

CHROMSYMP. 470

INFLUENCE OF WATER IN LIQUID-SOLID CHROMATOGRAPHIC SYSTEMS ON RETENTION DATA

II. FIXATION OF MONOLOCALIZED SOLUTES WITH CLASS N SOLVENTS AND SILICA GELS

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SUMMARY

A new model for monolocalized solute retention is presented in which silicas are used as adsorbent and class N solvents as mobile phase (diisopropyl ether, 1,2-dichloroethane, dichloromethane, chloroform, carbon tetrachloride and cyclohexane). It is based upon displacement of solvent molecules fixed simultaneously on free, bonded silanol groups and water molecules attached to free silanol groups by hydrogen bonding by a solute molecule. No distinction is made between solute molecules adsorbed on bonded silanol groups and those on free silanol groups deactivated by a monolayer of water. This model is valid for isoactivating solvents having a reduced water content lower than 0.13, corresponding to a water mole fraction on free silanol groups of 0.75. Application of the model to a large number of solutes shows good agreement between theory and experiment. The solute-solvent equilibrium constants on free silanol groups and bonded or free silanol groups deactivated by a water molecule are calculated. These values allow us to draw the following conclusions: bonded silanol groups have a lower energy than free silanol groups; the adsorption energy of a functional group depends on the proximity and spatial volume of other groups; the relative adsorption energies of class N solvents are in good agreement with the solvent strength parameter, ϵ_0 , defined by Snyder.

INTRODUCTION

Several solute retention models have already been proposed for liquid-solid chromatography (LSC). In 1968, a detailed model for LSC retention was proposed by Snyder¹ including the rôle of the mobile phase in the separation. Three classes of solvents were considered: class N, the less polar solvents with LSC solvent strength values, ϵ_0 , in the range from 0.00 to about 0.40 (for alumina); class P, the more polar solvents with ϵ_0 0.5-0.8; and class A B, the amphoteric polar solvents. A somewhat different retention model was presented a few years later by Soczewinski², but in 1974 Snyder³ demonstrated that the two models are essentially equivalent, and more

recently the Snyder–Soczewinski (S-S) model was described in full detail by Snyder and Poppe⁴. In 1973 a third model was presented by Scott and Kucera⁵. This (S-K) model differs almost diametrically from the S-S model. According to Scott^{6,7}, normal chromatographic silica (thermally activated at 150–200°C) contains free silanol groups, and a molecule of water is adsorbed onto each silanol group. This monomolecular layer of adsorbed water, when not displaced by anhydrous methanol, constitutes the surface of the stationary phase on which solute or solvent molecules are adsorbed from the mobile phase. A critical comparison of the S-K model with the S-S model was discussed by Snyder and Poppe⁴. Recently, a comprehensive and detailed physicochemical model was presented by Snyder⁸. This model is based on either classical adsorbents, such as silica or alumina, or on polar bonded-phase packings, such as aminoalkyl, diol, etc.⁹. It considers displacement and localization phenomena¹⁰ as the primary contribution to retention.

Few models take into account the solvent water content in a quantitative way. Therefore, we propose a simple retention model in LSC for isoactivating class N solvents and for monolocalized solute adsorption. Water is considered here as a polar solvent, so binary water–class N solvents will be studied. Isohydric or isoactivating solvents (solvents giving the same support activity) are defined as solvents having the same reduced water content¹¹.

THEORETICAL

In a previous paper¹¹ we have shown that, for class N solvents having a reduced water content lower than 0.13, the water adsorption takes place at strong silanol groups (or free silanol groups) and can be described by the simple Langmuir model. The silica gel surface can be visualized as in Fig. 1. The solute molecules, *s*, can be adsorbed on free silanol groups (●), on bonded silanol (○) or on free silanol groups deactivated by a monolayer of water (W).

