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

### I. ADSORPTION ISOTHERMS OF THE INTERFACE OF CLASS N SOLVENTS AND SILICA GELS

C. SOUTEYRAND, M. THIBERT, M. CAUDE\* and R. ROSSET

*Laboratoire de Chimie analytique de l'Ecole Supérieure de Physique et de Chimie de Paris, 10 Rue Vauquelin, 75231 Paris Cédex 05 (France)*

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#### SUMMARY

Adsorption isotherms are presented for the interface between binary water-class N solvent mixtures and various silica gels. Cyclohexane, carbon tetrachloride, diisopropyl ether, chloroform, methylene chloride and 1,2-dichloroethane were chosen as class N solvents and Partisil, LiChrosorb Si 60 and Si 100 as silica gels. The first part of the isotherms could be described by the simple Langmuir model. The corresponding solvent-water equilibrium constant,  $K$ , as well as the number of adsorption sites,  $N$ , per gram of silica have been calculated. The adsorption sites were identified as the free silanol groups, and it was observed that their number decreased with increasing specific surface area of the silica. Their nature is independent of the physical characteristics of the silica. At higher water contents, adsorption could take place by multilayer formation and adsorption of water on bonded silanol groups. The thermodynamic constant corresponding to the adsorption on the free silanol groups is independent of the solvent nature. Consequently, isohydric or isoactivating solvents are those having the same reduced water content and it is then very easy to link the water content of class N solvents to the silica activity.

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#### INTRODUCTION

Large variations in capacity factors and selectivity with the water content in the mobile phase are observed in liquid-solid chromatography (LSC) on polar inorganic adsorbents such as silica and alumina<sup>1-6</sup>. They are particularly pronounced if class N solvents<sup>5</sup>, that is solvents having strengths,  $\varepsilon^0$ , in the range 0.00-0.40, are used as eluents. For instance, with heptane as the mobile phase, with 10 or 20 ppm of water the retention times are quite different.

By carefully controlling the water content of the eluent, reproducible retention times can be obtained. In order to enhance reproducibility, Boehme and Engelhardt<sup>4</sup> developed an inexpensive glass moisture-control system to stabilize the water content

TABLE I

LSC MOBILE PHASES (NON-POLAR AND MODERATELY POLAR SOLVENTS)<sup>6,7</sup>

Solvent	$\epsilon_{(\text{SiO}_2)}^0$
Cyclohexane	0.03
Carbon tetrachloride	0.11
Diisopropyl ether	0.32
Chloroform	0.26
Methylene chloride	0.30
1,2-Dichloroethane	0.33

of class N solvents. Thomas *et al.*<sup>3</sup> introduced the concept of isoactivating solvents, *i.e.*, solvents with defined water contents adjusted so that the water content of silica gel in equilibrium with these solvents is exactly the same.

There are few studies linking the water content of class N solvents to the silica activity. Therefore we propose to study the mechanism of partition of water between stationary and mobile phases in the case of class N solvents (Table I). The aims of the present paper include:

- (1) The description of an experimental method for the determination of adsorption isotherms in the water–class N solvent systems
- (2) The development of a model to explain isotherm shapes and to derive the corresponding thermodynamic constants
- (3) The demonstration that adsorption isotherms of water in class N solvents can be used to predict solute retention and its dependence on mobile phase composition.

#### THEORETICAL

Assuming that the silica surface contains silanol groups having strong and homogeneous interaction energy, it is possible to predict the shape of the first part of the adsorption isotherm assuming water–solvent (S) equilibrium (Langmuir isotherm):



Here subscripts a and m refer to molecules in the stationary phase and the mobile phase respectively. This equilibrium is characterized by the corresponding thermodynamic equilibrium constant,  $K_{\text{th}}$  (refs. 8 and 9)

$$K_{\text{th}} = \frac{[a_{\text{H}_2\text{O}}]_{\text{a}} [a_{\text{S}}]_{\text{m}}}{[a_{\text{H}_2\text{O}}]_{\text{m}} [a_{\text{S}}]_{\text{a}}} \quad (2)$$

where  $[a_i]_{\text{a}}$  and  $[a_i]_{\text{m}}$  are the activities of the  $i$ th species in the stationary and the mobile phase respectively. The activity of the  $i$ th species is defined as

$$\begin{aligned} [a_i]_{\text{a}} &= \gamma_{i,\text{a}} | x_i |_{\text{a}} \\ [a_i]_{\text{m}} &= \gamma_{i,\text{m}} | x_i |_{\text{m}} \end{aligned} \quad (3)$$

where  $\gamma_{i,a}$  and  $\gamma_{i,m}$  are the activity coefficients of the  $i$ th species in the stationary and mobile phase and  $|x_{i,a}|$  and  $|x_{i,m}|$  the corresponding mole fractions.

Thermodynamic studies of adsorption isotherms have shown<sup>10-14</sup> that as the stationary phase becomes more ideal the adsorption phenomenon is more localized. Localization prevents interaction between adsorbed water molecules (during initial coverage of the surface) and prevents cooperative adsorption. Consequently polar adsorbents such as silica may be assumed to be ideal:

$$\gamma_{i,a} = 1 \quad (4)$$

Concerning the mobile phase, it is obvious that the mixture is not ideal due to the high polarity of water as compared to that of class N solvents. However, the water content in the mixture is always very low (some hundreds of ppm) and taking the pure solvent S as the standard state, we can write:

$$\gamma_{S,m} = 1 \quad (5)$$

$$\gamma_{H_2O,m} = \text{constant} \quad (6)$$

Eqn. 2 can then be transformed into

$$K_{th} = \frac{|x_{H_2O}|_a |x_S|_m}{\gamma_{H_2O,m} |x_{H_2O}|_m |x_S|_a} \quad (7)$$

and we can define an equilibrium constant:

$$K = K_{th} \cdot \gamma_{H_2O,m} = \frac{|x_{H_2O}|_a |x_S|_m}{|x_{H_2O}|_m |x_S|_a} \quad (8)$$

