

Reinforcement of Siloxane Elastomers by Silica. Interactions Between an Oligomer of Poly(Dimethylsiloxane) and a Fumed Silica

G. BERROD, A. VIDAL, E. PAPIRER, and J. B. DONNET, *Centre de Recherches sur la Physico-Chimie des Surfaces Solides, 68200 Mulhouse, France*

Synopsis

The study of the adsorption of an organosiloxane onto a fumed silica was undertaken in order to improve our knowledge of the reinforcement of silicon rubbers by silica. IR and gas-phase chromatography techniques were used to characterize the adsorption of octamethyltetracyclosiloxane. At room temperature, the occurrence of hydrogen bonding between the solute and the adsorbent was shown. The amount of material adsorbed according to this mechanism was shown to be strongly dependent on temperature. The heats of adsorption at various covering ratios were calculated from the isotherms measured at temperatures close to 150°C.

INTRODUCTION

As a consequence of their poor mechanical properties, organosiloxane elastomers cannot be used on their own. To compensate for this defect they have to be compounded with several fillers, particularly fumed silicas. The occurrence of very strong interactions at the silica-polymer interface is then a characteristic of the resulting materials, and during recent years much research has been devoted to the explanation of these phenomena.

Thus and in order to study the influence of the fillers on the mechanical properties of the composites, Boonstra et al.¹ tried to modify the interaction level between a hydrocarbon rubber and a filler. After grafting or adsorption of small molecules onto silica, they showed the important part played by its surface chemistry in the reinforcement process. However, very few studies so far have directly examined the nature of the processes occurring at the poly(dimethylsiloxane) (PDMS)-silica interface.

For example, Chahal and Saint-Pierre² studied the interactions of PDMS oligomers with several silicas, the surfaces of which were eventually modified with alkoxy, alkylsilane, or fluoroethyl groups. They determined their interfacial energies by measure of their heats of adsorption, and they observed a decrease in the interfacial energies proportional on the one hand to the amount of grafted groups and on the other hand to the length of the grafted chains when the number of groups retained on the surface was kept constant.

Ashmead and Owen³ as well as Perkell and Ullman⁴ have also studied the influence of several parameters such as moisture ratio, temperature, molecular weight of the polymer, and nature of solvents on the adsorption isotherms of PDMS on glass powder. However, no hypothesis could be derived from the results obtained by these authors about the interaction mechanisms between the tested material and the fillers.

IR spectroscopy was the technique used by Aristova and Coll^{5,6} to examine the dimethylsiloxane–silica interactions at high temperature. They particularly pointed at an important catalytic activity of water containing traces of HCl in the chemisorption of hexamethyldisiloxane. They also recognized the part played by two active centers in this chemisorption process, namely, the isolated hydroxyl groups and the siloxane bridges.

Thus, while several authors have tried to control the siloxane–silica interaction level by use of reactive molecules or oligomers able to mainly react with the surface of silica, very few have actually tried to characterize and quantify the created bonds. For these reasons, our work using model siloxanes has been aimed at the understanding of the nature of the bonds formed between the elastomer and the filler. From the knowledge of the part played by some functional groups in these interactions, we then planned to try to modify their number or their amount in order to produce fillers of different surface energy and to observe the influence of these modifications on the physical properties of the composites.

EXPERIMENTAL

Reactants

Studies were performed with a fumed silica of specific surface area 300 m²/g; Aerosil 300 (A 300; Degussa).

Octamethylcyclotetrasiloxane (D4) was used as a model for siloxane rubbers. It was supplied by Rhône Poulenc Industries and was used without previous purification. Its low boiling point made its use easier in the techniques we employed for our work, i.e., IR spectroscopy and gas-phase chromatography.

