	0	6	0	0	0	0	0	0
	5	83	74	0	12	0	2	0	0	3	0
	10	88	80	3	20	0	5	3	0	6	0
	15	—	90	8	30	3	12	7	0	10	0
	20	—	—	12	40	7	20	14	2	14	3
	30	—	—	24	50	12	32	26	3	19	7
	50	—	—	48	66	30	62	50	10	34	20
70	—	—	63	78	48	78	66	18	46	32	
Diisoamyl ether (iAm ₂ O)	1	63	52	0	1	0	0	0	0	0	0
	3	70	62	0	4	0	0	0	0	1	0
	5	78	66	0	8	0	1	0	0	3	0
	10	86	78	2	14	0	3	1	0	5	0
	15	90	84	4	20	2	6	5	0	8	1
	20	—	86	7	26	4	10	8	1	10	2
	30	—	90	16	38	8	26	18	2	16	5
	50	—	—	32	50	18	44	34	6	26	12
70	—	—	50	63	34	62	52	12	38	22	
Methyl isopropyl ketone (MeCOiPr)	1	74	62	1	4	0	0	1	0	1	0
	3	72	70	2	10	1	3	1	0	2	0
	5	88	80	5	19	2	10	4	1	7	2
	10	92	86	13	35	7	20	14	3	14	7
	15	—	92	29	54	15	36	44	7	30	20
	20	—	—	44	62	25	59	51	14	36	32
	30	—	—	72	78	51	82	76	32	55	54
	50	—	—	89	91	89	92	90	72	83	80
70	—	—	—	—	92	—	—	84	90	90	
Diisobutyl ketone (iBu ₂ CO)	1	—	—	0	4	0	0	0	0	1	0
	3	—	—	2	10	0	1	1	0	3	0
	5	—	—	3	18	1	4	4	0	5	1
	10	—	—	10	33	6	17	12	2	12	3
	15	—	—	28	54	14	34	31	4	21	8
	20	—	—	40	60	23	50	46	6	30	12
	30	—	—	66	73	46	73	70	16	42	28
	50	—	—	82	88	74	86	84	40	60	54
70	—	—	92	—	88	92	90	56	72	72	

123HB	135HB	DMPG	AZ	M	GA	PCA	VA	CGA	CA	PhA	THCA	2AP	3AP	4AP
0	0	0	15	0	0	0	0	0	0	0	0	0	0	0
0	0	0	16	0	0	0	0	0	0	0	0	0	0	0
0	0	0	18	0	0	0	0	0	0	0	0	0	0	0
0	0	0	22	0	0	0	0	0	0	0	0	0	0	0
0	0	0	30	0	0	0	0	0	0	2	2	9	0	0
0	0	0	34	0	0	0	3	0	0	5	4	12	0	0
0	0	0	44	0	0	0	8	0	0	10	11	18	3	0
4	0	0	64	6	0	2	20	0	3	28	34	34	10	2
10	1	3	74	16	0	8	38	0	14	48	60	50	20	9
0	0	0	14	0	0	0	0	0	0	0	0	0	0	0
0	0	0	16	0	0	0	0	0	0	0	0	0	0	0
0	0	0	18	0	0	0	0	0	0	0	0	0	0	0
0	0	0	20	0	0	0	0	0	0	0	0	0	0	0
0	0	0	28	0	0	0	0	0	0	0	0	4	0	0
0	0	0	30	0	0	0	3	0	0	4	2	8	0	0
0	0	0	40	0	0	0	6	0	0	10	8	12	2	0
2	0	0	56	4	0	1	13	0	2	20	18	22	4	0
4	0	3	68	8	0	4	20	0	3	28	33	32	8	2
0	0	0	12	0	0	0	0	0	0	0	0	0	0	0
0	0	0	14	0	0	0	0	0	0	0	0	0	0	0
0	0	0	16	0	0	0	0	0	0	0	0	0	0	0
0	0	0	18	0	0	0	0	0	0	0	0	1	0	0
0	0	0	24	0	0	0	0	0	0	1	0	2	0	0
0	0	0	28	0	0	0	2	0	0	3	2	5	0	0
0	0	0	36	0	0	0	6	0	0	5	4	9	2	0
1	0	0	52	2	0	0	12	0	1	12	14	14	3	0
3	0	0	64	6	0	2	18	0	2	23	25	18	5	1
0	0	0	16	0	--	--	--	--	--	--	--	0	0	0
0	0	0	20	0	--	--	--	--	--	--	--	0	0	0
0	0	0	30	0	--	--	--	--	--	--	--	3	0	0
1	0	0	50	3	--	--	--	--	--	--	--	6	1	0
2	0	0	60	6	--	--	--	--	--	--	--	9	2	0
3	1	1	70	8	--	--	--	--	--	--	--	18	6	0
10	2	5	80	26	--	--	--	--	--	--	--	38	12	1
43	6	35	92	70	--	--	--	--	--	--	--	50	24	2
64	33	66	--	82	--	--	--	--	--	--	--	78	50	8
0	0	0	14	0	0	0	0	0	0	0	0	0	0	0
0	0	0	18	0	0	0	0	0	0	0	0	0	0	0
0	0	0	20	0	0	0	0	0	0	0	0	3	0	0
0	0	0	34	0	0	0	1	0	0	2	1	5	0	0
0	0	0	42	0	0	0	5	0	0	4	3	12	1	0
1	0	0	48	1	0	0	8	0	0	6	10	16	3	0
2	0	0	62	6	0	1	18	0	1	20	24	26	8	3
8	2	1	78	16	0	5	38	0	9	42	52	46	20	8
20	8	9	86	28	1	15	60	0	24	60	72	54	32	12