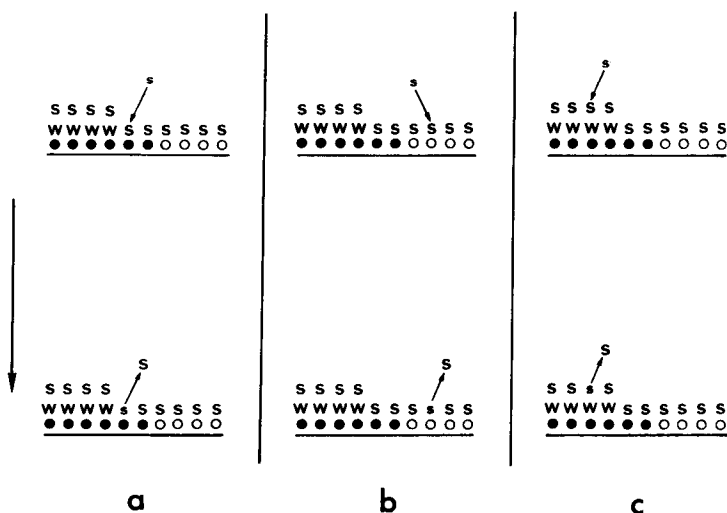
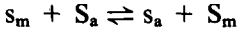


Fig. 1. Monolocalized solute retention mechanism for class N solvents. ● = Free silanol group; ○ = bonded silanol group; w = free silanol group covered by a water molecule; s = solute molecule; S = solvent molecule. a, b and c: see text.

The monolocalized retention mechanism can be represented by the following equilibria.

(a) *Interaction with free silanol groups (Fig. 1a)*



Here, subscript a refers to molecules adsorbed on free silanol groups, and m to molecules present in the mobile phase; S is a molecule of class N solvent. This equilibrium is characterized by the corresponding thermodynamic equilibrium constant

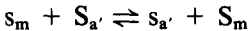
$$K_1^{\text{th}} = \frac{[a_s]_a [a_s]_m}{[a_s]_m [a_s]_a} \quad (1)$$

where $[a_i]_a$ and $[a_i]_m$ are the activities of the i th species in the stationary (for free silanol groups) and the mobile phase, respectively. The activity of the i th species is defined as

$$\begin{aligned} [a_i]_a &= \gamma_{i,a} |x_i|_a \\ [a_i]_m &= \gamma_{i,m} |x_i|_m \end{aligned}$$

where $\gamma_{i,a}$ and $\gamma_{i,m}$ are the activity coefficients of the i th species in the stationary (for free silanol groups) and mobile phase and $|x_i|_a$ and $|x_i|_m$ are the corresponding mole fractions.

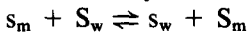
(b) *Interaction on bonded silanol groups (Fig. 1b)*



Here, subscript a' refers to molecules adsorbed on bonded silanol groups:

$$K_2^{\text{th}} = \frac{[a_s]_{a'} [a_s]_m}{[a_s]_m [a_s]_{a'}} \quad (2)$$

(c) *Interaction on free silanol groups deactivated by a monolayer of water (Fig. 1c)*



Here, subscript w refers to molecules adsorbed on free silanol groups deactivated by a molecule of water:

$$K_3^{\text{th}} = \frac{[a_s]_w [a_s]_m}{[a_s]_w [a_s]_m} \quad (3)$$

We have previously shown that the adsorption energy of water on bonded silanol groups is nearly the same as that for additional water on free silanol groups to which molecules of water are already attached by hydrogen bonding¹¹; it seems reasonable to make the same assumption for the adsorption energy of the solute.

Therefore:

$$K_3^{\text{th}} = K_2^{\text{th}}$$

Thermodynamic studies of adsorption isotherms have shown¹²⁻¹⁶ that as the stationary phase becomes more ideal the adsorption phenomenon is more localized. So polar adsorbents, such as silica, may be assumed to be ideal

$$\gamma_{i,a} = \gamma_{i,a'} = \gamma_{i,w} = 1$$

where $\gamma_{i,a'}$ and $\gamma_{i,w}$ are the activity coefficients of the i th species in the stationary phase for bonded silanol groups and for free silanol groups deactivated by a monolayer of water, respectively. In the mobile phase, the solute concentration is always very low, and taking the pure solvent S as the standard state, we can write:

$$\gamma_{s,m} = 1$$

$$\gamma_{s,m} = \text{constant}$$

Eqns. 1, 2 and 3 can then be transformed into:

$$K_1^{\text{th}} = \frac{|x_s|_a |x_s|_m}{\gamma_{s,m} |x_s|_m |x_s|_a} \quad (4)$$

$$K_2^{\text{th}} = \frac{|x_s|_{a'} |x_s|_m}{\gamma_{s,m} |x_s|_m |x_s|_{a'}} \quad (5)$$

$$K_2^{\text{th}} = \frac{|x_s|_w |x_s|_m}{\gamma_{s,m} |x_s|_m |x_s|_w} \quad (6)$$