IR Spectroscopy

Equipment. In order to degas silica at different temperatures, perform the adsorption of D4, and record the corresponding spectra without admitting atmospheric moisture onto the sample, we had to engineer a special device (Fig. 1). The silica samples were disc shaped (10 mg), agglomerated under 100 kg/cm². The cell had NaCl windows and a holder allowing the setting up of the sample on the axis of the IR beam. The upper part of the apparatus was made of a quartz tubing around which a movable oven could be set. By means of a magnetic device the sample could be transferred either to the cell or to the heated enclosure. The whole equipment was connected to a vacuum line and the absorbate container. In addition, it could be easily folded to be placed on the sample holder of a Beckman IR 12 spectrophotometer.

Experimental Procedure. After degassing under vacuum (5×10^{-5} torr) for 1/2 hr at 150°C, D4 vapor (saturated vapor pressure at 25°C) was admitted into the cell at room temperature. After a variable amount of time, desorption of the cyclosiloxane was obtained by pumping at room temperature. Each step of this treatment was controlled by the recording of the IR spectra between 4000 and 2600 cm⁻¹.

Method of Calculation. The adsorption of siloxane onto silica was followed by applying Lambert–Beer's law to the spectral lines characteristic of CH₃ groups (2960 cm⁻¹), associated hydroxyl groups (OH_{assoc} between 3700 and 3400 cm⁻¹),

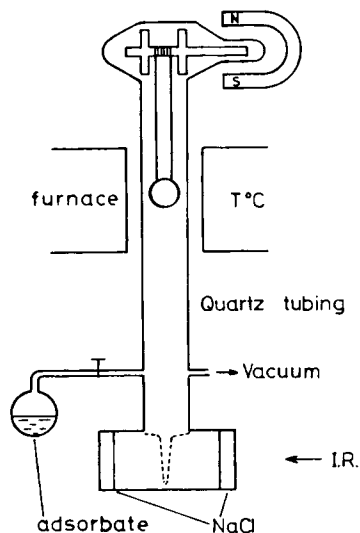


Fig. 1. IR cell diagram.

and free or isolated hydroxyls (OH_{free} , 3750 cm^{-1}). The method of calculation used to determine the absorbance values yielded nonzero values when there were no more free or associated hydroxyl groups. This was due to the overlapping of the different lines. In the particular case of OH_{assoc} it was somewhat difficult to measure I and I_0 since there was a shift of their spectral lines when the quantity of adsorbate changed. Moreover, several OH_{assoc} absorbing at different wavelengths could be obtained. In this case two methods of calculation were tested: (1) either I_0 and I were measured at the wavelength of the maximum absorbance, or (2) they were obtained by addition of the values measured at several wavelengths arbitrarily selected between 3700 and 3400 cm^{-1} (3700 , 3600 , 3500 , and 3400). Both methods gave comparable results. The comparison of the values obtained by IR spectroscopy with those derived from elemental analysis for samples having well-known amounts of adsorbed D4 permitted the plotting of a standard curve $\log(I_0/I)_{\text{CH}_3}$ versus quantity of adsorbed D4 (Fig. 2). It was used to quantify some of the results discussed below.

Gas-Phase Chromatography

Equipment. The experiments were performed with a Perkin-Elmer 881 chromatograph equipped with a catharometer. The stainless steel columns were 0.32 cm in diameter and 45 cm long. Aerosil 300 could not be used without pretreatment because of too small a granulometry. Thus, it first had to be agglomerated by a hydrothermal treatment. This resulted in the following sequence of procedures: dispersion of silica in distilled water, then vacuum drying (125°C), followed by grinding and sieving. The columns were filled with samples of grain size between 115 and 60 mesh. We made certain, of course, that the specific surface area of silica was not affected by this hydrothermal treatment. Helium was the carrier gas used at a rate of $20\text{ cm}^3/\text{min}$. Before any experiment, the column was conditioned by flushing with helium for 12 hrs at 200°C .