(Continued on p. 12|13)

TABLE II (continued)

Polar component (S)	Concentration of S (% v/v)	Phenol									
		1HN	2HN	16HN	23HN	27HN	13HN	15HN	13HB	12HB	O
Methyl	1	82	70	1	5	0	1	1	0	1	0
<i>n</i> -amyl	3	89	82	3	18	1	5	3	0	5	1
ketone	5	---	---	10	35	5	18	12	1	14	2
(MeCOAm)	10	---	---	40	63	24	50	44	6	28	10
	15	---	---	60	76	46	70	65	13	48	24
	20	---	---	74	82	53	80	76	24	53	44
	30	---	---	84	90	78	88	84	44	66	60
	50	---	---	90	---	90	---	92	72	81	82
	70	---	---	---	---	---	---	---	88	89	90
<i>n</i> -Propyl	1	74	---	0	5	0	1	1	0	1	0
acetate	5	84	---	2	14	1	3	2	0	4	0
(Pr Acet)	5	90	---	5	22	2	9	4	1	8	2
	10	---	---	16	42	6	30	22	3	20	5
	15	---	---	36	56	20	48	43	7	32	15
	20	---	---	50	64	25	64	52	13	40	24
	30	---	---	70	80	54	80	74	30	56	46
	50	---	---	90	90	82	92	90	60	78	70
	70	---	---	---	---	90	---	---	80	88	86

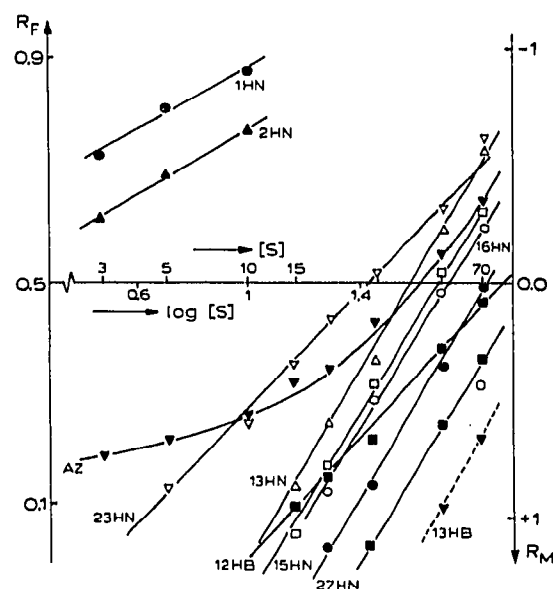
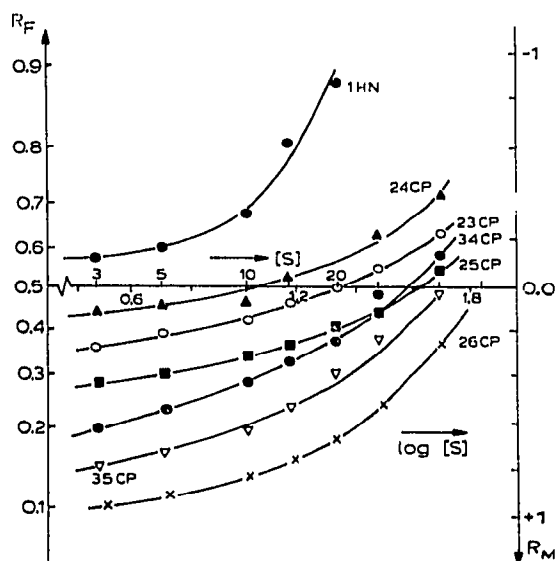