We also have the following relationships:

$$|x_{H_2O}|_a + |x_S|_a = 1 \quad (9)$$

$$|x_{H_2O}|_m + |x_S|_m = 1$$

With class N solvents the water concentration will be very small and consequently negligible, *i.e.*,  $|x_S|_m \approx 1$ . In that case the following relationship can be derived from eqn. 8:

$$K = \frac{|x_{H_2O}|_a}{|x_{H_2O}|_m (1 - |x_{H_2O}|_a)} \quad (10)$$

If  $N$  is the number of strong silanol groups (that is the free silanol groups) per gram of silica, we can write

$$|x_{H_2O}|_a = n_{H_2O,a}/N \quad (11)$$

where  $n_{\text{H}_2\text{O},a}$  is the number of water molecules adsorbed per gram of silica. Combination of eqns. 10 and 11 gives:

$$\frac{n_{\text{H}_2\text{O},a}}{[x_{\text{H}_2\text{O},m}]} = K(N - n_{\text{H}_2\text{O},a}) \quad (12)$$

This relationship enables us to calculate the equilibrium constant and  $N$  for a given chromatographic system.

## EXPERIMENTAL

### *Apparatus*

Experiments were performed with a liquid chromatograph assembled from an Orlita pump (Orlita, Giessen, G.F.R.), a Valco six-port sampling valve with a 10- $\mu\text{l}$  loop and an UV detector (Spectromonitor III Model; Laboratory Data Control, Riviera Beach, FL, U.S.A.). The temperature was set at 20 and  $25 \pm 0.1^\circ\text{C}$  with a constant temperature water-bath. The solute retention times were measured with a 33 80 A calculator integrator (Hewlett-Packard, Avondale, PA, U.S.A.).

### *Stationary phases*

Three porous silica gels (5  $\mu\text{m}$ ) were used: Partisil 5 (Whatman, Clifton, NJ, U.S.A.); LiChrosorb Si 60 and Si 100 (E. Merck, Darmstadt, G.F.R.). The surface area and pore volume respectively are 412  $\text{m}^2 \text{g}^{-1}$  and 1  $\text{cm}^3 \text{g}^{-1}$  for Partisil, 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 (surface area determined by BET method; space requirement for  $\text{N}_2$  molecule, 16.2  $\text{\AA}^2$ ).

### *Chemicals and reagents*

Methylene chloride, 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). All the solvents were dried over molecular sieve 4A then their water content was adjusted to the chosen value.

### *Water content in mobile phase*

The water contents of the solvents were measured coulometrically by the Karl Fischer titration method (Automate Bizot et Constant, Prolabo, France)<sup>15</sup>. The precision was about 5% for water contents of 2–10 ppm and 2% for those greater than 10 ppm.

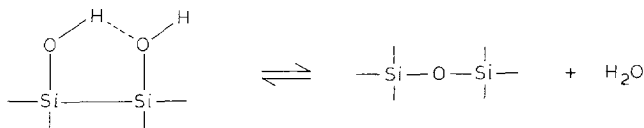
### *Water content in stationary phase*

The water contents in stationary phases are high (1–6%) and were determined by a standardized volumetric Karl Fischer method (automatic titrimeter E 547 Metrohm). Silica samples (0.5–1 g) equilibrated with the solvents were directly introduced into an excess of the Karl Fischer reagent. (The water content of the solvent contained in the porous volume of silica was negligible considering the low solubility of water in class N solvents.) The reagent was then back titrated with a 5% water-methanol mixture.

This technique has already been mentioned<sup>16</sup> and gives a rapid determination of the water contained in the porous silica volume. The precision was about 10% for water contents less than 1% and 5% for those greater than 1%. This rather low precision is due mainly to two effects:

Adsorption of water from the atmosphere during introduction of the silica samples into the cell

Very small extents of condensation, due to the Karl Fischer reagent, of bonded silanol groups, forming a siloxane bridge:



Consequently, the water content is generally measured as a slight excess. Nevertheless, we have verified that the mass of water lost per gram on heating at 150°C is the same (within experimental error) as the water content determined by the Karl Fischer titration.

### Adsorption isotherms

Considerable variations in solute retention times can be observed upon small variations of the solvent water content, especially with class N solvents. So we can assume that when the solute retention times are rigidly constant the system is truly in equilibrium. This has been exploited and adsorption isotherms have been determined using the device<sup>17</sup> shown in Fig. 1. The mobile phase (solvent plus water) is percolated in closed circuit into a chromatographic column connected to two small columns containing a weighed silica mass. When equilibrium is attained (solute retention times are constant) the mobile phase is withdrawn through the septum with a syringe and the two small columns are removed from the circuit. The mobile and the stationary phase water contents are then determined by Karl Fischer titration. This dynamic method gives a rapid equilibrium due to good contact between the two phases.

## RESULTS

The experimental measurements give two series of data:

the solvent water content (ppm) enabling calculation of the mole fraction of water in the mobile phase,  $x_{\text{H}_2\text{O},m}$

the water content of the adsorbent expressed as a weight percentage, permitting calculation of the number of adsorbed water molecules per gram of adsorbent,  $n_{\text{H}_2\text{O},a}$

The experimental values obtained at 20°C for the adsorption isotherm of water-methylene chloride on Partisil 5, at 25°C for water-chloroform on LiChrosorb Si 60 and Si 100 and for water-diisopropyl ether, -methylene chloride, -1,2-dichloroethane, -carbon tetrachloride and -cyclohexane on LiChrosorb Si 60 are shown in Tables II, III and IV, respectively.