With class N solvents the water concentration will be very small and consequently negligible; in the same way the amount of solute injected will be small and negligible. So we can write:

$$|x_{\text{H}_2\text{O}}|_a + |x_s|_a = 1$$

$$|x_s|_{a'} = 1$$

$$|x_s|_w = 1$$

$$|x_s|_m = 1$$

In that case, the following relationships can be derived from eqns. 4, 5 and 6, respectively

$$K_1^{\text{th}} = \frac{|x_s|_a}{\gamma_{s,m} |x_s|_m (1 - |x_{\text{H}_2\text{O}}|_a)} \quad (7)$$

$$K_2^{th} = \frac{|x_s|_{a'}}{\gamma_{s,m}|x_s|_m} \tag{8}$$

$$K_2^{th} = \frac{|x_s|_w}{\gamma_{s,m}|x_s|_m} \tag{9}$$

and we can write two equilibrium constants:

$$K_1 = K_1^{th}\gamma_{s,m} \tag{10}$$

$$K_2 = K_2^{th}\gamma_{s,m} \tag{11}$$

The *s* solute capacity factor, *k'*, can be defined as the ratio of the numbers of molecules in the stationary and mobile phase, respectively

$$k' = \frac{n_{s,a} + n_{s,a'} + n_{s,w}}{n_{s,m}} \tag{12}$$

where *n_{s,a}*, *n_{s,a'}* and *n_{s,w}* are the numbers of adsorbed solute molecules per gram of silica on free silanol groups, bonded silanol groups and free silanol groups deactivated by a monolayer of water, respectively; *n_{s,m}* is the number of solute molecules contained in the dead volume of the column per gram of silica. We have also the following relationships

$$|x_s|_a = n_{s,a}/N \tag{13}$$

$$|x_s|_{a'} = n_{s,a'}/N' \tag{14}$$

$$|x_s|_w = n_{s,w}/n_{H_2O,a} \tag{15}$$

$$|x_s|_m = n_{s,m}/N_m \tag{16}$$

where *N*, *N'* are the number of free and bonded silanol groups, respectively, per gram of silica, *n_{H₂O,a}* is the number of water molecules deactivating free silanol groups and *N_m* is the number of solvent molecules contained in the dead volume of the column per gram of silica. Eqn. 12 can then be transformed into:

$$k' = \frac{N}{N_m} \left[K_1 + K_2 \cdot \frac{N'}{N} - (K_1 - K_2)|x_{H_2O}|_a \right] \tag{17}$$

This relationship can be written in the simplified form

$$k' = a - b|x_{H_2O}|_a \tag{18}$$

where *a* and *b* are positive constants (*K₁* > *K₂*).

Previously¹¹ the following relationship was demonstrated

$$|x_{\text{H}_2\text{O}}|_a = \frac{K|x_{\text{H}_2\text{O}}|_m}{1 + K|x_{\text{H}_2\text{O}}|_m} \quad (19)$$

where K is the water-solvent equilibrium constant for adsorption on free silanol groups. So, combination of eqns. 17 and 19 gives

$$k' = \frac{N}{N_m} \cdot \frac{\frac{N'}{N} \cdot K_2 + K_1 + KK_2 \left(1 + \frac{N'}{N}\right) |x_{\text{H}_2\text{O}}|_m}{1 + K|x_{\text{H}_2\text{O}}|_m} \quad (20)$$

i.e., of the type:

$$k' = \frac{\alpha + \beta|x_{\text{H}_2\text{O}}|_m}{1 + K|x_{\text{H}_2\text{O}}|_m} \quad (21)$$

Eqns. 18 and 21 lead to simple expressions for the dependence of the k' values of monolocalized solutes on the water mole fraction in the stationary and mobile phase, respectively. We must emphasize that these two relationships are only valid for class N solvents having a reduced water content lower than 0.13.