Experimental Procedures. At a given temperature, for example, 60°C , we

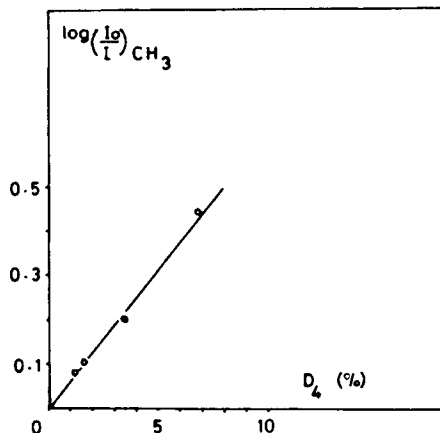


Fig. 2. Plot of $\log(I_0/I)_{\text{CH}_3}$ vs quantity of adsorbed D4.

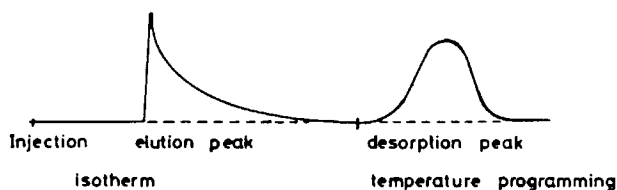


Fig. 3. Chromatograms.

used the following procedure to study the adsorption of the siloxane onto silica: (1) In order to saturate the adsorbent, a sufficiently large volume of D4 was injected ($60 \mu\text{l}$). After 2 hr this was followed by the recording of an elution peak. (2) The recording of the desorption peak, the area under which is proportional to the quantity of irreversibly adsorbed D4, was obtained by heating the column to 200°C in steps of $2^\circ\text{C}/\text{min}$. (3) In order to check that during this process no deviation of the baseline occurs which would alter the calculation of the surface of the desorption peak, a blank column was submitted to a similar temperature programming. (4) The heats of adsorption were deduced from the adsorption isotherms. These isotherms were plotted from the chromatograms obtained after injection of increasing quantities of adsorbate.

Method of Calculation. The quantity of adsorbed D4, proportional to the area under the desorption peak, is expressed by (Fig. 3)

$$Q_a = \frac{Q_1 S_{dp}}{S_{ep} + S_{dp}}$$

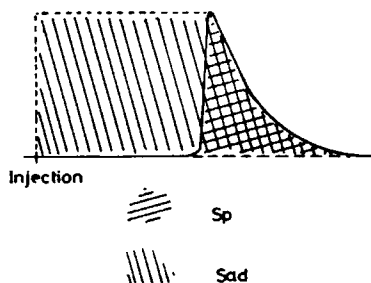


Fig. 4. Chromatograms.

where Q_a = amount of D4 retained through hydrogen bonding; Q_i = quantity of D4 injected; S_{dp} = area under the desorption peak; and S_{ep} = area under the peak obtained after saturation of the column. After assuming that the conditions of equilibrium chromatography were satisfied, the adsorption isotherms were calculated from the elution curve by applying the Glueckhau's method.⁷ The two quantities we had to know in order to plot an adsorption isotherm (a and p/p_0) were deduced from the following equations (Fig. 4):

$$a = \frac{Q_i S_{ad}}{m S_p S_0} \quad \frac{p}{p_0} = \frac{Q_i q h R T}{S_p W p_0}$$

where a = amount of D4 retained per m^2 of filler ($\mu\text{mol}/m^2$); Q_i = quantity of D4 injected (μmol); S_p = area under the elution peak (cm^2); m = quantity of silica (g); S_0 = specific surface area of silica (m^2/g); S_{ad} = area under the adsorption peak (cm^2); q = speed of the recording chart (cm/min); h = height of the elution peak (cm); R = perfect gas constant ($\text{atm cm}^3/\text{K mol}$); T = temperature (K); W = velocity of the carrier gas (cm^3/min); and p_0 = vapor pressure of D4 at temperature T (atm). Since each point of the isotherm necessitates an injection for its calculation, a series of injections of increasing volume had to be performed in order to calculate and plot the total isotherm.