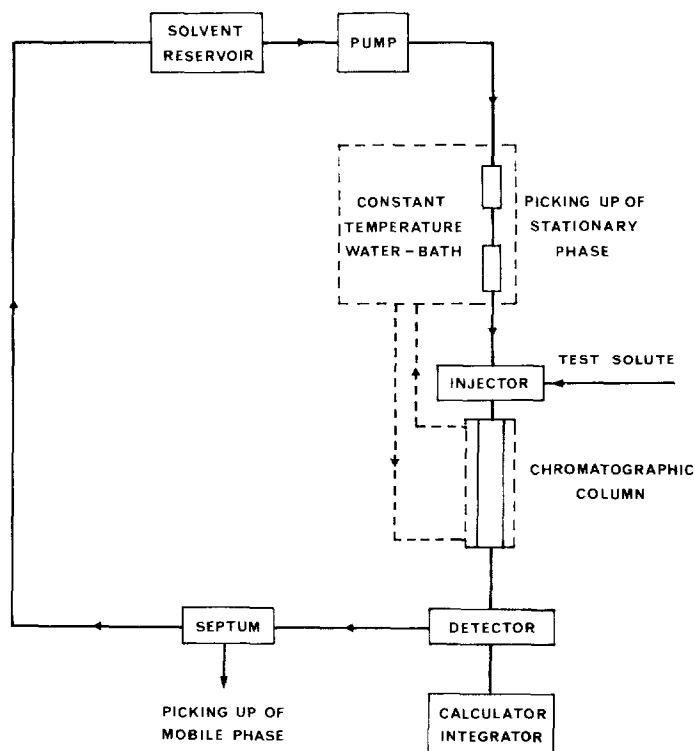


Fig. 1. Experimental device for obtaining water adsorption isotherm.

### *Isotherm representation*

The adsorption isotherms of water in methylene chloride on Partisil 5 and in chloroform on LiChrosorb Si 60 and Si 100 are shown in Figs. 2 and 3, respectively.

### *Adsorption isotherm according to the Langmuir model*

According to the relationship 12, the ratio  $n_{\text{H}_2\text{O},a}/|x_{\text{H}_2\text{O}}|_m$  has been plotted *versus*  $n_{\text{H}_2\text{O},a}$  for the adsorption isotherm of water-methylene chloride on Partisil 5 silica at

TABLE II

EXPERIMENTAL VALUES FOR ADSORPTION ISOTHERM OF WATER-METHYLENE CHLORIDE ON PARTISIL 5 AT 20°C

Water content in methylene chloride (ppm)	$ x_{\text{H}_2\text{O}} _m \times 10^4$	Water content in silica (weight percentage)	$n_{\text{H}_2\text{O},a}$
18.0	0.85	0.77	2.58
95	4.48	2.19	7.32
180	8.49	2.47	8.26
325	15.4	3.51	11.7
470	22.2	4.51	15.1
685	32.4	5.65	18.9

TABLE III

EXPERIMENTAL VALUES FOR ADSORPTION ISOTHERMS OF WATER-CHLOROFORM ON LICHROSORB Si 60 AND Si 100 AT 25°C

Water content in chloroform (ppm)	$ x_{H_2O} _m \times 10^4$	Water content in silica (weight percentage)		$n_{H_2^0,a} \times 10^{-20}$	
		Si 60	Si 100	Si 60	Si 100
22.5	1.49	1.27	0.91	4.25	3.04
42	2.79	1.73	1.32	5.79	4.41
61	4.05	2.09	1.57	6.99	5.25
109	7.23	2.62	1.93	8.76	6.45
182	12.1	3.38	2.34	11.3	7.83
285	18.9	4.38	3.22	14.7	10.8
360	23.9	5.14	3.90	17.2	13.0
565	37.5	10.05	6.69	33.6	22.0

20°C (Fig. 4), for water-chloroform on LiChrosorb Si 60 and Si 100 (Fig. 5) and for water-diisopropyl ether, -1,2-dichloroethane and -methylene chloride on LiChrosorb Si 60 at 25°C (Fig. 6). For all these isotherms a linear relationship is observed at the lowest water contents. In this range the water adsorption takes place at strong silanol groups, and can be described by the simple Langmuir model. From this linear relationship, the solvent-water equilibrium constant,  $K$ , and the value of  $N$  can easily be calculated;  $N$  values are collected in Table V.

The mean  $N$  value measured with LiChrosorb Si 60 (from the isotherms of

TABLE IV

EXPERIMENTAL VALUES FOR ADSORPTION ISOTHERMS OF WATER IN FIVE SOLVENTS ON LICHROSORB Si 60 AT 25°C

Solvent	Water content (ppm)	$ x_{H_2^0} _m \times 10^4$	Water content in silica (weight percentage)	$n_{H_2^0,a} \times 10^{-20}$
Diisopropyl ether	166	9.43	1.22	4.08
	375	21.3	1.84	6.15
	585	33.2	2.15	7.19
1,2-Dichloroethane	45	2.47	1.18	3.95
	63	3.46	1.44	4.82
	86	4.73	1.65	5.52
	113	6.21	1.90	6.35
	162	8.91	2.17	7.26
	220	12.1	2.38	7.96
Methylene chloride	43	2.03	1.19	3.98
	99	4.68	1.87	6.25
	179	8.45	2.25	7.52
Carbon tetrachloride	11.1	0.950	2.16	7.22
Cyclohexane	10.5	0.490	2.22	7.43