EXPERIMENTAL

Experiments were performed with a liquid chromatograph, Spectra Physics Model 8000 (Spectra Physics, Santa Clara, CA, U.S.A.). The UV detector was a Spectromonitor Model III (Laboratory Data Control, Riviera Beach, FL, U.S.A.). The temperature was kept at $25 \pm 0.1^\circ\text{C}$ with a constant-temperature water-bath. The solute retention times were obtained from two measurements and the results were averaged. Reproducibility of retention time was 1%.

Stationary phases

Two porous silica gels ($5 \mu\text{m}$) were used: LiChrosorb Si 60 and Si 100 (E. Merck, Darmstadt, F.R.G.). The surface area and pore volume, respectively, are $482 \text{ m}^2 \text{ g}^{-1}$ and $0.85 \text{ cm}^3 \text{ g}^{-1}$ for LiChrosorb Si 60 and $309 \text{ m}^2 \text{ g}^{-1}$ and $1.15 \text{ cm}^3 \text{ g}^{-1}$ for LiChrosorb Si 100. The columns ($250 \times 4.8 \text{ mm I.D.}$) were packed with 2.00 g of LiChrosorb Si 60 and 1.7 g of LiChrosorb Si 100. The mobile phase flow-rate was 1 ml min^{-1} .

Chemicals

The class N solvents and corresponding test solutes studied are listed in Table I. Dichloromethane, 1,2-dichloroethane, chloroform and carbon tetrachloride were of LiChrosorb grade and were purchased from Merck. Cyclohexane and diisopropyl ether were of Spectrosol grade and were obtained from SDS (Valdonne, Peypin, France).

Test solutes were of analytical grade and were purchased from various producers.

TABLE I
CLASS N SOLVENTS AND CORRESPONDING TEST SOLUTES

<i>Solvent</i>	<i>Test solutes</i>
Diisopropyl ether	Phenol, aniline, <i>o</i> -nitroaniline, <i>p</i> -nitroaniline, 1-phenyl-1-propanol, 1-phenyl-2-propanol, 3-phenyl-1-propanol
1,2-Dichloroethane	Phenol, <i>p</i> -cresol, <i>o</i> -nitroaniline, 1-phenyl-1-propanol, 1-phenyl-2-propanol, 3-phenyl-1-propanol
Dichloromethane	Same as with 1,2-dichloroethane
Chloroform	Phenol, <i>p</i> -cresol, β -naphthol, aniline, <i>o</i> -nitroaniline, <i>p</i> -nitroaniline
Carbon tetrachloride	Naphthalene, <i>o</i> -methylmethoxybenzene, <i>p</i> -methylmethoxybenzene, methoxybenzene, <i>o</i> -ethylnitrobenzene, <i>o</i> -methylnitrobenzene, <i>p</i> -methylnitrobenzene, nitrobenzene
Cyclohexane	Benzene, fluorobenzene, chlorobenzene, nonadecylbenzene, naphthalene

Water content of the mobile phase

The water contents of the solvents were measured coulometrically by the Karl Fischer titration method (Automate Bizot et Constant, Prolabo, France)¹⁷. Accuracy was about 5% for water contents of 2–10 ppm and 2% for those greater than 10 ppm.

Dead-volume determination

The dead volume was measured by using *n*-hexane as test solute.

RESULTS AND DISCUSSION

The capacity factor values of test solutes measured at 25°C for water–diisopropyl ether, –1,2-dichloroethane, –dichloromethane, –chloroform, –carbon tetrachloride and –cyclohexane as mobile phase are shown in Tables II, III, IV, V, VI and VII, respectively.

The water mole fraction on free silica groups was calculated from the water–solvent equilibrium constant published previously¹¹.