The Brunauer Emmett and Teller transformation of the isotherms yielded the amount of adsorbate corresponding to a monolayer and as a consequence the covering ratio of the filler by D4 could be deduced. When the calculations were performed with an adsorbed phase of constant composition and for isotherms obtained at very close temperatures, it was possible by use of the Clayperon equation to calculate the differential heat of adsorption (ΔH_a):

$$\Delta H_a = R \left(\frac{\partial \ln P}{\partial (1/T)} \right)_a$$

RESULTS AND DISCUSSION

IR Spectroscopy

The spectrum of Aerosil 300 degassed for $1/2$ hr at 150°C is presented in Figure 5. One can see particularly at 3750 cm^{-1} the line due to the free hydroxyl groups and between 3700 and 3400 cm^{-1} the one due to the hydrogen-bonded vicinal hydroxyls. The total disappearance of the free OH band is obtained at room temperature after 13 hr of reaction between the D4 vapor and silica (Fig. 6). On the one hand, the height and width of the OH_{assoc} line are increasing and its maximum corresponds to a wavelength of 3745 cm^{-1} ; on the other hand, a sharp band due to the CH_3 of adsorbed D4 is appearing at 2960 cm^{-1} .

Presented in the order of increasing degassing times, the different spectra of Figure 7 show a decrease of the CH_3 and OH_{assoc} lines and a reappearance and then an increase in the OH_{free} band. Moreover, while the desorption process is still in progress, one notes a shifting of the maximum of the OH_{assoc} line toward shorter wavelengths. This is proof of the existence of hydrogen bonding of different levels of energy. After degassing for 3 hr, some quantity of D4 is still adsorbed on the filler, and it can be recovered by heating the sample at 150°C for $1/2$ hour.

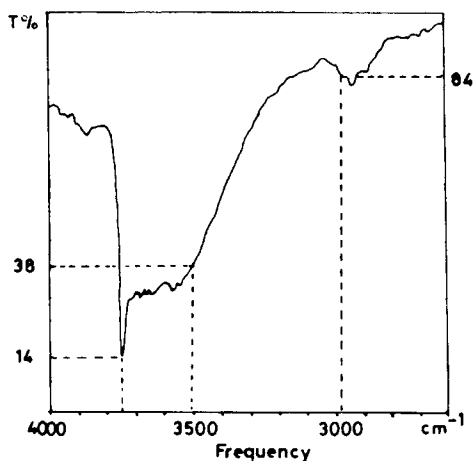


Fig. 5. IR spectrum of A 300 degassed for $\frac{1}{2}$ hr at 150°C .

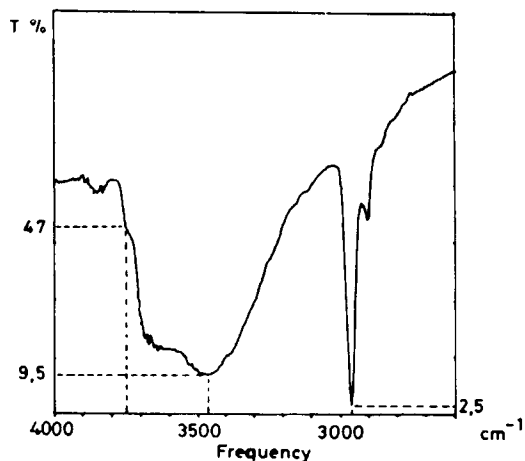


Fig. 6. IR spectrum of degassed A 300 after reaction with D4 for 13 hr.

After each period of degassing, the absorbances of the CH_3 , OH_{assoc} and OH_{free} lines were calculated and their evolutions compared. The curve corresponding to the absorbance of OH_{free} versus absorbance of OH_{assoc} (Fig. 8) reveals an inversely proportional variation of these two quantities. As chemisorption is not occurring since the whole D4 can be desorbed by vacuum degassing for $\frac{1}{2}$ hr at room temperature, the disappearance of one OH_{free} group must necessarily correspond to the appearance of one OH_{assoc} group.