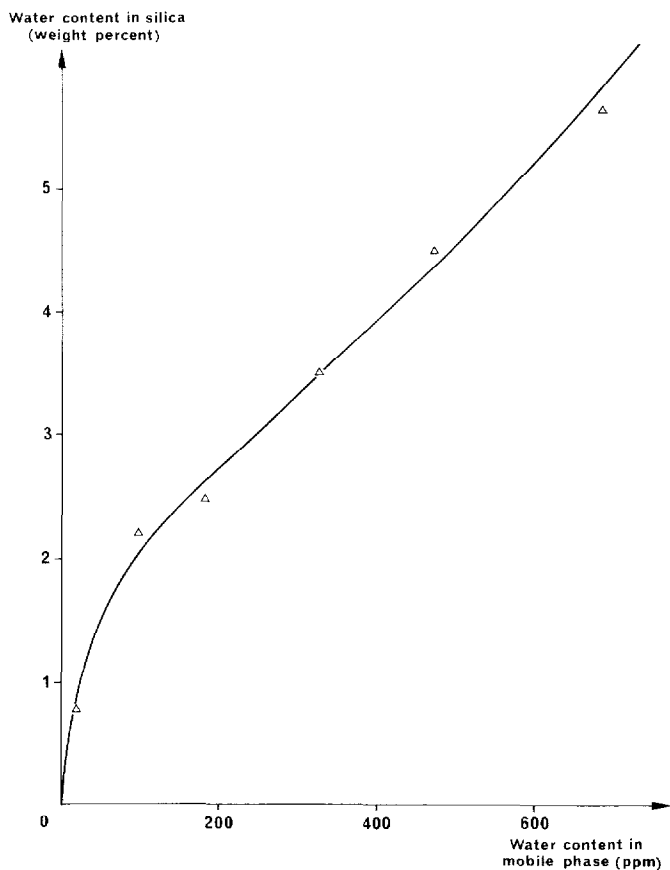


Fig. 2. Water-methylene chloride adsorption isotherm on Partisil 5 at 20°C.

water-diisopropyl ether, -1,2-dichloroethane and -methylene chloride) is equal to  $(10.5 \pm 1) \cdot 10^{20} \text{ g}^{-1}$ , that is  $2.2 \pm 0.2$  strong silanol groups per  $\text{nm}^2$ .

Taking into account the experimental errors, these results demonstrate the validity of our theoretical model. Also, the  $N$  value measured with LiChrosorb Si 60 has been used to calculate the equilibrium constant,  $K$ , in the case of cyclohexane and carbon tetrachloride (thus only one experimental measurement is necessary). The values of  $K$  are shown in Table VI. That of water-chloroform has been measured with both LiChrosorb Si 60 and Si 100. The value reported in Table VI (3500) is the mean value (3600 on LiChrosorb Si 60 and 3400 on LiChrosorb Si 100). The similarity of these two experimental results shows that the adsorption energy of strong silanol groups is independent of the nature of the silica, and particularly of its specific surface area.

From Table VI, it is seen that the higher is the solvent strength,  $\epsilon^0$ , the smaller is the equilibrium constant, except for diisopropyl ether, which will be discussed below.



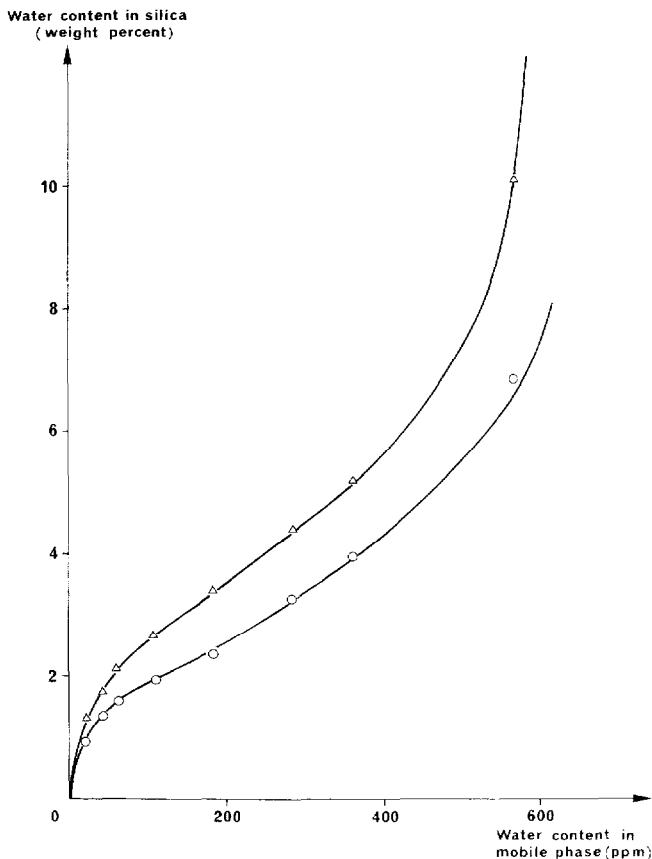


Fig. 3. Water-chloroform adsorption isotherms on LiChrosorb Si 60 ( $\Delta$ ) and Si 100 ( $\circ$ ) at 25°C.