Fig. 1. R_M versus $\log [S]$ relationships for chlorophenols. Stationary phase: ca. 10% aqueous solution of NaHCO_3 . Developing solvent: solutions of chloroform (S) in cyclohexane. For notation of solutes, see text.

Fig. 2. R_M versus $\log [S]$ relationships for polyhydroxy compounds for systems of the type [cyclohexane + electron-donor solvent (S)]-water. Polar solvent: di-*n*-butyl ether.

123HB	135HB	DMPG	AZ	M	GA	PCA	VA	CGA	CA	PhA	1HCA	2AP	3AP	4AP
0	0	0	16	—	0	0	0	0	0	0	0	0	0	0
0	0	0	18	—	0	0	0	0	0	0	0	3	0	0
0	0	0	34	—	0	0	3	0	0	0	2	7	1	0
1	0	0	52	—	0	0	9	0	0	4	8	16	4	0
3	0	0	64	—	0	0	16	0	0	12	17	23	7	2
5	1	4	72	—	0	1	24	0	2	20	27	36	13	3
9	5	9	80	—	1	6	42	0	10	40	58	52	22	8
32	14	32	—	—	4	28	60	0	42	70	80	70	46	21
54	27	52	—	—	12	48	72	3	62	86	92	78	64	28
0	0	0	16	0	0	0	0	0	0	—	0	1	0	0
0	0	0	22	0	0	0	0	0	0	—	0	3	0	0
0	0	0	28	0	0	0	1	0	0	1	0	4	0	0
0	0	0	42	0	0	0	4	0	0	4	3	10	1	0
1	0	0	54	0	0	0	9	0	0	12	8	18	4	2
3	0	1	68	1	0	0	17	0	1	18	16	25	8	3
8	1	3	80	10	1	3	32	0	4	42	38	44	17	8
24	7	12	90	28	3	20	64	0	24	70	72	66	40	21
48	20	42	—	40	14	48	79	3	50	86	84	78	60	38

higher and less steep than those for the corresponding isomers without a chlorine atom in the *ortho* position. The lowest R_F values of 2,6-dichlorophenol, in spite of the shielding of the hydroxyl group from two sides, are probably caused by the higher acidity of the isomer.

The line for 1-naphthol is parallel to those of 3,4- and 3,5-dichlorophenol up to 10% of chloroform in the developing solvent. At higher chloroform concentrations, the line rises more steeply, which may indicate the formation of 1:2 solvation complexes, the second chloroform molecule probably interacting with the π -electron system. The R_F values are too high, however, for this effect to be considered as definite evidence of the formation of higher solvation complexes.

Similar R_M versus $\log [S]$ curves were obtained for 1,2-dichloroethylene as the polar component of the developing solvent.

The results indicate that in aqueous systems, chlorophenols are extracted by proton-donor solvents with the formation of simple 1:1 solvates, as found earlier for halogenophenols and methylphenols in formamide systems⁸. The solvates dissociate easily when chloroform or dichloroethane is diluted with an inert solvent, especially at concentrations below 10%. The *ortho*-effect (steric shielding or formation of internal hydrogen bonds) is manifested by higher R_F values and less steep R_M versus $\log [S]$ relationships (lower values of n).