According to eqn. 18 a linear decrease of capacity factor values is observed for all these solutes *versus* water mole fraction on free silica groups up to a maximum of 0.75. (In this range water adsorption takes place at free silanol groups only, see Figs. 2–4.) Beyond this point, water adsorption takes place simultaneously at bonded silanol groups and free silanol groups having a water molecule already attached by hydrogen bonding. So, eqn. 18 is not valid, and a steep decrease in capacity factor values is observed (Fig. 2). A non-linear regression has been used to fit the experimental points with eqn. 21, giving the values sought. A short program for a Hewlett-Packard 9825 A computer has been used to obtain the α , β and K values. As an example, water–chloroform equilibrium constant values calculated for six test solutes are shown in Table VIII. A close fit between the average value obtained from Table VIII (3400) and the value obtained from the experimental adsorption isotherm (3500)¹¹ is observed. These overall results support the validity of our theoretical model.

TABLE VI

VARIATIONS OF CAPACITY FACTOR VALUES OF TEST SOLUTES *VERSUS* WATER CONTENT IN CARBON TETRACHLORIDE

Solute	Capacity factor on LiChrosorb Si 60				
Naphthalene	1.20	0.98	0.825	0.715	0.43
<i>o</i> -Methylmethoxybenzene	6.68	5.36	4.70	3.85	1.76
<i>p</i> -Methylmethoxybenzene	14.7	11.55	9.85	7.98	3.72
Methoxybenzene	11.05	8.73	7.32	6.07	2.97
<i>o</i> -Ethylnitrobenzene	6.18	5.29	4.74	4.26	2.73
<i>o</i> -Methylnitrobenzene	8.56	7.20	6.38	5.63	3.49
<i>p</i> -Methylnitrobenzene	12.2	10.2	9.04	7.89	4.99
Nitrobenzene	9.99	8.28	7.12	6.29	4.07
Water content in mobile phase (ppm)	2.4	4.7	7.5	10.0	27.5
$ x_{H_2O} _m \cdot 10^4$	0.205	0.402	0.642	0.856	2.35
Water mole fraction on free silanol groups, $ x_{H_2O} _a$	0.321	0.481	0.596	0.663	0.844

We can also remark that selectivity is affected by the water content of the solvent. It is seen that, in a general way, the higher the water mole fraction on the free silanol groups, the smaller is the selectivity. Once again, from the foregoing, in LSC the water must be considered as a polar solvent and its content must be carefully controlled. As a rigorously anhydrous solvent does not exist, we always have a binary mixture: solvent plus water.

Solute-solvent equilibrium constant values

From eqns. 17 and 18 the equilibrium constants K_1 , K_2 can be calculated. The

TABLE VII

VARIATIONS OF CAPACITY FACTOR VALUES OF TEST SOLUTES *VERSUS* WATER CONTENT IN CYCLOHEXANE

Solute	Capacity factor on LiChrosorb Si 60							
Benzene	2.66	2.33	2.18	1.66	1.35	1.30	1.25	0.74
Fluorobenzene	1.70	1.53	1.45	1.17	1.01	0.995	0.965	0.67
Chlorobenzene	1.36	1.21	1.18	0.945	0.835	0.82	0.795	0.57
Nonadecylbenzene	1.48	1.28	1.21	0.87	0.755	0.72	0.685	0.305
Naphthalene	4.86	4.27	3.99	2.94	2.53	2.38	2.28	1.19
Water content in mobile phase (ppm)	1.8	2.8	3.3	5.9	8.1	8.9	9.4	20.5
$ x_{H_2O} _m \cdot 10^4$	0.084	0.131	0.154	0.275	0.378	0.415	0.439	0.957
Water mole fraction on free silanol groups, $ x_{H_2O} _a$	0.296	0.395	0.435	0.579	0.654	0.675	0.689	0.827