## DISCUSSION

It is well known that various types of silanol groups of different retention activities are present in silica<sup>18,19</sup>, and it is possible to classify them as one of two principal types:

hydrogen bonded silanol groups, the oxygen atoms of which are located within a distance of less than 0.31 nm<sup>20</sup>

free silanol groups, the oxygen atoms of which are located within a distance of greater than 0.31 nm

Several authors<sup>1,21,22</sup> consider that the physisorbed water is totally removed by heating to 150°C for 8 h. Beyond 200°C the water lost comes from the condensation of bonded hydroxyl groups<sup>1,23,24</sup>. They also agree on a total silanol group concentration of about 5 per nm<sup>2</sup> (whatever the specific surface area)<sup>1,25,26</sup> and that the number bonded silanol groups increases with increasing specific surface area of the silica gel<sup>23,27</sup>. On the other hand, the quantitation of the two types of silanol group and their reactivity are the subject of much controversy. According to Kiselev and co-workers<sup>28,29</sup>, infrared spectroscopic measurements show that adsorption takes

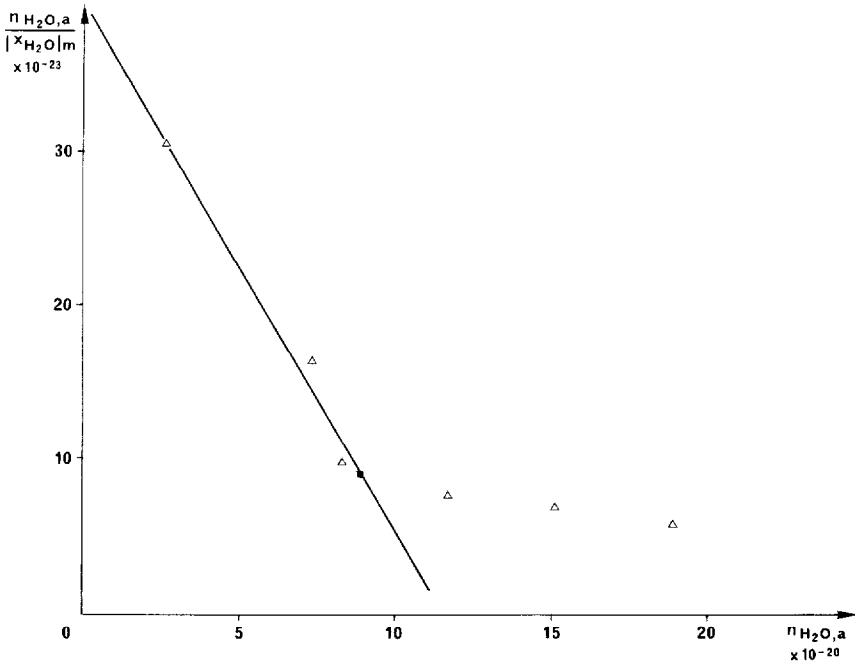


Fig. 4. Linear representation according to the Langmuir model of the water-methylene chloride adsorption isotherm on Partisil 5.

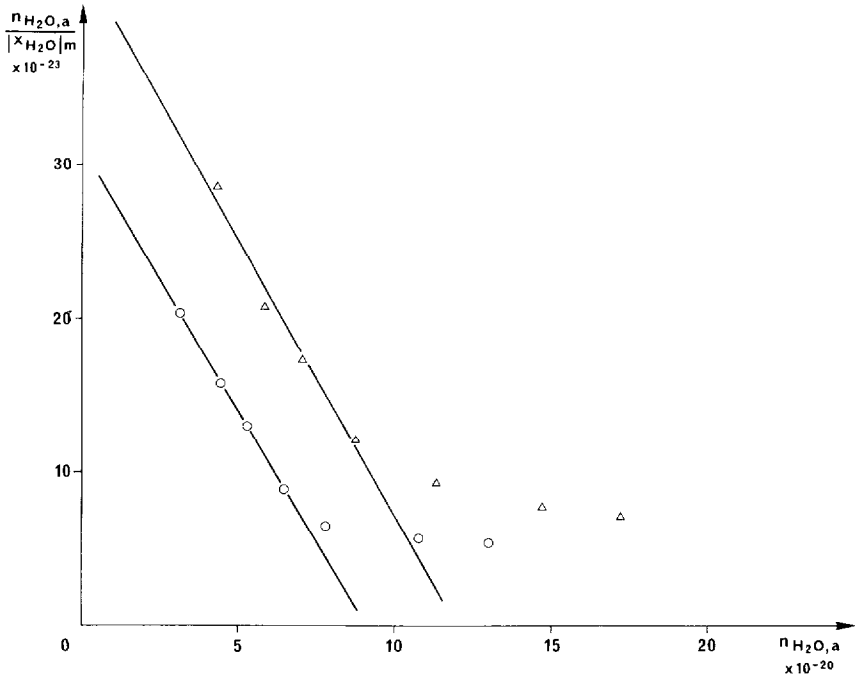


Fig. 5. Linear representation according to the Langmuir model of the water-chloroform adsorption isotherms on LiChrosorb Si 60 ( $\Delta$ ) and Si 100 ( $\circ$ ).

