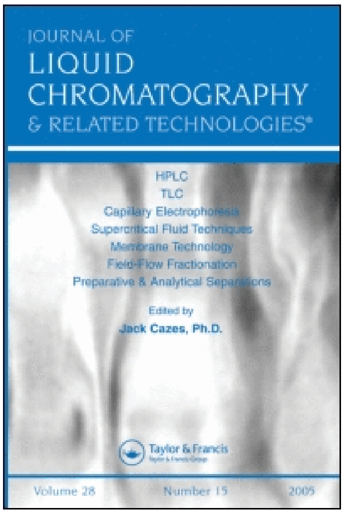

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Chromatographic Separation on Silica of Polar Aromatic Compounds

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CHROMATOGRAPHIC SEPARATION ON SILICA OF POLAR AROMATIC COMPOUNDS

I) STUDY OF SOME FACTORS INFLUENCED BY DIFFERENT CONDITIONS OF PRELOADING SILICA

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ABSTRACT

Our goal in this work, was to seek the best experimental conditions which allow the migration and partition in thin layer chromatography of numerous aromatic compounds, essentially those of polar character, according to a predominating adsorption process. We then studied the modification of different coefficients intervening in these chromatographies according to accepted experimental conditions. The results with different modes of adsorbent deactivation show that the adsorption process is possible and must be interpreted by the SNYDER Model.

I) INTRODUCTION

Polar aromatic compounds, of which benzoic acid derivatives are examples, cannot be chromatographied on polar adsorbents such as silica, since their degree of adsorption is too great.

It appeared interesting to us to modify the activity of the adsorbent thus permitting the desired migrations and separations. We envisaged controlling the silica deactivation with the help of water molecules, followed by acid or basic polar molecules such as formic acid or diethylamine.

We studied the different silica modifications in relation to characteristic parameters of adsorbent and solute. The mechanism and the most important factors in the obtained chromatographic separations are discussed in this paper.

II) EXPERIMENTAL STUDY

The principal solutes studied are indicated in table 1.

Chromatographic separations were carried out with weak solvent strength benzene as the mobile phase in a VARIO KS (Camag) (Ref 1-2) tank, which allowed the use of Merck HPTLC silica plates with fluorescent indicator as the stationnary phase with well determined preloading. The separated compounds were visualized under U.V. radiations at 254 nm. We determined easily their Rf.

Various silica preloadings using the vapor phase as an intermediate are employed during a predetermined period with the solution "c" containing the factor of deactivation in various concentrations. In our experiments we used a water like deactivant (diluted concentred sulfuric acid) ; formic acid and diethylamine. For the two latter, we diluted with water or diethylene glycol monoethyl ether (DEGMEE).

Deactivation by water is insufficient in assuring the migration of benzoic acids. Preloading with formic acid gives better results. A detailed study of this deactivant follows.

TABLE 1 : STUDIED COMPOUNDS Ø = C_6H_5 or C_6H_4

BENZOIC ACIDS	PHENOLS	ACETOPHENONES	BENZALDEHYDES	ANILINES
Ø-COOH	Ø-OH	Ø-$COCH_3$	O-CHO	Ø-NH_2
2 NH_2-Ø-COOH	2 NH_2-Ø-OH	2 NH_2-Ø-$COCH_3$	2 Cl-Ø-CHO	2 NH_2-Ø-NH_2
3 NH_2-Ø-COOH	3 NH_2-Ø-OH	3 NH_2-Ø-$COCH_3$	3 Cl-Ø-CHO	3 NH_2-Ø-NH_2
4 NH_2-Ø-COOH	4 NH_2-Ø-OH	4 NH_2-Ø-$COCH_3$	4 Cl-Ø-CHO	4 NH_2-Ø-NH_2
2 Cl-Ø-COOH	2 Cl-Ø-OH	2 Cl-Ø-$COCH_3$	2 HO-Ø-CHO	2 Cl-Ø-NH_2
3 Cl-Ø-COOH	3 Cl-Ø-OH	4 Cl-Ø-$COCH_3$	4 HO-Ø-CHO	3 Cl-Ø-NH_2
4 Cl-Ø-COOH	4 Cl-Ø-OH	2 HO-Ø-$COCH_3$	2 CH_3-Ø-CHO	4 Cl-Ø-NH_2
2 HO-Ø-COOH	2 CH_3-Ø-OH	3 HO-Ø-$COCH_3$	4 CH_3-Ø-CHO	2 NO_2-Ø-NH_2
3 HO-Ø-COOH	4 CH_3-Ø-OH	4 HO-Ø-$COCH_3$	2 OCH_3-Ø-CHO	3 NO_2-Ø-NH_2
4 HO-Ø-COOH	2 NO_2-Ø-OH	2 CH_3-Ø-$COCH_3$	3 OCH_3-Ø-CHO	4 NO_2-Ø-NH_2
2 NO_2-Ø-COOH	3 NO_2-Ø-OH	4 CH_3-Ø-$COCH_3$	4 OCH_3-Ø-CHO	
3 NO_2-Ø-COOH	4 NO_2-Ø-OH	2 OCH_3-Ø-$COCH_3$	2 NO_2-Ø-CHO	
4 NO_2-Ø-COOH		3 OCH_3-Ø-$COCH_3$	3 NO_2-Ø-CHO	
		4 OCH_3-Ø-$COCH_3$		
		2 NO_2-Ø-$COCH_3$		
		3 NO_2-Ø-$COCH_3$		
		4 NO_2-Ø-$COCH_3$		