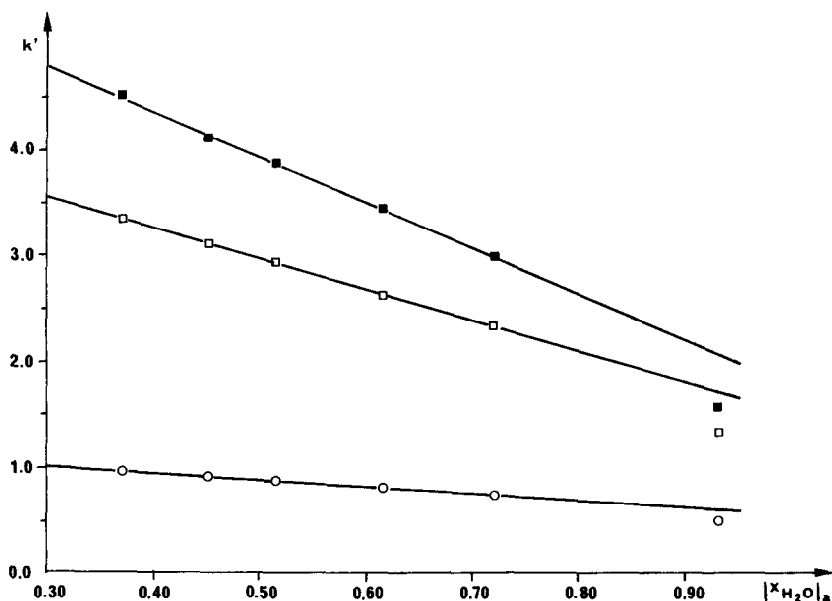


Fig. 2. Variations of monolocalized solute capacity factors, k' , on LiChrosorb Si 60 versus water mole fraction, $|x_{H_2O}|_a$, on free silanol groups. Mobile phase: diisopropyl ether. Temperature: 25°C. Solutes: \circ = 1-phenyl-1-propanol; \square = 1-phenyl-2-propanol; \blacksquare = 3-phenyl-1-propanol.

numbers of free (N) and bonded (N') silanol groups are known¹¹; N_m (number of solvent molecules contained in the dead volume of the column per gram of silica) is easily calculated from V_0 (dead volume of the column) and m (mass of silica in the chromatographic column) according to

$$N_m = \frac{V_0}{m} \cdot \frac{d}{M} \cdot \mathcal{N}$$

where d , M and \mathcal{N} are the density, molecular mass of solvent and Avogadro's number respectively. Thus, for each solute a and b in eqn. 18 are calculated by linear

TABLE VIII

WATER-CHLOROFORM EQUILIBRIUM CONSTANT VALUES CALCULATED FROM VARIATIONS OF SOLUTE CAPACITY FACTOR VALUES VERSUS WATER CONTENT IN THE CHLOROFORM

Solute	K
Aniline	3400
<i>p</i> -Nitroaniline	3300
<i>o</i> -Nitroaniline	3600
Phenol	3400
<i>p</i> -Cresol	3300
β -Naphthol	3500
Average value	3400

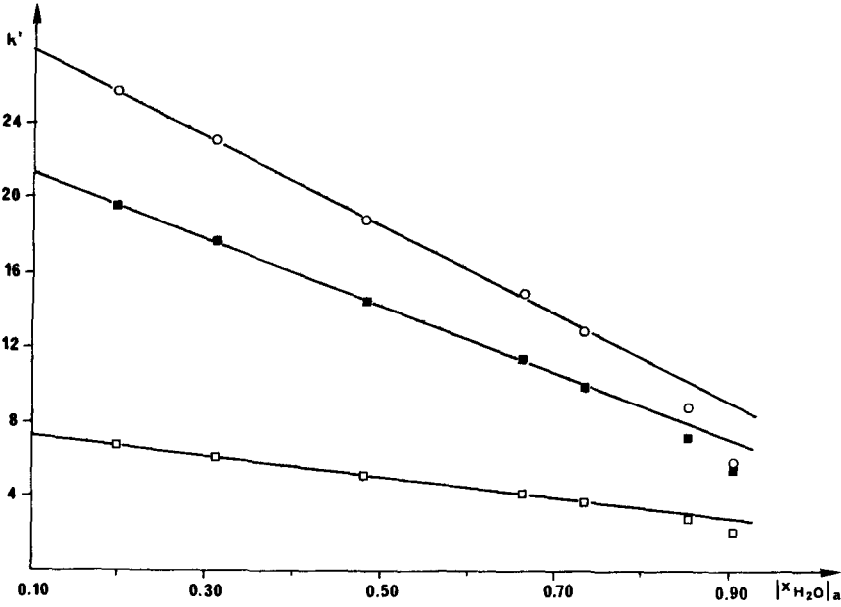


Fig. 3. Variations of monolocalized solute capacity factors, k' , on LiChrosorb Si 60 versus water mole fraction, $|x_{H_2O}|_a$, on free silanol groups. Mobile phase: chloroform. Temperature: 25°C. Solutes: ○ = aniline; ■ = *p*-nitroaniline; □ = *o*-nitroaniline.