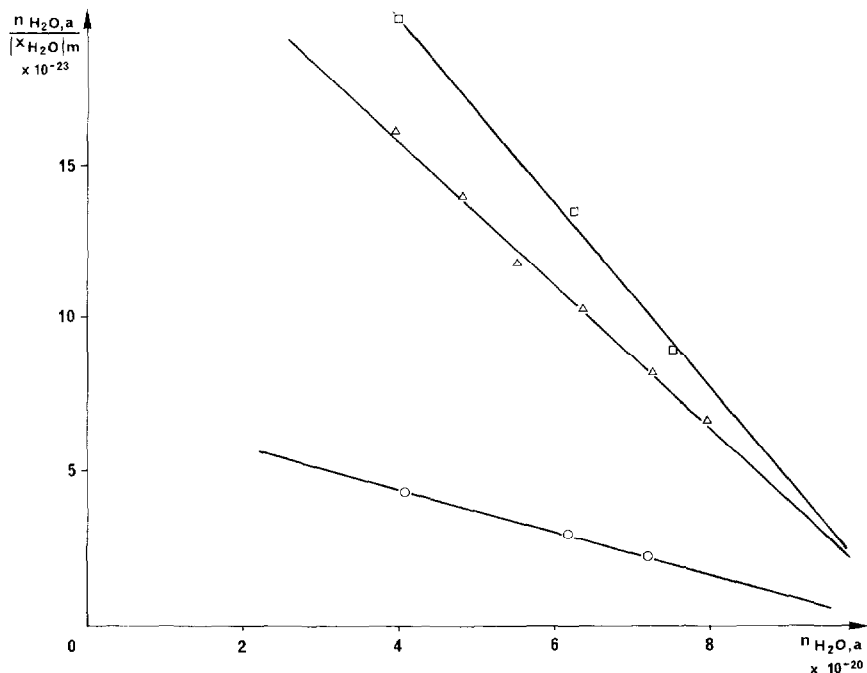


Fig. 6. Linear representation according to the Langmuir model of the water-diisopropyl ether (○), -1,2-dichloroethane (△) and -methylene chloride (□) adsorption isotherms on LiChrosorb Si 60.

place exclusively on free silanol groups. These authors consider that bonded hydroxyl groups are totally condensed at 400°C. On this assumption, it can be calculated that there are 2.6 free silanol groups per nm<sup>2</sup> and 2.2 bonded silanol groups per nm<sup>2</sup> for an Aerosil silica. Bather and Gray<sup>30</sup> consider that for Spherisorb S10W a temperature of about 500°C is needed to remove all molecular water resulting from the condensation of bonded hydroxyl groups. On this assumption, the numbers of free and bonded hydroxyl groups are respectively 1.2 and 3.4 per nm<sup>2</sup>. Furthermore, they believe that free hydroxyl groups are more energetic than bonded hydroxyl groups.

TABLE V

VARIATIONS IN THE NUMBER OF STRONG SILANOL GROUPS WITH THE SPECIFIC SURFACE AREA

Adsorbent	Specific surface area (m <sup>2</sup> g <sup>-1</sup> )	Solvent	No. of strong silanol groups per gram of silica, <i>N</i>	Mean value of <i>N</i> per	
				nm <sup>2</sup>	μmol m <sup>-2</sup>
LiChrosorb Si 100	309	Chloroform	9.1 × 10 <sup>20</sup>	2.95	4.9
Partisil 5	412	Methylene chloride	11.6 × 10 <sup>20</sup>	2.7	4.5
Partisil 5	412	Hexane	10.8 × 10 <sup>20</sup>		
LiChrosorb Si 60	482	Diisopropyl ether	10.3 × 10 <sup>20</sup>	2.2	3.6
LiChrosorb Si 60	482	1,2-Dichloroethane	10.7 × 10 <sup>20</sup>		
LiChrosorb Si 60	482	Methylene chloride	10.6 × 10 <sup>20</sup>		

TABLE VI

WATER-SOLVENT EQUILIBRIUM CONSTANT FOR ADSORPTION ON STRONG SILANOL GROUPS AT 25°C AND SOLVENT STRENGTH PARAMETER,  $\epsilon^0$ , DEFINED BY SNYDER<sup>6,7</sup>

<i>Solvent</i>	<i>K</i>	$\epsilon^0_{(SiO_2)}$
Diisopropyl ether	690	0.32
1,2-Dichloroethane	2300	0.33
Methylene chloride	3000	0.30
Chloroform	3500	0.26
Carbon tetrachloride	21,000	0.11
Cyclohexane	50,000	0.03

However, according to Snyder and Ward<sup>23</sup> the bonded hydroxyl groups are the strongest silica sites for adsorption of polyfunctional solutes such as polycyclic aromatics, while monofunctional solutes or solutes having one very strongly adsorbing group adsorb equally as strongly on both bonded and free hydroxyl groups.

According to Scott<sup>31,32</sup> a temperature of 650°C is needed to remove all physisorbed water. A monolayer of strongly hydrogen bonded water would not be lost by heating at 150°C, would not be titrated by the Karl Fischer method and not removed by anhydrous solvents such as methanol. Consequently, the adsorption phenomenon would then take place on this water monolayer on the silica surface. If this were true the silica surface would be energetically homogeneous and for Partisil 20 it can be calculated that there are  $8.5 \cdot 10^{20}$  hydroxyl groups per gram of silica. Unfortunately, all Scott's results can be interpreted differently, particularly those of the infrared measurements. Consequently, it is not surprising that this work has been severely criticized<sup>5</sup>.

Our results show that free hydroxyl groups have approximately equal energy and that their number decreases when the specific surface area increases (Table V).

Beyond the range of low water contents, the mechanism of adsorption of water is much more difficult to elucidate because two phenomena can take place simultaneously: (i) multilayer formation of water on free hydroxyl groups, and (ii) adsorption of water on bonded hydroxyl groups. The experimental data cannot be interpreted in terms of two Langmuir isotherms associated with two kinds of adsorption sites<sup>17</sup>. So, in the case of class N solvent-water mixtures the multilayer isotherm model has been studied. We have chosen the BET isotherm<sup>33</sup>, assuming that the class N solvent plays the same rôle as the inert gas in a gas-solid equilibrium.