TABLE 2

COMPOUNDS	0% HCOOH	20% HCOOH	40% HCOOH	60% HCOOH	80% HCOOH	100% HCOOH
PHENOL	0,20	0,24	0,30	0,38	0,50	0,59
ORTHO CRESOL	0,45	0,46	0,49	0,57	0,70	0,87
CHLORO-2-PHENOL	0,66	0,68	0,71	0,77	0,86	0,90
ACETOPHENONE	0,40	0,42	0,53	0,58	0,67	0,79
CHLORO-4-ACETOPHENONE	0,49	0,49	0,50	0,54	0,70	0,91
METHYL-4-ACETOPHENONE	0,45	0,48	0,50	0,54	0,70	0,91
BENZALDEHYDE	0,04	0,10	0,12	0,30	0,66	0,84
METHYL-4-BENZALDEHYDE	0,04	0,10	0,19	0,36	0,70	0,93
CHLORO-2-BENZALDEHYDE	0,66	0,76	0,84	0,86	0,88	0,96
BENZOIC ACID	0,07	0,30	0,37	0,52	0,71	0,95
CHLORO-4 BENZOIC ACID	0,05	0,10	0,12	0,32	0,71	0,94
NITRO-4 BENZOIC ACID	0,02	0,04	0,07	0,10	0,48	0,55

Studied Series Solutes R_f on silica

TABLE 3

COMPOUNDS	0% HCOOH	20% HCOOH	40% HCOOH	60% HCOOH	80% HCOOH	100% HCOOH
PHENOL	1,19	1,19	0,86	0,80	0,67	0,26
ORTHO CRESOL	∞	∞	∞	2,80	0,71	0,57
CHLORO-2-PHENOL	114,50	15,29	2,43	2,05	0,75	4,60
ACETOPHENONE	∞	5,5	20,10	4,11	2,64	0,85
CHLORO-4-ACETOPHENONE	∞	6,31	2,18	2,26	1,08	0,70
METHYL-4-ACETOPHENONE	17,46	3,08	2,20	1,79	1,21	0,54
BENZALDEHYDE	10,36	13,08	4,63	3,43	2,61	1,17
METHYL-4-BENZALDEHYDE	∞	97,71	4,86	29,40	2,86	1,00
CHLORO-2-BENZALDEHYDE	35,36	16,2	2,84	7,89	5,65	0,81
BENZOIC-ACID	2,08	1,94	1,63	1,56	1,50	0,82
CHLORO-4 BENZOIC ACID	8,09	3,55	3,76	2,57	2,20	1,66
NITRO-4 BENZOIC ACID	0,89	0,75	0,69	0,48	0,61	0,50

Partition Coefficient K' For Formic Acide-water Preloading For Studied Series Solutes Solutes

III) STUDY OF PARTITION MECANISM

In the case of a partition mechanism between the benzenic mobile phase and the stationnary phase, impregnated with the deactivant which is obtained by the vapor phase produced by different preloading solutions, we determined the solute (X) partition coefficient (K') between these last "c" and organic phase "org" which in this case is benzene.

$$K' = \frac{[X]\,\mathrm{org}}{[X]\,\mathrm{c}} \quad (1)$$

For the results given in table (3), formic acid is used as the deactivant. These results are compared to Rf obtained (table 2) with preloading which correspond to silica plates. We can see that the Rf vary inversely to K' values. This result allows us to eliminate the partition mechanism in the chromatographic process, mentioned in this work and leads us to the adsorption mechanism hypothesis. Also, various models of adsorption are cited in the literature (Ref 8,9,10). We choose the SNYDER (3) representation to interpret the different separations.

