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SOME FEATURES OF THE INTERACTION OF SILICA GEL WITH ORGANIC BASES

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ABSTRACT

The acid groups attached to a silica gel surface were calorimetrically and chromatographically titrated by *N,N*-dimethylformamide; *N,N*-dimethylacetamide; pyridine; methanol; acetone, and acetonitrile in 1,2-dichloroethane. The chromatographic titration furnished the number of moles of solute which reacted with the silanol groups. From the net isotherm fitted to a modified Langmuir equation, the variation of enthalpy and the equilibrium distribution constant of the hydrogen bonding were calculated. The results correlated with the donor number of the bases. The following order of the interaction in forming hydrogen bonding was established: pyridine > *N,N*-dimethylacetamide > *N,N*-dimethylformamide > acetone > acetonitrile.

INTRODUCTION

Active silica gel is covered by silanol groups attached to a SiO_2 skeleton. These groups easily adsorb water and many organic molecules with polar centres onto the surface, through hydrogen bonding. An extensive investigation has been devoted to this kind of material, in order to clarify the nature of the adsorption sites [1].

Dehydration of the surface has been the subject of many discussions [1], but, in general, the water adsorbed physically [1,2] or by hydrogen bonding [3,4], can be distinguished by its characteristic temperature of adsorption, 420 K and 670 to 870 K, respectively. These arguments are in agreement with the adsorption of water in multilayers [5–7], being dried at 420 K in atmosphere or at ordinary temperatures in vacuum [1].

The degree of dehydration of the silica surface increases with the temperature, but the number of silanol groups per unit area of silica is not consistent in the literature, due to the fact that different silicas vary enormously in structure. However, many publications indicate the existence of four to five silanol groups per square nanometer [1,7], for a fully hydroxylated silica surface, when the sample has been dried at 390 to 420 K.

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The purpose of this work was to titrate the acid silanol groups at the solid–solution interface. Silica gel was titrated calorimetrically and chromatographically with bases suspended in 1,2-dichloroethane, which is a poor interacting solvent. The resulting isotherms from these titrations were fitted to a modified Langmuir equation in order to obtain parameters involved with the heterogeneous equilibrium.

EXPERIMENTAL

Materials

The pure grade solvents *N,N*-dimethylformamide (Merck); *N,N*-dimethylacetamide (Merck); pyridine (Reagen); methanol (QEEL); acetone (Carlo Erba) and acetonitrile (Merck) were stored over appropriate dehydrating agents overnight, distilled through an efficient column under reduced pressure and then stored over molecular sieves [8].

Silica gel (Merck) 70–230 mesh, with an average pore diameter of 60 Å, was degassed at 150°C for several hours in high vacuum and stored in a desiccator. The specific area of 579 m^2 g^{-1} was determined by a BET method, by using a CG 2000 Instrumentos Científicos CG Ltda apparatus. All samples for measurement were manipulated in a drybox.

Calorimetric and chromatographic experimental procedures

The calorimetric measurements were performed in the 1,2-dichloroethane solvent by means of a LKB 8700-2 precision calorimetric system. The thermostatted solute in 1,2-dichloroethane at (298.15 ± 0.05) K was incrementally added to 90.0 cm^3 of the desired suspension of silica in the same solvent and at the same temperature, in the calorimetric vessel and the heat of interaction recorded. The calorimeter's performance and details of operation were described previously [8]. Different masses of silica gel were titrated with the same solute with the objective of checking the reproducibility of the measurements.

In a typical example, a 0.49019 g-portion of silica gel was titrated with a solution containing 0.5854 mol l^{-1} of *N,N*-dimethylacetamide. The final volume was ca. 102 cm^3, and at least eight increments were necessary to give an outline of the saturation of the surface (Table 1). Due to the low heat of dilution, a relatively high volume of the solute solution was added in each increment, only five additions being necessary to bring the initial 90.0 cm^3 of 1,2-dichloroethane to the final volume (Table 2).