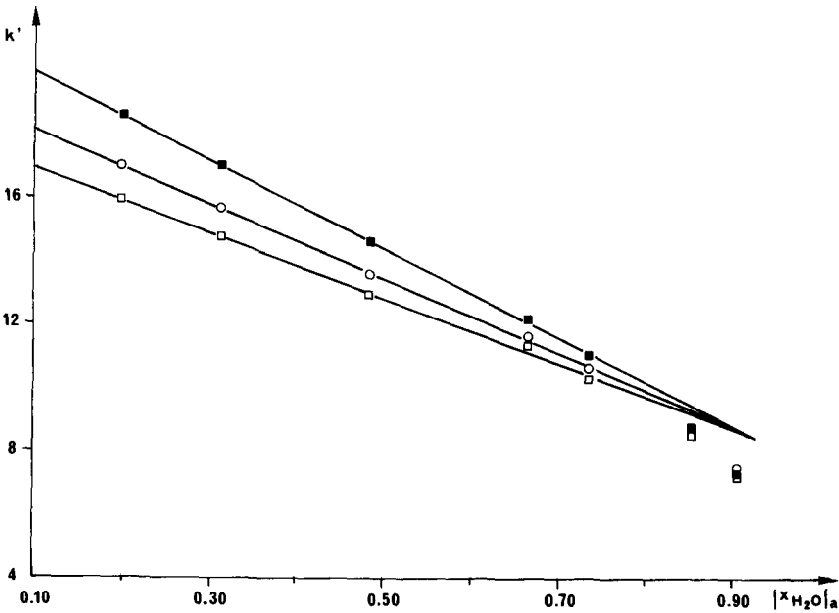


Fig. 4. As Fig. 3 except test solutes: ○ = phenol; ■ = *p*-cresol; □ = β -naphthol.

TABLE IX

SOLUTE-CLASS N SOLVENT EQUILIBRIUM CONSTANT VALUES ON FREE SILANOL GROUPS (K_1) OR ON BONDED AND FREE SILANOL GROUPS DEACTIVATED BY A MONO-LAYER OF WATER (K_2) FOR LICHROSORB Si 60 and Si 100

Solute	Solvent	Si 60		Si 100	
		K_1	K_2	K_1	K_2
Phenol	Diisopropyl ether	2.7	1	3.1	1.2
	1,2-Dichloroethane	26	11	34	10
	Dichloromethane	55	22	68	21
	Chloroform	160	36	155	44
Aniline	Diisopropyl ether	36	3.2	33	3.9
	Chloroform	280	32	210	40
<i>o</i> -Nitroaniline	Diisopropyl ether	5.2	2.5	5.4	2.8
	1,2-Dichloroethane	9.9	4.0	11	4.1
	Dichloromethane	24	7.4	27	7.4
	Chloroform	70	10	61	11
<i>p</i> -Nitroaniline	Diisopropyl ether	38	6.8	37	7.7
	1,2-Dichloroethane	24	7.7	22	7.9
	Dichloromethane	60	16	55	14
	Chloroform	215	25	160	26
1-Phenyl-1-propanol	Diisopropyl ether	6.6	1.8	6.4	2.1
	1,2-Dichloroethane	68	28	70	28
	Dichloromethane	140	43	140	47
1-Phenyl-2-propanol	Diisopropyl ether	26	5	25	5.5
	1,2-Dichloroethane	165	45	160	46
	Dichloromethane	300	77	355	80
3-Phenyl-1-propanol	Diisopropyl ether	37	6.8	33	6.6
	1,2-Dichloroethane	200	54	200	56
	Dichloromethane	365	77	355	80
<i>p</i> -Cresol	1,2-Dichloromethane	29	12	35	11
	Dichloromethane	63	22	71	23
	Chloroform	170	35	165	45
β -Naphthol	Chloroform	145	37	140	43
Naphthalene	Carbon tetrachloride	16	1.2	—	—
	Cyclohexane	58	0.8	—	—
<i>o</i> -Methylmethoxybenzene	Carbon tetrachloride	89	6.2	—	—
<i>p</i> -Methylmethoxybenzene		205	8.7	—	—
Methoxybenzene		155	6.6	—	—
<i>o</i> -Ethylnitrobenzene		67	12	—	—
<i>o</i> -Methylnitrobenzene		100	14	—	—
<i>p</i> -Methylnitrobenzene		145	19	—	—
Nitrobenzene		125	13	—	—
Benzene	Cyclohexane	32	0.5	—	—
Fluorobenzene		18	1.5	—	—
Chlorobenzene		14	1.3	—	—
Nonadecylbenzene		18	0.2	—	—