Dihydroxy and trihydroxy derivatives of benzene and naphthalene

As these compounds are only weakly extracted from water by solvents of class A, the following solvents of classes B and AB were used as polar components of the developing solvent: diisopropyl ether, di-*n*-butyl ether (Fig. 2), diisoamyl ether, methyl isopropyl ketone, diisobutyl ketone, methyl amyl ketone (Fig. 3), *n*-propyl

TABLE III

$R_F \times 100$ VALUES OF PHENOLS, PHENOLIC ACIDS AND AMINO PHENOLS FOR VARIOUS CONCENTRATIONS OF CLASS AB SOLVENTS (ALCOHOLS) IN CYCLOHEXANE

Polar component (S)	Concentration of S (% v/v)	Phenol								
		16HN	23HN	27HN	15HN	13HN	13HB	12HB	O	
<i>n</i> -Hexanol	1	2	14	1	2	3	0	3	2	
	3	8	38	5	12	20	2	12	6	
	5	19	52	12	24	38	6	20	12	
	10	46	72	30	52	66	14	35	30	
	15	62	80	48	68	78	26	48	44	
	20	74	86	59	80	86	36	57	56	
	30	82	—	74	86	92	52	66	68	
	50	88	—	86	92	—	68	74	80	
70	—	—	—	—	—	80	84	90		
<i>n</i> -Octanol	1	2	16	1	2	3	0	3	1	
	3	9	40	6	12	22	2	11	5	
	5	23	56	13	22	40	5	20	12	
	10	48	75	28	52	64	17	36	30	
	15	58	80	42	62	70	26	48	48	
	20	72	86	58	78	82	34	54	54	
	30	82	92	74	88	90	50	64	68	
	50	90	—	82	—	—	66	72	78	
70	—	—	—	—	—	78	88	86		
<i>n</i> -Decanol	1	2	12	1	1	2	0	2	1	
	3	5	32	3	7	14	2	8	3	
	5	14	46	7	18	32	4	15	8	
	10	27	62	19	42	56	10	30	22	
	15	48	72	30	52	62	18	40	34	
	20	60	82	48	70	78	24	48	44	
	30	78	89	62	78	86	44	62	62	
	50	86	—	78	86	92	62	74	76	
70	—	—	88	92	—	74	82	82		

TABLE IV

ABSOLUTE SLOPES OF R_M versus LOG [S] LINES

Polar component (S)	Phenol										
	1HN	2HN	16HN	23HN	27HN	13HN	15HN	13HB	12HB	O	123HB
iPr ₂ O	0.7	0.6	1.9	1.1	2.6	1.9	2.2	2.6	1.7	2.4	3.0
Bu ₂ O	0.5	0.6	2.0	1.4	2.1	2.0	2.0	2.2	1.4	2.2	—
iAm ₂ O	0.7	0.7	2.0	1.2	2.4	2.1	2.3	2.2	1.4	2.4	—
MeCOiPr	1.6	1.3	2.4	1.7	2.8	2.4	1.5	2.6	1.9	2.8	3.6
iBu ₂ CO	—	1.1	2.1	1.6	2.4	2.2	2.3	2.3	1.6	2.2	3.1
MeCOAm	—	—	2.1	1.6	2.4	2.2	2.2	2.4	1.6	2.4	3.6
Pr Acet	0.7	—	2.2	1.6	2.6	2.2	2.1	2.6	1.8	2.4	2.8
Bu Acet	1.0	—	2.2	1.3	2.4	2.1	2.0	2.2	1.6	2.4	2.8
Am Acet	—	—	2.0	1.5	2.2	1.9	2.0	2.5	1.6	2.1	2.1
HxOH	—	—	1.7	1.2	1.7	1.4	1.7	1.7	1.2	1.6	1.7
OcOH	—	—	1.6	1.1	1.7	1.5	1.8	1.6	1.1	1.5	2.0
DcOH	—	—	1.5	1.1	1.7	1.5	1.6	1.6	1.1	1.5	2.1