IV) ADSORPTION MECHANISM

According to SNYDER (Ref 3) when a solute is fixed on an adsorbent surface, the relation can be expressed in this form :

$$R'_M = \log \frac{V_a W}{V_0} + \alpha f(X,S) \quad (2) \quad \text{with } R'_M = \log \left(\frac{1}{\xi R_f} - 1\right)$$

ξ is the correcting coefficient which takes into account the preloading adsorbent with solvent vapors. It is equal to unity under these experimental conditions

V_a = volume of solvent per monolayer fixed per gramme of adsorbent.

W = adsorbent weight in grams of the silica layer used

V_0 = free volume of the accesible layer at the mobil phase in milliliters

α = adsorbent activity

$f(X,S)$ = relation which depends on the difference between the adsorption energy of the solute (X) and the solvent S.

The terms V_a, W, V_o and α depend on the adsorbent, the active solvent used as the mobile phase, and the additional modifications by preloading (They can be determined experimentally). Finally, we used hexane as the solvent in different preloading cases studied with three reference compounds : naphtalene, phenanthrene and benzo-3,4 pyrene, for which SNYDER gave the values of f(X,S). Rf was measured and R'_M deduced, which allowed us, using formula 2, to obtain the different values of α and the term log $\frac{V_aW}{V_o}$ for the different preloadings (table 4).

In addition, we determined gravimetrically the quantity of fixed deactivant formic acid and others deactivants of W and V_o. In this manner, we calculate V_a from the preceding term : log $\frac{V_aW}{V_o}$.

We know from recent studies of silica the number of accesible hydroxyl active groups for 100 Å^2 and also specific area : 500 $m^2g^{-1}$is known and we deduced form this that the existence of 25.10^{20} active hydroxyl groups per m^2. If we assume that during preloading the deactivant is fixed (as is formic acid which is frequently used in this work) occupies one active hydroxyl site, we can then calculate the hydroxyl number (n_{OH}) which remains free for solute adsorption (table 5 and 6).

Considering the problem qualitatively, we noticed that there was a correlation between the variation of Va and that of the free hydroxyl number (n_{OH}) depending on the concentration of the deactivant used (table 5 and 6,fig 1). We have 1-1 a fixation for the deactivant. These results agree with the definition of Va given by SNYDER.

However, for free $n_{(OH)}$ = 0 which corresponds to a blocking of all active sites, V_a is still active. This indicates, that for a definite quantity of formic acid, we are not definitely in the presence of the formation monolayer of this acid. Nevertheless we can assume that the silica surface is partially deactivated and possess hydroxyl sites for an adsorption mechanism.

TABLE 4 : VALUES OF α AND $\frac{V_a W}{V_o}$

FORMIC ACID %	0	20	40	60	80	100
WATER %	100	80	60	40	20	0
α	0,58	0,62	0,63	0,66	0,83	+
$\log \frac{VaW}{Vo}$	-1,58	-1,65	-1,80	-2,29	-2,97	+

FORMIC ACID %	0	20	40	60	80	100
DEGMEE %	100	80	60	40	20	0
α	0,73	0,7	0,61	0,7	0,8	+
$\log \frac{VaW}{Vo}$	-1,45	-1,63	-1,86	-2,48	-3,22	+