However, the OH_{free} absorbance is strongly dependent on the absorbance of CH_3 , that is, on the covering ratio θ of the filler by D4 (Fig 9); θ is measured by assuming that the surface covered by an adsorbed molecule of D4 is equal to 100 \AA^2 .⁸ Indeed, when $0 < \log (I_0/I)_{\text{CH}_3} < 0.25$, i.e., when $0 < \theta < 0.3$, the absorbances are inversely proportional to each other. For $\theta > 0.3$, the experimental points lie off a straight line and the curve is heading toward a constant value of $\log (I_0/I)_{\text{OH}_{\text{free}}}$. This value is obtained when all the free OH groups have disappeared.

When $\theta = 1$, almost all the OH_{free} groups have disappeared, which means that

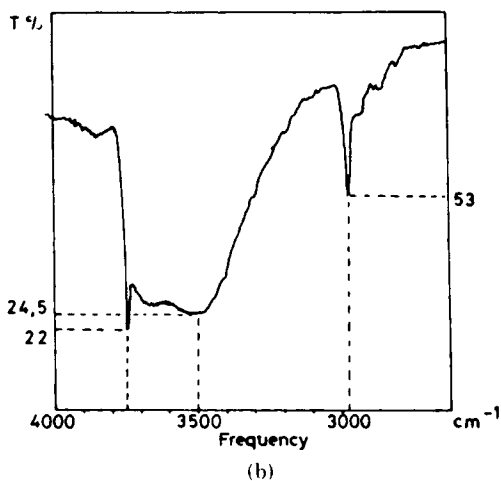
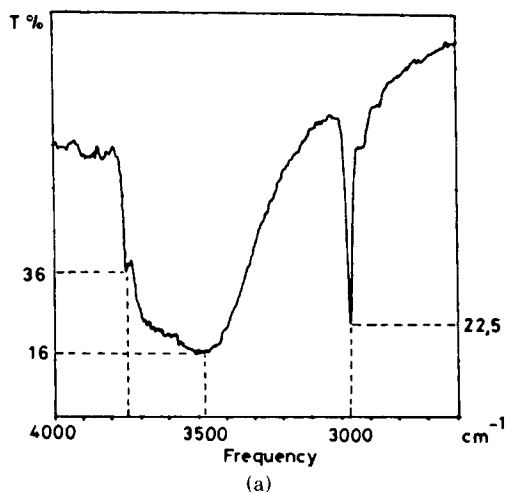
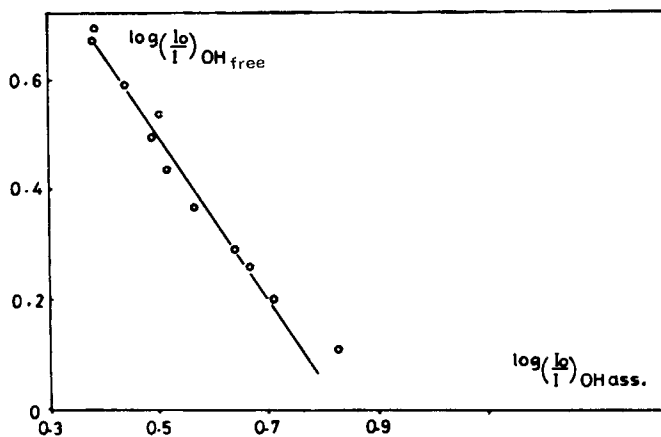
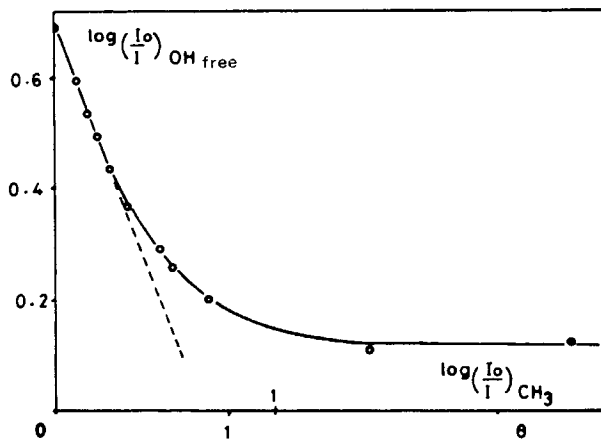


Fig. 7. (a) IR spectrum of A 300 modified with adsorbed D4, degassed for 2 min 30 sec; (b) IR spectrum of A 300 modified with adsorbed D4, degassed for 15 min 30 sec.

the A 300 surface is carrying enough silanol groups to allow its total coverage by hydrogen-bonded D4.