<i>123HB</i>	<i>135HB</i>	<i>DMPG</i>	<i>AZ</i>	<i>M</i>	<i>GA</i>	<i>PCA</i>	<i>VA</i>	<i>CGA</i>	<i>CA</i>	<i>PhA</i>	<i>tHCA</i>
0	0	0	22	—	0	0	2	0	0	3	0
0	0	0	36	—	0	0	10	0	0	14	14
1	0	0	42	—	0	2	18	0	1	20	18
3	1	1	54	—	3	6	20	0	6	36	38
6	2	3	64	—	6	12	40	0	12	46	58
10	4	6	70	—	9	18	54	0	20	56	68
16	8	16	74	—	18	32	68	2	40	72	78
34	21	36	78	—	34	56	82	9	62	82	88
54	36	54	88	—	52	72	92	22	76	90	—
0	0	0	20	—	0	0	1	0	0	3	6
0	0	0	34	—	0	0	8	0	0	11	14
1	0	0	40	—	0	3	15	0	1	19	20
4	1	2	48	—	3	7	30	0	7	34	40
6	2	4	52	—	6	12	42	0	12	50	58
9	4	6	62	—	12	18	50	0	20	54	66
19	7	15	70	—	20	32	66	1	37	70	76
34	20	34	76	—	34	54	80	8	60	80	88
48	38	52	86	—	50	68	90	22	72	90	—
0	0	0	12	—	0	0	1	0	0	2	2
0	0	0	28	—	0	0	6	0	0	8	5
1	0	0	42	—	0	1	10	0	1	14	13
2	0	1	58	—	2	3	18	0	4	22	27
4	1	2	60	—	4	7	30	0	10	36	46
6	2	3	68	—	6	12	40	0	15	46	56
12	5	10	78	—	14	25	58	2	30	58	70
28	14	28	86	—	27	44	72	5	54	76	86
40	26	42	—	—	42	60	82	10	64	82	92

<i>135HB</i>	<i>DMPG</i>	<i>AZ</i>	<i>M</i>	<i>GA</i>	<i>PCA</i>	<i>VA</i>	<i>CGA</i>	<i>CA</i>	<i>PhA</i>	<i>tHCA</i>	<i>2AP</i>	<i>3AP</i>	<i>4AP</i>
—	—	0.4–2.0	4.0	—	—	2.7	—	—	2.4	3.0	1.6	2.0	—
—	—	0.3–1.4	—	—	—	1.6	—	—	1.8	2.2	1.4	—	—
—	—	0.7–1.5	—	—	—	2.2	—	—	1.2	1.6	1.1	—	—
4.0	4.0	1.0–1.2	3.5	—	—	—	—	—	—	—	—	—	—
—	—	1.5	2.4	—	2.4	2.4	—	3.0	2.4	2.8	1.6	1.8	1.6
3.0	3.0	1.3	2.6	—	2.6	2.4	—	3.6	1.9	3.0	1.6	2.0	2.2
3.4	3.4	—	—	—	—	—	—	—	—	—	—	—	—
—	2.6	0.8–2.0	—	—	—	—	—	—	—	—	—	—	—
—	3.8	—	—	—	—	—	—	—	—	—	—	—	—
2.4	2.4	—	—	1.8	2.1	1.4	3.2	1.9	1.5	1.4	—	—	—
2.4	2.5	—	—	1.8	2.2	1.3	2.6	2.3	1.3	1.7	—	—	—
2.4	2.5	—	—	1.9	1.9	1.3	2.6	1.9	1.3	1.3	—	—	—