The chromatographic determinations were carried out with a CG 35 Instrumentos Científicos CG Ltda apparatus, equipped with a thermal conductivity detector, using a Porapak Q column as the stationary phase

TABLE 1

Titration of 0.49019 g of silica gel suspended in 90.0 cm^3 of 1,2-dichloroethane with a 0.5854 M dma solution

V (cm^3)	$-Q_{obs}$ (J g^{-1})	$-\Sigma\ Q_{obs}$ (J g^{-1})
90.00	0	0
90.10	2.57	2.57
90.43	4.35	6.92
90.86	2.79	9.71
91.77	2.86	12.57
93.64	2.61	15.18
95.94	1.65	16.83
98.84	1.59	18.42
102.33	1.37	19.79

with hydrogen as carrier gas. The main purpose of these measurements, called by us chromatographic titration, was to determine the unreacted solute concentration dispersed in solution after the interfacial solid–solution interaction. This experiment followed, as closely as possible, the calorimetric measurements. To illustrate a set of determinations, a portion of 0.81146 g of silica gel was introduced in 90.0 cm^3 of 1,2-dichloroethane in a calibrated volumetric flask of 100.0 cm^3. Immediately, 1.0 cm^3 of 0.5032 mol l^{-1} solution of acetone in 1,2-dichloroethane was pipetted into the volumetric flask. After shaking and then allowing the solid settle, 8.3 μl of this solution was injected into the chromatograph and the area of the peak recorded. A new 1.0 cm^3 portion of the 0.5032 mol l^{-1} solution of the acetone solution was added to the previous mixture in the volumetric flask, which was then shaken and allowed to stand. Again, 8.3 μl of the solution was injected into the chromatograph and the area of the peak recorded. To complete this experiment the same procedure was followed for eight more additions and the respective area of the peaks recorded. A second set of determinations, without silica gel in the volumetric flask, was done, following the same procedure. The unadsorbed acetone in the surface can be determined from

TABLE 2

Dilution of 90.0 cm^3 of a 0.5854 M dma solution with 1,2-dichloroethane

V (cm^3)	Q_{obs} (J)	$\Sigma\ Q_{obs}$ (J)
90.00	0	0
91.06	0.83	0.83
93.57	0.89	1.72
96.13	0.80	2.52
99.24	0.77	3.29
102.18	0.77	4.06

the area vs. volume (or number of moles of acetone) plotted. The acetone which was not adsorbed by the silica surface was determined from a calibration curve of peak area vs. number of moles injected.

RESULTS

The reaction of silica gel with pyridine (py), *N,N*-dimethylacetamide (dma), *N,N*-dimethylformamide (dmf), acetone (ac) and acetonitrile (at) was carried out in 1,2-dichloroethane, due to its poor ability for interacting. The results of a typical calorimetric titration, carried out as described in experimental section, are listed in Table 1 and the enthalpy of dilution is given in Table 2. The net heat obtained is plotted for all solutes used in Fig. 1. This net enthalpy for each increment of titrand (Q_A) was calculated after subtracting the heat of dilution (Q_B). Thus, from the net variation of the enthalpy due to the reaction (Q_{obs}) and the number of moles of the solute adsorbed on the surface (n_f), the variation of the enthalpy was calculated, i.e., $\Delta H = Q_{obs}/n_f$.

During the process of adsorption it is always admitted that the solvent molecules on the surface are continuously displaced by the solute, depending on its concentration in solution, until a dynamic equilibrium is reached [9]. Thus, for this equilibrium, parameters of the adsorption isotherms can be determined through the equation [10–12]