SNYDER Model Study
+ Solute Migrate With Solvent Front

TABLE 5 : FORMIC ACID/WATER

% in HCOOH	FORMIC ACID or H_2O fixed in g.	WEIGHT SiO_2	PERCENTAGE HCOOH or H_2O fixed	OH BLOCKED	REMAINING OH	WEIGHT C_6H_6 in g.	VOL. C_6H_6 in ml.	$\frac{W}{V_o}$	Va in ml.
80	0,0376	0,1424	26,40	$34,5\ 10^{20}$	0	0,129	0,162	0,876	$1,22\ 10^{-3}$
60	0,0270	0,1430	18,90	$24,7\ 10^{20}$	$0,3\ 10^{20}$	0,1319	0,165	0,866	$5,89\ 10^{-3}$
50	0,0186	0,1377	13,50	$17,6\ 10^{20}$	$7,3\ 10^{20}$	0,1337	0,168	0,824	
40	0,0173	0,1380	12,50	$16,3\ 10^{20}$	$8,7\ 10^{20}$	0,1417	0,178	0,777	$20,3\ 10^{-3}$
30	0,0166	0,1402	11,84	$15,5\ 10^{20}$	$9,5\ 10^{20}$	0,1473	0,184	0,760	
20	0,0152	0,1458	10,42	$13,6\ 10^{20}$	$11,4\ 10^{20}$	0,1443	0,180	0,811	$27,6\ 10^{-3}$
10	0,0159	0,1680	9,46	$12,4\ 10^{20}$	$12,6\ 10^{20}$	0,1423	0,178	0,946	
0	0,0135	0,1685	8,01			0,158	0,197	0,855	$30,7\ 10^{-3}$

TABLE 6 : FORMIC ACID/DIETHYLENEGLYCOLMONOETHYLETHER

% in HCOOH	FORMIC ACID fixed in g. or loss H_2O	WEIGHT $Si\ O_2$	PERCENTAGE HCOOH or loss H_2O	OH BLOCKED	REMAINING OH	WEIGHT C_6H_6 in g .	VOL. C_6H_6 in ml.	$\frac{W}{V_o}$	Va in ml
80	0,0652	0,165	39,65	51,9 10^{20}	0	0,135	0,169	0,97	0,63 10^{-3}
60	0,0458	0,1561	29,34	38,4 10^{20}	0	0,1458	0,182	0,85	3,89 10^{-3}
50	0,0193	0,1384	13,94	18,24 10^{20}	6,76 10^{20}	0,1507	0,188	0,736	
40	0,0104	0,1424	7,30	9,55 10^{20}	15,45 10^{20}	0,1596	0,199	0,716	19,27 10^{-3}
30	0,0046	0,1483	3,10	4,05 10^{20}	20,95 10^{20}	0,1626	0,203	0,730	
20	0,0024	0,1594	1,50	1,96 10^{20}	23,04 10^{20}	0,150	0,187	0,85	27,5 10^{-3}
10	-0,0002	0,1398	-0,143			0,155	0,194	0,720	
DEGMEE	-0,0026	0,1373	-1,89			0,129	0,161	0,852	41,7 10^{-3}

SNYDER Model Study Free OH and V_a Determination

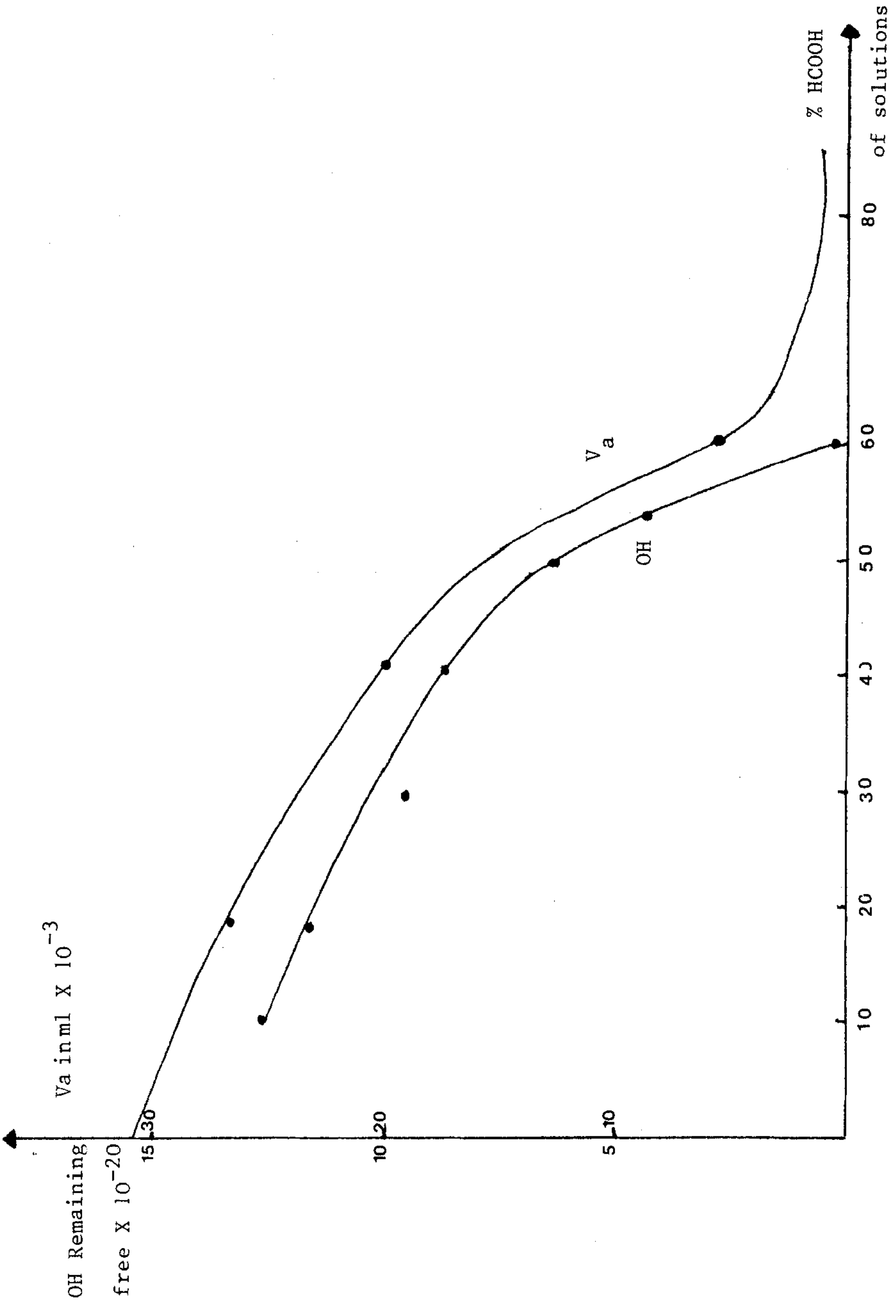
Va in ml X 10^{-3}
OH Remaining free X 10^{-20}
15
10
5
30
20
10
% HCOOH of solutions
10
20
30
40
50
60
80
V_a
OH