When $\theta > 1$, D4 condenses on the surface giving a multilayer. The OH_{free} absorbance then remains constant while the CH_3 absorbance increases. Similar conclusions can be drawn from Figure 10, where absorbance of CH_3 is plotted versus absorbance of OH_{assoc} . A confirmation of these results is presented in Figure 11, where the desorption kinetics is deduced from the evolution of the CH_3 line and shows the occurrence of several mechanisms in the reaction of siloxane with silica.

Thus, the different curves show that at room temperature the adsorption of D4 on silica is followed by a decrease in the amount of free hydroxyl groups and simultaneously by an increase in the quantity of associated hydroxyls. This means that the attachment of D4 onto the silica surface is the consequence of the formation of hydrogen bonding. Some work actually performed is aimed

Fig. 8. Plot of $\log(I_0/I)_{\text{OH free}}$ vs $\log(I_0/I)_{\text{OH assoc}}$.Fig. 9. Plot of $\log(I_0/I)_{\text{OH free}}$ vs covering ratio θ and $\log(I_0/I)_{\text{CH}_3}$.

at the understanding of the reaction mechanisms and will be presented in another paper.

Since the irreversible adsorption of D4 onto the surface of Aerosil 300 at room temperature has been clearly shown by means of IR spectroscopy, we tried to confirm it by gas-phase chromatography and to examine its behavior with temperature variation.

Gas-Phase Chromatography

First we checked that an irreversible adsorption of D4 was obtained at 25°C. The covering ratio is then equal to 0.82, i.e., a monolayer is nearly completed. Figure 12 shows the adsorbed quantity of D4 versus temperature between 25 and 140°C. One notes that whatever the temperature at which the adsorption was performed, the desorption of the siloxane begins as soon as the temperature increases. The conclusions derived from IR studies are thus confirmed, i.e., more or less energetic hydrogen bonds are created between the siloxane and the surface silanol groups. Of course, the higher the temperature at which desorption occurs, the stronger the hydrogen bonds.

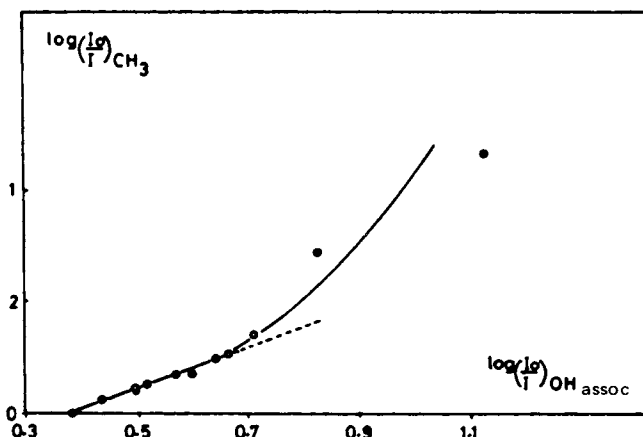


Fig. 10. Plot of $\log(I_0/I)_{CH_3}$ vs $\log(I_0/I)_{OH_{assoc}}$.

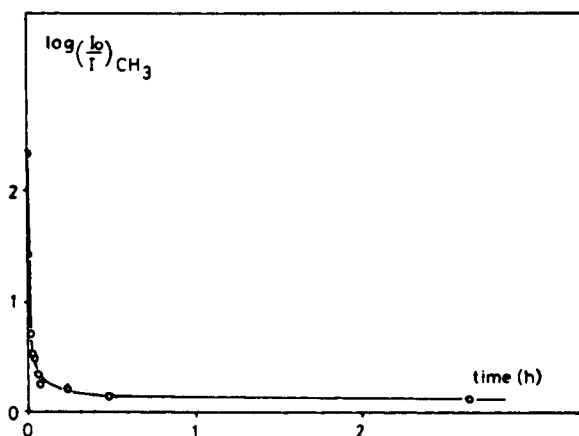


Fig. 11. Kinetics of desorption of D4: $\log(I_0/I)_{CH_3}$ vs time.