$$\frac{N}{X} = \frac{1}{X_m(K-1)} + \frac{1}{X_m}N \qquad (1)$$

where X is the mole fraction of the solute adsorbed per gram of adsorbate,

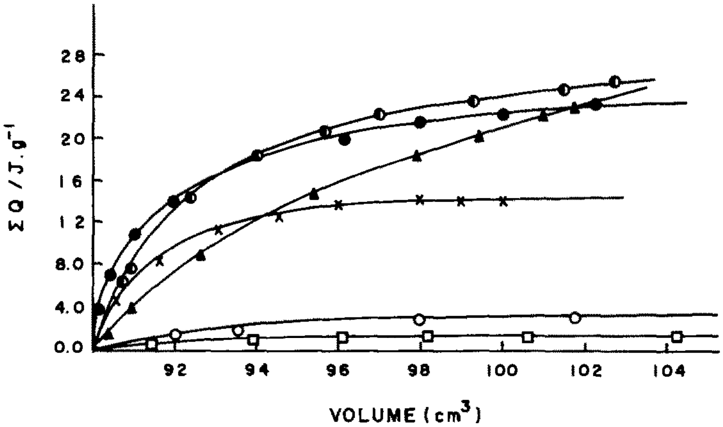

Fig. 1. Net adsorption isotherms of the bases on silica gel at 298.15 K: ◐ *N,N*-dimethylformamide, ▲ methanol, ● *N,N*-dimethylacetamide, × pyridine, ○ acetone and □ acetonitrile.

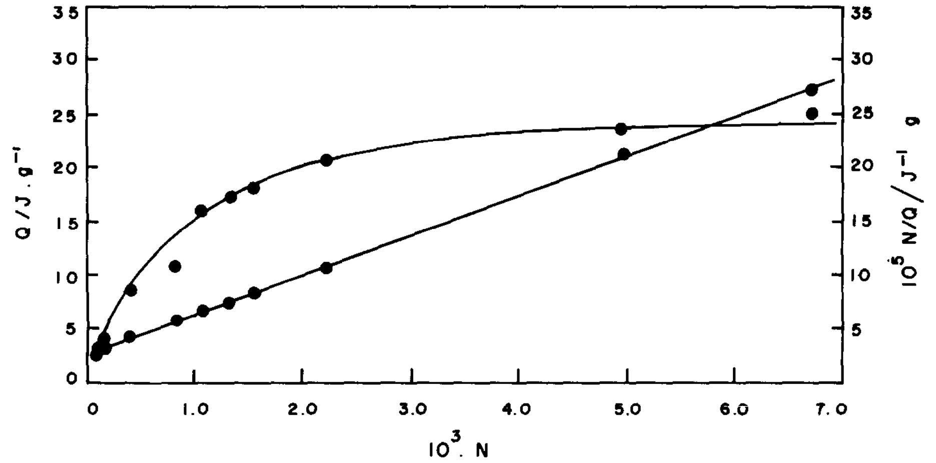

Fig. 2. Amount of acetonitrile adsorbed from 1,2-dichloroethane at 298.15 K on silica gel versus the mole fraction of the adsorbate in solution. The straight line is the linearized form of the adsorption isotherm.

N is the mole fraction of the solute in solution, X_m is the total number of moles of solute adsorbed per gram of adsorbate and K denotes the equilibrium distribution constant. A plot relating N/X vs. N gave a straight line, as is shown for acetonitrile in Fig. 2.

The mole fraction in the above equation was calculated bearing in mind that there is not only a variation in volume, but also in mass in both the calorimetric and chromatographic titrations. Thus, to correlate the results obtained in both titrations, the following expression (2) was adapted to calculate the number of moles of solute (n_s) in equilibrium [13]

$$bn_s^2 + (m + aV - bn_0)n_s - aVn_0 = 0 \tag{2}$$

where n_0, m and V are the moles of solute added in each increment, the mass of adsorbate in grams and the total volume in liters at each point of the titration, respectively. The values of a and b represent coefficients of the slope and intercept of the Langmuir equation $\frac{C}{n_f} = a + bC$. These values are obtained by plotting the concentration of the solute in solution (C) vs. the fixed number of moles of solute per gram of silica.