FIGURE 1

If we now have V_a, W,V_0 values and α we can further study the function f(X,S) which affects different solutes which leads to a better interpretation of their retention.

V) STUDY OF THE FUNCTION f(X,S) ACCORDING TO THE SNYDER MODEL

Using SNYDER'S theory, we can represent $f(X,S) = S^0 - \varepsilon_0 A_x$ (3) where S^0 is a dimension bound to solute (X) adsorption strength with the considered adsorbent, ε_0, to that of solvent (S) ("solvent strength") and A_x is the surface covered by adsorption of solute (X)

Taking into account the molecule (X), groups of atoms, can react on the adsorbent surface and intereact. This relation can be developed in the following manner (Ref, 3,5,6,7)

$$f(X,S) = \sum_i Q_i^{\circ} - \beta f(Q_k^{\circ}) \sum_{i \neq k} Q^{\circ}_i + \rho_k \sigma_i + \delta - \varepsilon_0 \Big(\sum_i a_{i(cal)} + \gamma \Delta a_k (SiO_2) \Big)$$

(4) where the solute can be represented by i-Ø-k (Ø = C_6H_4 or C_6H_5)
Q°_i = is a dimension linked to adsorption of free energy of group i only if the group k is localised (absorption strength is higher than for others groups) $f(Q^{\circ}_k)$ is the localization function, that its value is larger than Q°_k is important. The term $\beta f(Q^{\circ}_k) \sum_{i \neq k} Q^{\circ}_i$ links localization effect of group k on the active sites. These values were supplied by SNYDER.

The coefficient β takes into consideration a certain mobility of silica active sites. The term $\rho_k \sigma_i$ takes into account intramolecular electronic effects of group i on adsorption strength of group k.

σ_i is Hammett's constant bound to donner or attracter electron pover of group i.

ρ_k is a coefficient which depends upon group k and the solvent used.

δ is a correcting term for solute and solvent interactions.

$\sum a_i$ points out the contribution of the non localized groups or the recovery by a solute.