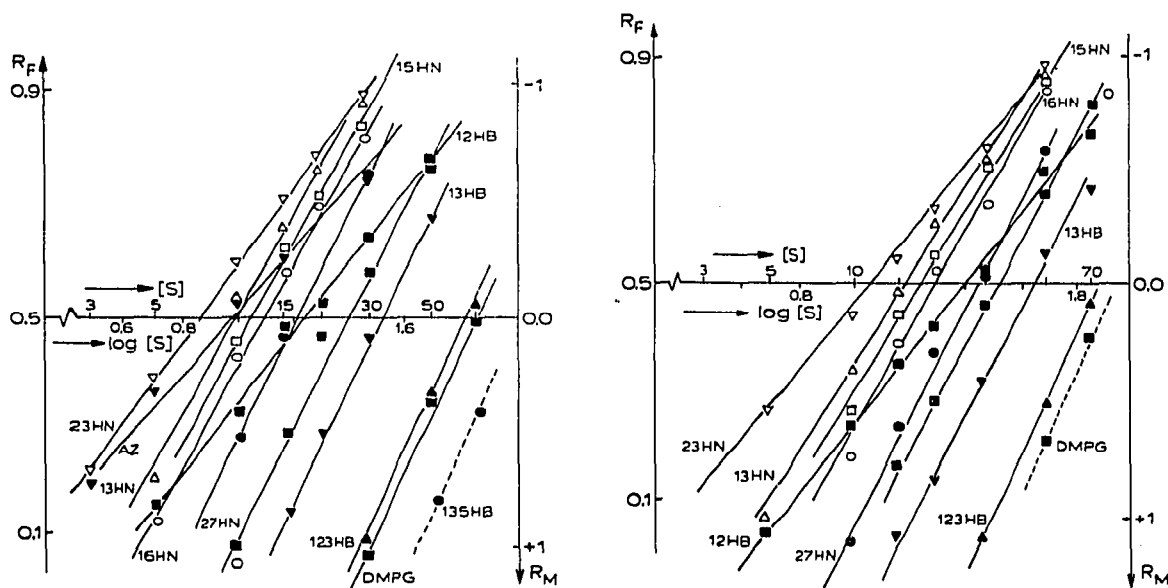


Fig. 3. As Fig. 2, with methyl *n*-amyl ketone as polar solvent.

Fig. 4. As Fig. 2, with *n*-propyl acetate as polar solvent.

acetate (Fig. 4) and butyl acetate. In these solvent systems, the two naphthols had high R_F values at low concentrations of the polar solvent: the slope of the R_M versus $\log [S]$ line obtained for the di-*n*-butyl ether system is *ca.* 0.8, indicating the formation of 1:1 solvation complexes. The R_F values for trihydroxybenzenes are low, except for high concentrations of the polar solvent, and are therefore also less accurate. Only the results obtained for dihydroxy compounds are based on a larger number of points. The relationships are similar to those obtained for cyclohexanone and tri-*n*-butyl phosphate as polar solvents⁵; thus, for 2,3-dihydroxynaphthalene and 1,2-dihydroxybenzene, the lines are less steep owing to the interaction of two vicinal hydroxyl groups.

The sequence of R_F values for isomeric dihydroxynaphthalenes is similar for all of the solvent systems investigated. The highest R_F values were obtained for 2,3- and 1,3-dihydroxy derivatives, lower values for 1,5- and 1,6-dihydroxynaphthalenes, and the lowest values for 2,7-dihydroxynaphthalene. The R_F values are therefore related to the distance between the two hydroxyl groups and, in the last compound, to the better accessibility of β -hydroxyl groups¹² (see also the lower R_F values for 2-naphthol shown in Fig. 2, owing to a better interaction with water). The experimental solvation numbers for dihydroxy compounds are higher than expected, by as much as 0.6 unit, except for 2,3-dihydroxynaphthalene and pyrocatechol, for which the slopes are decreased owing to the formation of internal hydrogen bonds and difficulties in achieving the simultaneous solvation of both groups⁶. For trihydroxybenzenes also the slopes are higher than expected (3.4–4.0). The highest slopes are obtained for methyl isopropyl ketone, whereas the replacement of ketones with the less polar ether decreases the R_F values and the apparent solvation numbers. However, the results for

trihydroxybenzenes are less accurate owing to their low R_F values and the fewer experimental points determined for these compounds.

More complex compounds, such as alizarin and morin, behaved in a similar manner to the simpler compounds in the systems investigated, the slopes of their R_M versus $\log [S]$ lines being related to the number of hydroxyl groups, taking into account the possibility of internal hydrogen bonding; for example, for alizarin, the slope is *ca.* 1.5.