The adsorption process is accompanied by a change in enthalpy and a similar equation could be written [10–12]

$$\frac{N}{Q} = \frac{1}{Q_m(K_e - 1)} + \frac{1}{Q_m}N \tag{3}$$

In expression (3), N has the same meaning as before, Q is the enthalpy of adsorption observed per unit mass of adsorbed material, Q_m is the integral enthalpy of the adsorption of the solute in the monolayer of one gram of

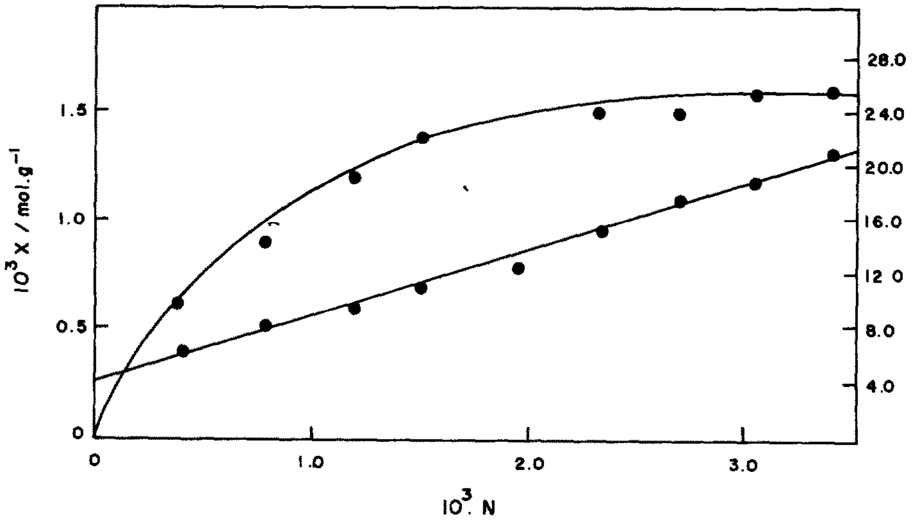

Fig. 3. Heat of adsorption of dmf on silica gel from 1,2-dichloroethane at 298.15 K versus the mole fraction of the adsorbate in solution. The straight line is the linearized form of the adsorption isotherm.

adsorbent. The constant K_e includes a proportionality factor and is not necessarily numerically identical with eqn. (1). As established before, the slope and the intercept of N/Q vs. N give Q_m and K, respectively. The heat of adsorption of dmf on the surface is represented in Fig. 3 and the thermodynamic parameters of adsorption involving all equilibria are listed in Table 3. The free energy of adsorption and the corresponding entropy were calculated by means of the following expressions: $\Delta G = -RT \ln K$ and $\Delta G - \Delta H = -T\Delta S$.

TABLE 3

Thermodynamic parameters for the adsorption on silica gel of bases dissolved in 1,2-dichloroethane at 298.15 K

Base	log K_e	Q_m (J g^{-1})	$-\Delta H^\ominus$ (kJ mol^{-1})	$\Delta S^\ominus$ (J mol^{-1} K^{-1})	$-\Delta G^\ominus$ (kJ mol^{-1})	DN [a]	RME [b]
Acetonitrile	2.40	2.62	1.28	4.03	2.24	14.1	6
Methanol	2.59	37.07	12.78	−34.56	2.40	19.0	30
Acetone	2.90	3.88	1.29	3.98	2.69	17.0	17
N,*N*-dimethylformamide	3.11	27.43	2.25	0.77	2.89	26.6	25
N,*N*-dimethylacetamide	3.31	24.51	5.84	−11.26	3.07	27.8	41
Pyridine	3.31	16.31	7.09	−15.50	3.07	33.1	42

[a] Donor number.

[b] Relative molar effectiveness.