regression and identified with their expression given by eqn. 17. The results are collected in Table IX.

It must be pointed out, first that, within the experimental errors, the values of K_1 and of K_2 are identical on both silicas (Si 60 and Si 100). Secondly, K_2 is always smaller than K_1 . This observation, again, demonstrates that the adsorption energy of the strong groups is higher than the adsorption energy on bonded groups or strong groups deactivated by a monolayer of water. Thirdly, for a given functional group, alcohol for instance, its equilibrium constant value and, consequently, its adsorption energy depends on the proximity and spatial volume of other groups. The influence of steric hindrance, due to a phenyl group, on the K_1 , K_2 values of phenylpropanol position isomers is evident from Table IX: the closer the phenyl group is to the alcohol group, the smaller are the equilibrium constants K_1 and K_2 .

Relative adsorption energy of class N solvents

Considering the solute-solvent equilibrium on free groups of silica, we can write

$$K_1^{\text{th}} = e^{-\frac{\Delta G}{RT}} = e^{\Delta E}$$

where ΔG is the net free energy and ΔE the net dimensionless free energy corresponding to eqn. 1 with:

$$\Delta E = E_{s,a} + E_{S,m} - E_{s,m} - E_{S,a}$$

For class N solvents, the interaction energies for s and S with the mobile phase are cancelled by corresponding stationary phase interactions. The dimensionless free energy of adsorption is then:

$$\Delta E = E_{s,A} - E_{S,a}$$

Considering the system as ideal, we can write:

$$\ln K_1 = E_{s,a} - E_{S,a} \quad (22)$$

In a similar manner:

$$\ln K_2 = E_{s,a'} - E_{S,a'}$$

$$\ln K_2 = E_{s,w} - E_{S,w}$$

From the K_1 experimental values in Table IX, the reduced adsorption energy of class N solvents falls in the order:



This classification is in good agreement with the solvent strength parameter, ϵ_0 , defined by Snyder and Glajch¹⁸.

Conversely, the reduced adsorption energy of diisopropyl ether depends on the

solute nature. For example, $E_a^{C_6H_{14}O} > E_a^{C_2H_4Cl_2}$ for phenol and phenylpropanols as solutes and $E_a^{C_6H_{14}O} < E_a^{C_2H_4Cl_2}$ for *p*-nitroaniline as solute. This indicates that eqn. 22 is not valid with diisopropyl ether. This system must be considered as non-ideal. In that case, the equilibrium constants K_1 and K_2 can be correlated with the thermodynamic equilibrium constant according to eqns. 10 and 11. Eqn. 22 can then be transformed into:

$$\ln K_1 = \ln \gamma_{s,m} + E_{s,a} - E_{s,a}$$

Consequently, with diisopropyl ether, the calculation of the solute adsorption energy involves the knowledge of the solute activity coefficient in this solvent.

CONCLUSIONS

A simple retention model for monolocalized solutes and for class N solvents is proposed. This model gives a good agreement with experimental results for solvents having a reduced water content lower than 0.13, corresponding water mole fraction on free silanol groups of 0.75. In this range, water adsorption takes place only at free silanol groups. The solute molecule interaction with free, bonded and free silanol groups deactivated by a monolayer of water has been demonstrated.

Water is considered as a polar solvent, and selectivity variations *versus* the water content of class N solvents are measured. It is seen that, in a general way, the higher the water mole fraction on free silanol groups, the smaller is the selectivity.

From solute-solvent equilibrium constants, we have shown that the adsorption energy of a functional group depends on the proximity and spatial volume of other groups.

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