The three aliphatic alcohols investigated gave R_M versus $\log [S]$ relationships similar to those for solvents of class B. However, the slopes were lower (Figs. 5–8), indicating a lower solvation ability owing to auto-association of the alcohols^{7,8}.

Aminophenols

The isomeric aminophenols chromatographed in N + B and N + AB systems behaved in a similar manner to dihydroxybenzenes owing to the proton-donor nature of the amino groups. Thus the slopes of the R_M versus $\log [S]$ lines were *ca.* 2.0, except for *o*-aminophenol, which gave higher R_F values and lower apparent solvation numbers (like pyrocatechol) owing to the formation of an internal hydrogen bond (Fig. 5, Table IV).

Phenolic acids

In order to reduce the dissociation of phenolic acids, which tends to cause tailing, the paper strips were impregnated with 1% citric acid instead of pure water (the

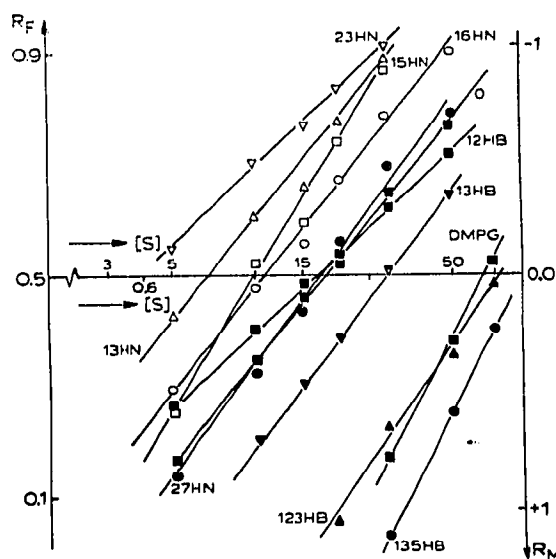
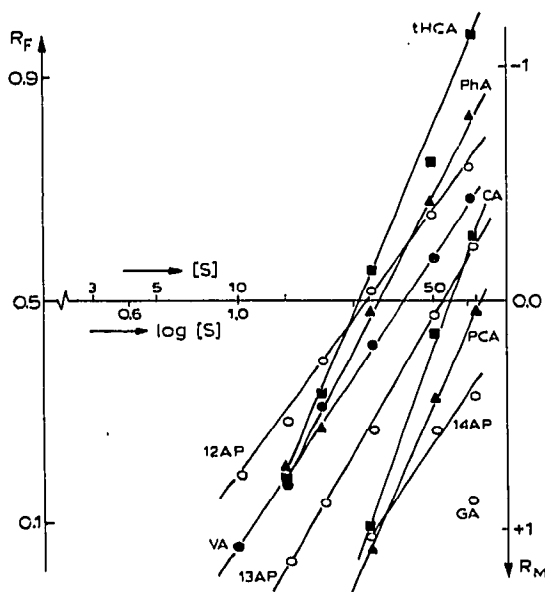


Fig. 5. R_M versus $\log [S]$ relationships for phenolic acids and aminophenols. Developing solvent: cyclohexane + methyl *n*-amyl ketone (S). Stationary phase: *ca.* 2% aqueous solution of citric acid (phenolic acids) or water (aminophenols).

Fig. 6. R_M versus $\log [S]$ relationships for polyhydroxy compounds for systems of the type [cyclohexane + *n*-octanol (S)]-water.