DISCUSSION

During the process of adsorption of the organic molecule at the 1,2-dichloroethane solution/silica gel interface, the bases displace the solvent on the surface, being held by the silanol groups, an interaction which can be interpreted by applying the Lewis acid–base concept [14]. Therefore, the acid centre represented by the hydrogen of a silanol group must be linked to a basic centre of the solute to give typical hydrogen bonding. In fact, all bases present a basic atom in their molecules available for this interaction; an oxygen centre in dma, dmf, acetone or a nitrogen centre in pyridine and acetonitrile [15].

For this adsorption the following equilibrium might be written:

$$\text{adsorbed} - \text{solvent} + \text{solute in solution}$$
$$\rightleftarrows \text{adsorbed} - \text{solute} + \text{solvent in solution}$$

Experimentally, this exchange is kinetically favourable. The evidence of this fact, is demonstrated in the rapidity with which the baseline is reached after each incremental addition in the calorimetric determinations. On the other hand, the results are perfectly reproducible in calorimetric and chromatograph titrations.

A calculation of the variation of the enthalpy of acid–base interaction from the net calorimetric curve is not possible since the number of moles of reactant solute in each increment was unknown. However, this amount was determined by means of the chromatographic titrations. From this technique, samples of the supernatant, after each increment was equilibrated with the adsorbate, were injected into the chromatograph. The difference in area of the peaks with and without the silica gel in the sample allows calculation of the number of moles of solute fixed in the surface. The net isotherm, after this sort of correction, was fitted by using a modified Langmuir equation [10–12] and the results are summarized in Table 3.

The data in Table 3 show an increase of log K from acetonitrile to pyridine and, consequently, increasing ΔG values. There is not any trend in ΔS or Q_m values. However, it is quite reasonable to interpret these results by means of the variation of the enthalpy [8]. This parameter describes the chemical interactive process involving the formation of the hydrogen bond.

The basicity or donor ability of the solvent defines its donor number in homogeneous medium, when the base interacts with the standard acid in 1,2-dichloroethane, to give a negative variation of enthalpy [16]. In changing the standard acid for phenol or *p*-fluorophenol, the exothermic enthalpy correlates reasonably with the ability for interaction of the bases, in the formation of the hydrogen bonding [17].

Although our system involves reactions in heterogeneous medium, with the exception of methanol, the increase in the variation of enthalpy follows the increase of donor-number from acetonitrile to pyridine as is indicated in

Table 3. On the other hand, the adsorption isotherm determined by spectral and calorimetric methods indicated the equivalence of the hydrogen bond strengths, in both heterogeneous and homogeneous media. Based on the strength of interaction of the bases with the silica gel surface, acetonitrile and acetone gave ΔH values of -1.28 and 1.29 kJ mol^{-1}, which permits their classification as median bases, while dmf and py, with ΔH values 2.25, 5.84 and 7.09 kJ mol^{-1} are ordered as strong bases [1].

The association of the polysilicic acid with organic compounds is an argument used to compare the relative molar effectiveness, of various organic compounds, in relation to the structure and activity of the hydrogen bond formed. For a given number of carbon atoms in the molecules, the activity increases with a decrease in the number of hydrogen atoms attached to the polar oxygen or nitrogen atoms. These relative numbers are listed in Table 3. With the exception of methanol, they increase from acetonitrile to pyridine, as was observed with the donor number and, consequently, this is also the sequence of increasing variation of the enthalpy in the series of bases [1].

The greatest variation of the enthalpy was observed with methanol, whose value did not correlate with the donor number, nor with the relative effectiveness (see Table 3). This discrepancy might be associated with the great ability of this molecule to form hydrogen bonds or by some esterification of the surface. Moreover, its small size can facilitate its diffusion through the pores of silica. An illustration of this point of view is shown in the summation of heats vs. volume plot (Fig. 1), where a plateau is not reached, even with high concentrations of the alcohol.

Taking into account the neutralization of the silanol groups by the organic molecules studied during the formation of hydrogen bonding, the following basicity order was established.

pyridine > *N,N*-dimethylacetamide > *N,N*-dimethylformamide
> acetone > acetonitrile.

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