This model can be represented by the usual equation

$$\frac{1}{n_{H_2O,a}} \cdot \frac{\alpha}{1 - \alpha} = \frac{1}{NC} + \frac{C - 1}{NC} \cdot \alpha \quad (13)$$

where:

$$\alpha = \frac{|x_{H_2O}|_m}{|x_{H_2O}|_m^{sat}} \quad (14)$$

$|x_{H_2O}|_m^{sat}$  is the solubility of water in the solvent, expressed as the mole fraction;  $C$  is

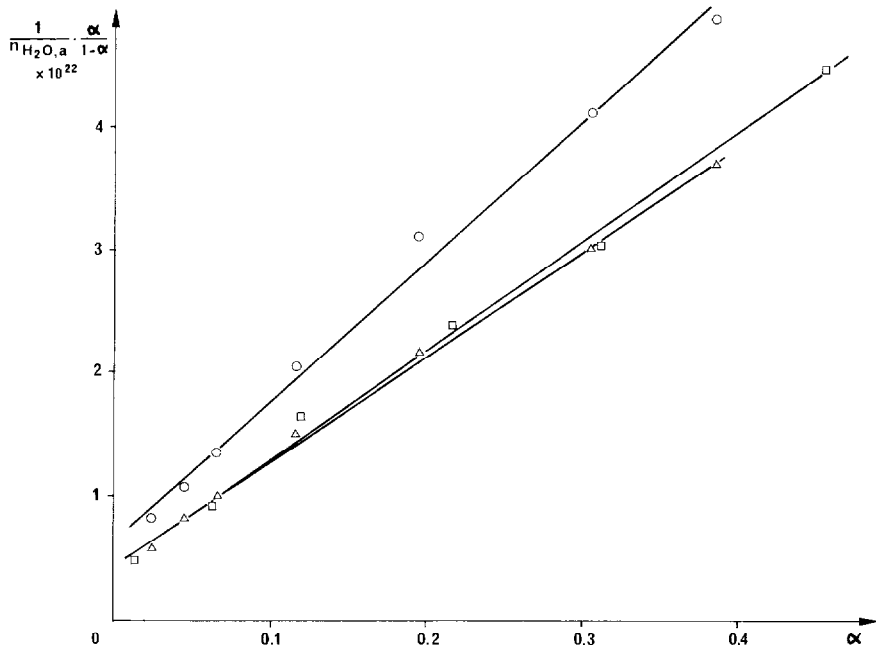


Fig. 7. Representation according to the BET multilayer model of the chloroform–water adsorption isotherms on LiChrosorb Si 60 ( $\Delta$ ) and Si 100 ( $\circ$ ) and of methylene chloride–water on Partisil 5 ( $\square$ ).

a constant taking into account the difference in adsorption energy between the water monolayer at the silica surface and the other layers. Plots of the left-hand side of eqn. 13 against  $\alpha$  values for several binary mixtures such as methylene chloride–water on Partisil 5 (as the stationary phase) and chloroform–water on LiChrosorb Si 60 and Si 100 are shown in Fig. 7. The solubilities of water in pure methylene chloride and chloroform measured in our laboratory are respectively 1500 ppm (20°C) and 930 ppm (25°C).

In all cases a linear range larger than that of a Langmuir isotherm is observed. The value of  $N$  can be calculated by linear regression: LiChrosorb Si 60,  $11.3 \cdot 10^{20} \text{ g}^{-1}$ ; LiChrosorb Si 100,  $8.4 \cdot 10^{20} \text{ g}^{-1}$ ; Partisil 5,  $10.9 \cdot 10^{20} \text{ g}^{-1}$ . These values are in accord with those obtained from the Langmuir model. The  $C$  values obtained from water–chloroform isotherms on LiChrosorb Si 60 and Si 100 are respectively 19.6 and 18.6. This again demonstrates that the adsorption energy of the strong sites is independent of the nature of the silica and particularly of its specific surface area.

The good fit of the multilayer model to the experimental results allows us to draw the following conclusions:

- (1) the bonded silanol groups (sites having a lower energy than free silanol groups) are not involved in the bounding of water molecules
- (2) the adsorption energy of water on bonded silanol groups is nearly the same as that of additional water on free silanol groups to which molecules of water are already attached by hydrogen bonding

In the second conclusion no distinction is made between solute molecules adsorbed on bonded silanol groups or on free silanol groups deactivated by a monolayer of water.

From the foregoing, the equilibrium constant,  $K$ , can be correlated with the thermodynamic equilibrium constant

$$K = K_{th} \cdot \gamma_{H_2O,m}$$

where  $\gamma_{H_2O,m}$  is the activity coefficient of water in the mobile phase, the standard state being pure water. Taking into account the low solubility of water in class N solvents, we have assumed that the water content in these solvents is ideal in the sense of Henry's law, *i.e.*,  $\gamma_{H_2O,m}$  is constant over the entire solubility range. With this assumption eqn. 6 is applicable. If this relationship can be verified, for a given solvent over the entire range of water solubility, then

$$\gamma_{H_2O,m} = \text{constant} = \frac{1}{|x_{H_2O}|_m^{sat}} \quad (15)$$

and we can write:

$$K|x_{H_2O}|_m^{sat} = K_{th} \quad (16)$$

The water contents in class N solvents have been determined at 25°C. The binary water-solvent mixture was shaken vigorously in a separating funnel until equilibration. The separating funnel was maintained at 25°C using a water-bath. The water content in the solvent was titrated according to the Karl Fischer method. Except for cyclohexane, the results are in good agreement with those published<sup>34-36</sup>. For cyclohexane, many difficulties were encountered and we could not obtain a reproducible experimental result. The published solubilities of water in cyclohexane vary from 75 ppm<sup>36,37</sup> to 130 ppm<sup>38,39</sup>, probably due to the formation of water micelles.

The water contents in Table VII are a mean values from to a large number of measurements.