The different kinds of bonds may result on the one hand in a more or less easy accessibility of the free hydroxyl groups due to heterogeneous silica surface and the other hand in the arrangement of the adsorbed D4 molecules and of the filler surface hindrance which increases with its covering ratio. This is confirmed by a continuous decrease in the amount of adsorbed D4 when the temperature rises and by the existence of different kinds of associated OH_s yielding a broad IR spectral line instead of one sharp band between 3700 and 3400 cm⁻¹.

Since beyond 140°C the adsorption of D4 is reversible, we have been able to plot adsorption isotherms. Two of them (153 and 158°C) were plotted for $0 < p/p_0 < 1$ (Fig. 13) in order to calculate the heat of adsorption of D4. According to Brunauer Emmett and Teller's definitions, these isotherms are of type II, which means strong adsorbate-adsorbent interactions. Thus, the use of the BET equation allows the calculation of a_0 . The a_0 is the amount of siloxane necessary to complete a monolayer on the surface of the filler. We found $a_0 = 1.6 \mu\text{mol}/\text{m}^2$. The surface area of an adsorbed D4 molecule could then be calculated and was 100 \AA^2 , which is in agreement with the value determined from Zismann's figures.⁸

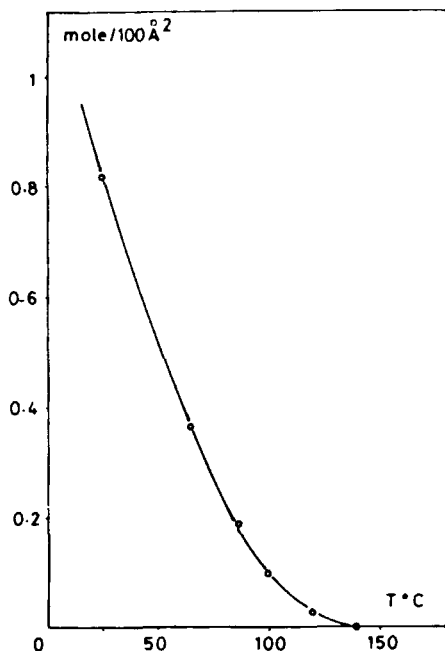


Fig. 12. Quantity of D4 adsorbed vs temperature.

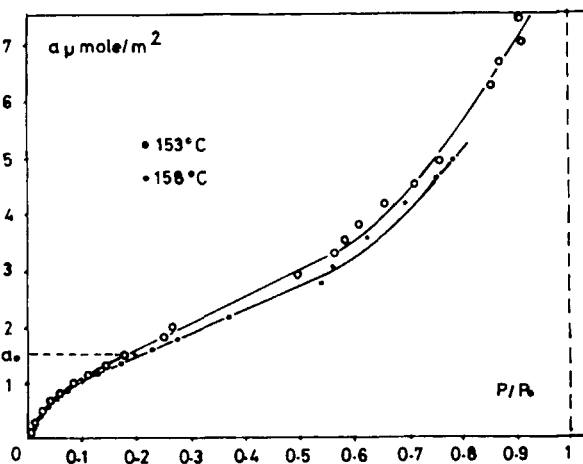


Fig. 13. Adsorption isotherm of D4 onto A 300.

Heats of adsorption (ΔH_a) were deduced from Clapeyron's equation, and Figure 14 gives their variation with covering ratio θ . When $\theta = 0.1$, $\Delta H_a = 32$ kcal/mol. ΔH_a decreases very rapidly when θ increases and is heading toward a plateau obtained for $0.6 < \theta < 2$. ΔH_a is then equal to 21 kcal/mol. But this value, which should correspond to the heat of condensation of D4, is higher than that given by Chahal and Saint-Pierre,² 11 kcal/mol.