TABLE 7

FUNCTION F(X,S), EXPERIMENTAL VALUES OF ρ, β and δ FOR DIFFERENT PRELOADING IN FORMIC ACID

PRELOADING SOLUTIONS	WATER	20% HCOOH 80% H_2O	40% HCOOH 60% H_2O	60% HCOOH 40% H_2O	80% HCOOH 20% H_2O
α	0,58	0,62	0,63	0,66	0,83
BENZOIC ACID	0,58	0,53	0,30	0,28	-0,32
ACETOPHENONES	-0,005	-0,04	-0,43	-0,48	-0,48
BENZALDEHYDES	-0,83	-0,86	-0,91	-0,91	-0,77
PHENOLS	1,25	0,62	0,15	0,10	0,05
ANILINES	-0,47	-4,84	-6,55	-7,22	-3,2

PRELOADING SOLUTIONS	DEGMEE	20% HCOOH 80% DEGMEE	40% HCOOH 60% DEGMEE	60% HCOOH 40% DEGMEE	80% HCOOH 20% DEGMEE
α	0,73	0,70	0,61	0,70	0,80
BENZOIC ACID	0,48	0,45	0,50	-0,22	-0,35
ACETOPHENONES	-0,30	-0,40	-0,73	-0,75	-0,66
BENZALDEHYDES	-0,54	-0,67	-0,97	-0,83	-0,58
PHENOLS	-0,05	0,12	0,06	0,21	0,70
ANILINES	-0,51	-0,65	1,86	-2,09	-1,85

VALUES OF ρ

(continued)

TABLE 7 (Continued)

PRELOADING SOLUTIONS	WATER	20% HCOOH / 80% H_2O	40% HCOOH / 60% H_2O	60% HCOOH / 40% H_2O	80% HCOOH / 20% H_2O
α	0,58	0,62	0,63	0,66	0,83
BENZOIC ACIDS	1,73	1,73	1,79	1,49	1,52
ACETOPHENONES	1,4	1,66	1,65	1,60	1,62
BENZALDEHYDES	1,76	1,78	1,73	1,60	1,44
PHENOLS	1,54	1,72	1,57	1,54	1,51
ANILINES	-0,18	0,26	0,02	0,09	1,39

PRELOADING SOLUTIONS	DEGMEE	20% HCOOH / 80% DEGMEE	40% HCOOH / 60% DEGMEE	60% HCOOH / 40% DEGMEE	80% HCOOH / 20% DEGMEE
α	0,73	0,70	0,61	0,70	0,80
BENZOIC ACIDS	1,95	1,50	1,37	1,29	1,21
ACETOPHENONES	1,65	1,51	1,51	1,28	1,18
BENZALDEHYDES	1,80	1,34	1,24	1,32	1,38
PHENOLS	1,33	1,49	1,57	1,40	1,17
ANILINES	1,86	1,92	2,32	2,48	2,37

VALUES OF β

TABLE 7 (Continued)

PRELOADING SOLUTIONS	WATER	20% HCOOH / 80% H_2O	40% HCOOH / 60% H_2O	60% HCOOH / 40% H_2O	80% HCOOH / 20% H_2O
α	0,58	0,62	0,63	0,66	0,83
BENZOIC ACIDS	-0,034	0,28	0,75	0,63	0,32
ACETOPHENONES	0,37	0,39	0,27	0,28	0,03
BENZALDEHYDES	-1,134	-0,81	-0,94	-0,61	-0,35
PHENOLS	-0,09	0,03	0,12	0,13	0,12
ANILINES	1,04	0,92	1,70	2,10	0,90

PRELOADING SOLUTIONS	DEGMEE	20% HCOOH / 80% DEGMEE	40% HCOOH / 60% DEGMEE	60% HCOOH / 40% DEGMEE	80% HCOOH / 20% DEGMEE
α	0,73	0,70	0,61	0,70	0,80
BENZOIC ACIDS	-0,92	0,45	0,43	0,34	0,20
ACETOPHENONES	0,43	0,51	-1,07	0,25	0,05
BENZALDEHYDES	-0,23	-0,06	-0,01	-0,24	0,16
PHENOLS	0,11	-0,001	-0,02	0,006	-0,12
ANILINES	-0,44	-0,27	0,01	0,33	0,37

VALUES OF δ

$\gamma \Delta a_k$ takes into account the higher contribution on silica Δa_k for a group k which is localized and modulated by the coefficient γ describing deactivation state ; finally we have :

$$R'_M = \log \frac{VaW}{Vo} + \alpha \left[\sum_i Q^\circ_i - \beta f(Q^\circ_k) \sum_{i \neq k} Q^\circ_i + \rho_k \sigma_i + \delta \right.$$

$$\left. - \varepsilon_0 \left[\sum_i a_{i\,(cal)} + \gamma \Delta a_k (SiO_2) \right] \right] \quad (5)$$