From the water contents in class N solvents and the  $K$  values (Table VI) the thermodynamic equilibrium constant,  $K_{th}$ , has been calculated. The results are given in Table VII. It must be pointed out that the thermodynamic constants corresponding

TABLE VII

WATER CONTENTS IN CLASS N SOLVENTS AND THERMODYNAMIC CONSTANT VALUES FOR ADSORPTION ON STRONG SITES AT 25°C

Solvent	Solubility		$K_{th}$
	ppm	$ x_{H_2O} _m^{sat} \times 10^2$	
Diisopropyl ether	6350	3.60	24.8
1,2-Dichloroethane	1860	1.02	23.5
Methylene chloride	1710	0.808	24.2
Chloroform	930	0.617	21.6
Carbon tetrachloride	105	0.0898	20.7
Cyclohexane	95	0.0443	22.2

to the water-solvent equilibrium on strong sites of silica are independent of the solvent nature:  $K_{th} = 22.8 \pm 2.0$ . It is well known that

$$K_{th} = e^{-\Delta G^0/RT} = e^{\Delta E^0} \quad (17)$$

where  $\Delta G^0$  is the net free energy and  $\Delta E^0$  the net dimensionless free energy corresponding to reaction 1 with  $\Delta E^0 = E_{H_2O,a}^0 + E_{S,m}^0 - E_{H_2O,m}^0 - E_{S,a}^0$ , *i.e.*, the sum of the energies for the species on the right of eqn. 1 minus the sum of the energies for the species on the left. The fact that  $K_{th}$  values are identical whatever the nature of the type N solvent implies that  $E_{H_2O,a}^0 - E_{H_2O,m}^0 \gg E_{S,a}^0 - E_{S,m}^0$ , *i.e.*, the molar free enthalpy of adsorption of pure water (or the interfacial tension of pure water in contact with the adsorbent) is much higher than that of class N solvents. Consequently it is possible to deduce the standard molar free enthalpy of adsorption of water on silica gel:  $\bar{\Delta}G_{H_2O}^0 = \bar{G}_{H_2O,a} - \bar{G}_{H_2O,m} = -RT \log K_{th} = -7.8 \text{ kJ mole}^{-1}$ .

From eqns. 10 and 16 we can write:

$$K_{th} = K |x_{H_2O}|_m^{\text{sat}} = \frac{|x_{H_2O}|_a}{\frac{n_{H_2O,m}}{|x_{H_2O}|_m^{\text{sat}}} \cdot (1 - |x_{H_2O}|_a)} \quad (18)$$

Since  $K_{th}$  is independent of the nature of the class N solvent, isoactivating or isohydric solvent series can easily be identified with eqn. 18. For a given adsorbent activity,  $|x_{H_2O}|_a = \text{constant}$ . The isohydric solvents correspond to  $|x_{H_2O}|_m / |x_{H_2O}|_m^{\text{sat}} = \text{constant}$ , they have the same reduced water content.

From the water contents in class N solvents we can immediately identify an isohydric solvent series whatever the silica activity. As an example, Table VIII shows three isohydric solvent series for three adsorbent activities. This important result must make it easier to choose the optimal conditions in adsorption chromatography. From Table VI, a relationship exists between the solvent strength parameter,  $\varepsilon^0$ , defined by Snyder (which reflects the relative interaction energy of mobile phase molecules with the adsorbent surface) and the water-solvent equilibrium constant,  $K$ , determined by us. Except for diisopropyl ether, the greater  $\varepsilon^0$  is, the smaller  $K$  is.

From the Snyder-Soczewinski model<sup>5</sup> the distribution constant of a solute,  $K^0$ , is given by

$$\log K^0 = \log V_a + S^0 - \varepsilon^0 A_s + A_{\text{eas}}$$

Here,  $V_a$  is the volume of the adsorbed monolayer per gram of adsorbent,  $S^0$  is a parameter which reflects the relative interaction energy of solute molecules with the adsorbent surface,  $A_s$  is the relative area of the solute molecule when adsorbed and  $A_{\text{eas}}$  is a second order term. If water is considered to be the solute, we can write:

$$\log K^0 = a - b \varepsilon^0$$

This relationship shows that the greater the solvent strength is, the smaller is the water-solvent equilibrium constant.

The irregular behaviour of diisopropyl ether may be explained by the high solubility of water in this solvent. Solutions of water in diisopropyl ether no longer have a constant  $\gamma_{H_2O,m}$ .

TABLE VIII  
 SERIES OF ISOACTIVATING CLASS N SOLVENTS CORRESPONDING TO THREE SILICA ACTIVITIES

<i>Water mole fraction on strong silica sites</i>   $x_{H_2O} _a$	<i>Reduced water content (%)</i>	<i>Water content of class N solvent (ppm)</i>					
		<i>Diisopropyl ether</i>	<i>1,2-Dichloro-ethane</i>	<i>Methylene chloride</i>	<i>Chloroform</i>	<i>Carbon tetrachloride</i>	<i>Cyclohexane</i>
0.25	1.16	93	27	25	14	1.5	1.4
0.50	4.39	280	82	75	41	4.6	4.2
0.75	13.2	840	245	225	123	14	12.5



## CONCLUSIONS

The presence of free silanol groups having equal energies has been demonstrated by the rigorous determination of adsorption for isotherms water-class N solvent systems. The number of free silanol groups per gram of adsorbent decreases with increasing specific surface area of the adsorbent.

The first part of the adsorption isotherms corresponds to a deactivation of free silanol groups. They are covered by a water monolayer according to a Langmuir isotherm. Beyond the Langmuir region, the BET isotherm allows a good description of the experimental adsorption behaviour.

The thermodynamic equilibrium constant for water-class N solvent systems is independent of the solvent and reflects the adsorption of water on the strong adsorptive sites of silica. Consequently, isohydric or isoactivating solvents (solvents giving the same support activity) can be defined as solvents having the same reduced water content. With these observations it is easy to link each water content in class N solvents to the silica activity. Thus we will be able to study precisely solute adsorption. The solute adsorption model will be the subject of a subsequent paper.

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