What is important for the characterization of an adsorption process, however, is the neat heat of adsorption ΔH_{neat} for a given value of θ . It is defined by the difference between the heat of adsorption measured at a certain value of θ and

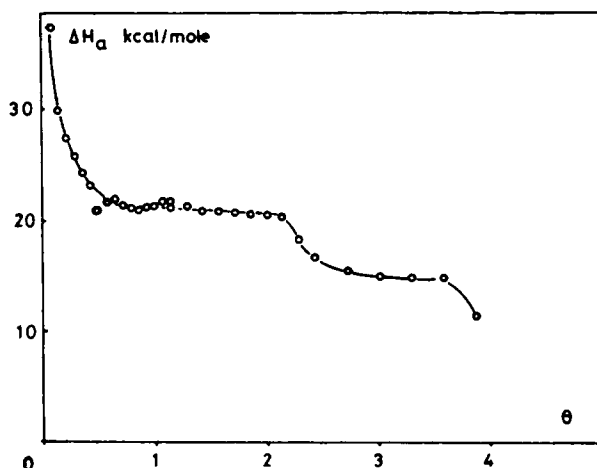


Fig. 14. Differential heats of adsorption of D4 vs covering ratio of A 300.

the heat of condensation measured for $\theta = 1$. Thus, for $\theta = 0.1$, the ΔH_{neat} is 11 kcal/mol, which is in close agreement with the value determined by Chahal and Saint Pierre.²

The decrease of ΔH_a for $\theta > 2$ has to be considered because it could mean that interactions can occur between the surface of the filler and the second layer of D4. However, one can note with Eirich⁹ that what we call a second layer is in fact the quantity of adsorbate corresponding to this covering ratio, but usually the adsorbate forms clusters on the surface of the filler.

Beyond the third layer, ΔH_a approaches 12 kcal/mol. These chromatographic studies thus confirm the irreversible adsorption of D4 onto silica at 25°C previously shown by IR spectroscopy. The adsorbed quantity is strongly dependent on the temperature, which points toward the creation of hydrogen bonding of different levels of energy.

CONCLUSIONS

The examination of silica-siloxane interactions by means of IR spectroscopy and gas-phase chromatography has shown that between 25 and 140°C the adsorption of D4 onto Aerosil 300 is due to hydrogen bonding. Since the adsorption is reversible above 140°C, we were able to plot the adsorption isotherms and to measure the heats of interaction. We also found indications for adsorption through hydrogen bonding of different levels of energy.

The authors wish to acknowledge financial help from the Délégation Générale à la Recherche Scientifique et Technique (Contract No. 7670481) and are grateful to D. J. Jagoda for help in preparing the manuscript.

References

1. B. B. Boonstra, H. Cochrane, and E. M. Dannenberg, *Rubber Chem. Tech.*, **48**(4), 558 (1975).
2. R. S. Chahal and L. E. Saint Pierre, *Macromolecules*, **1**(2), 152 (1968).
3. B. V. Ashmead and M. J. Owen, *J. Polym. Sci. A* **2**(9), 331 (1971).
4. P. Perkel and R. Ullman, *J. Polym. Sci.*, **54**, 127 (1961).

5. V. G. Aristova, I. M. Zimmer, A. I. Gorbunov, and K. A. Andrianov, *Dokl. Akad. Nauk SSSR*, **211**(1), 130 (1973).
6. V. G. Aristova, K. K. Popkov, and M. L. Galashina, *Koll. Zh.*, **36**(1), 123 (1974).
7. E. G. Glueckauf, *Discuss. Faraday Soc.*, **7**, 199 (1949).
8. H. W. Fox, P. W. Taylor, and W. A. Zisman, *Ind. Eng. Chem.*, **39**(11), 1401 (1947).
9. F. R. Eirich, *J. Coll. Int. Sci.*, **58**(2), 423 (1977).

Received April 11, 1978