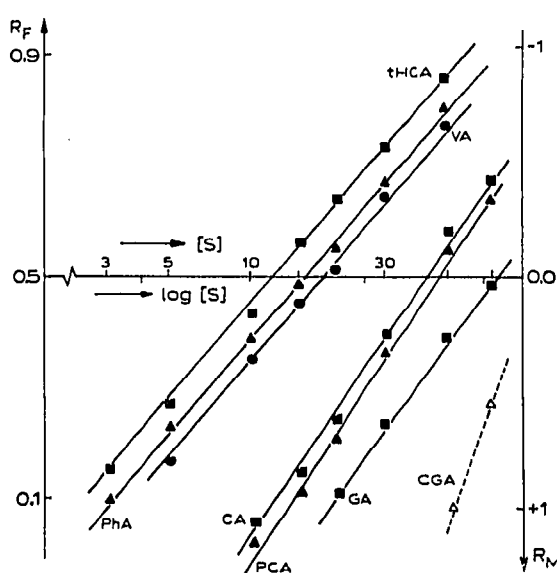


Fig. 7. R_M versus $\log [S]$ relationships for phenolic acids for systems of the type [cyclohexane + *n*-hexanol]-ca. 2% aqueous solution of citric acid.

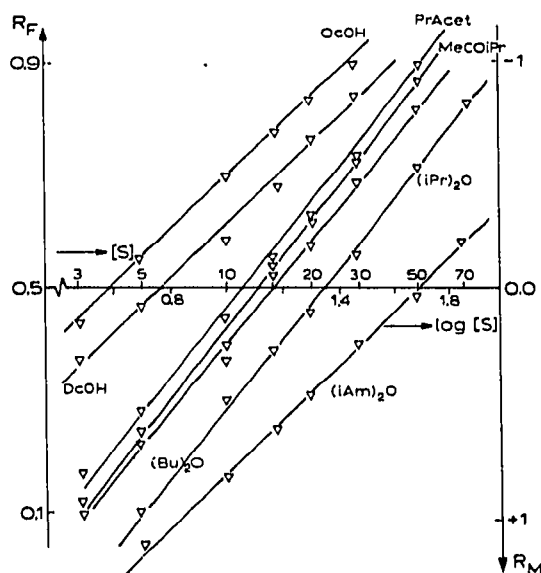


Fig. 8. Comparison of R_M versus $\log [S]$ relationships for 2,3-dihydroxynaphthalene for various polar solvents.

concentration of citric acid in the stationary phase during development was thus ca. 2.0–2.5%). The phenolic acids were only weakly extracted by ethers. For ketones and alcohols, straight R_M versus $\log [S]$ lines were obtained, their slopes and vertical positions being dependent on the number of hydrophilic groups present. Thus, the lines of *trans*-4-hydroxycinnamic acid, vanillic acid and pherulic acid are parallel and well separated from the lower and steeper lines of caffeic and protocatechuic acids. The lowest R_F values were obtained for gallic and chlorogenic acids. The slopes of the lines are given in Table IV. The apparent solvation numbers were correlated satisfactorily with the total number of carboxyl and hydroxyl groups present if interactions of vicinal hydroxyl groups are taken into account; for analogous compounds, the lines are parallel (Fig. 7).

In Fig. 8, the extraction and solvation strengths of the polar solvents are compared for a single compound (2,3-dihydroxynaphthalene). In spite of their tendency to undergo auto-association, alcohols are the best extractants at moderate and high dilutions; however, for ketones and diisopropyl ether, the lines are steeper.

Although liquid-liquid partition data obtained by "dilution analysis" should be interpreted with caution in terms of the presumable molecular solvation mechanism involved^{9,10} (especially when obtained by paper chromatography, where various complicating effects can distort the picture), the results are reasonably consistent. In particular, the parallelism of the R_M versus $\log [S]$ relationships for analogous compounds is striking, so that confirmation of the hypothetical solvation mechanism for a typical compound can be generalized for a whole group of related solutes. The conclusions concerning solvation of hydroxyl groups are now extended to include other

proton-donor groups (class AB¹¹) such as -COOH and -NH₂. Class B groups, such as -OCH₃ and =CO, are weakly solvated by solvents of classes B and AB and their effect on the slope of the R_M versus log [S] lines is insignificant. The results also provide a further illustration of the similar properties of lipophilic alcohols and solvents of class B such as ketones, ethers and esters⁶⁻⁸. The less steep relationships obtained for alcohols may be due to steric shielding of the lone electron pairs of the oxygen atoms in the association chains⁷ and/or to the dissociation of the chains at lower concentrations of the alcohol.

In general, the aqueous systems investigated were found to be more selective than analogous formamide systems⁸.

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