So studying a solute series, one solute couple i-Ø-k and Ø-k for which we measure the R'_M, according to different preloadings and using the expression :

$$\left(R'_M (i\text{-}Ø\text{-}k) - R'_M (Ø\text{-}k) \right) \frac{1}{\alpha} - (Q^\circ_i - \varepsilon_0 a_i) = \delta - \beta f(Q^\circ_k) Q^\circ_i + \rho_k \sigma_i$$

we can calculate the coefficients values by multiple linear regression ρ_k, β and δ (table 7) which refer to solute behaviour with the adsorbent. In reality α can be evaluated before and the Q°_i, a_i, ε_0 and $f(Q^\circ_k)$ values were given by SNYDER. Ref (3).

IV) DISCUSSION

Accordingly a good correlation is found between obtained V_a and free calculated n_{OH}, we can now assume an adsorption possibility of different solutes on active free silanol. We discuss the other coefficients α, ρ_k, β , δ , variations to which we have access.

* α

Given the value of α = 1,12 proposed by SNYDER (Ref 3) for a non deactivated silica with average pores like these of HPTLC, the value obtained in our experiments were smaller, which indicates an adsorbent activity decrease by formic acid fixation. Active sites of the adsorbent then, are not available to fix a solute. However the obtained values increase slightly in percentage as a function of the volume of deactived compound of preloading solution. This leads us to think that the formic acid (or diethylamin)fixation on the silica blocks partially the activated sites but leaves others which are available for the fixation on solute.

$*\rho_k$

The obtained values are positive for the benzoic acids and phenols. The group k includes here carboxylic acids and phenols hydroxyls groups which accept electrons easier than the adsorbent. This coefficient is less than zero for anilines, benzaldehydes and acetophenones which behave then like electrons donors or Lewis bases compared to the adsorbent. ρ_k is important when the donor or acceptor effect is more characteristic.
For phenols, the ρ_k values decrease with the formic acid percentage of preloading solutions which involve , a hydrogen bonding decrease. For small formic acid percentages, molecules like i-0-OH may bind to silica by the two extremities where the distance between the two reactive groups are close to silica free sites.
If again it is a matter of adsorption, for benzoic acid (from 80%, for formic acid as preloading solution), we notice a sign change of ρ_k and the acids become electrons donors. This we can explain considering their acidity constants. Indeed, the benzoic acids except for two m and p. nitrobenzoic acids isomers, are weaker acids than formic acid. In this last case, benzoic acid must fix to the silica by the formic acid molecule intermediate.

$*\beta$

Except for preloading using only water, the obtained values for β are perceptibly constant for a given preloading which confirms that it depends little on substituent k. If we compare the obtained values to those found by SNYDER (Ref 3) on alumina, it seems that which the preloading used in our experience the silanol active groups are blocked to a greater degree and more strongly than active groups of alumina.

$*S$

This coefficient explains secondary effects of solvent. It has a significant value when solute and solvent are polar. We see greater values, although few are homogeneous for benzoic acids and phenols cases.

CONCLUSION

The SNYDER theory adopted by HAMMERS and Coll (Ref 5,6,7) gives a good representation of observed phenomenon. The different chromatographic factors calculation makes clear modifications in the different experimental conditions used.

The coefficient which plays a great part is α which explains adsorbent activity and allows the use of a preloading compound which acts as a greffon, to block the very active silanol groups of a silica. It gives also a quantitative idea of the number of free groups **remains** for solute adsorption.

The suggested chromatographic type favors then, polar compounds migration since the latter give strong interaction with adsorbents like silica. In the few remaining compounds migration is less influenced by the preloading type considering as in the case of benzaldehyde and acetophenons. However if the concentration in the preloading compound fixed on the adsorbent is very high, it is not possible to consider a simple adsorption. Thus if only this intervened, all silica hydroxyl active groups would be blocked, and all solute must migrate with the solvent front, this was not observed. The acting mechanism must be a partition mechanism and the solute divides between solvent and the preloading solution fixed on a silica. It must also have hydrogen bonding formation between solute and preloading compound fixed on the silica by monolayer formation. In the case where the preloading compound is formic acid , it has many free sites to make up hydrogen bondings ; It must then fix both to silica and to the solute.

The numerous experimental conditions for pratical applications fo this method show the possibility of using one system of solvent for analysing a mixture of complex compounds.
The study that we undertook, allowed us to consider the chromatographic separation of polar compounds by an adsorption mechanism.

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