

An infrared study of the interaction between Aerosil-200 and polydimethylsiloxane (dimethicone-1000)

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The individual hydrogen-bonds formed between Aerosil-200 and dibutyl ether are stronger than those formed between the Aerosil and dimethicone-1000 (PMS). Nevertheless, because there is multiple hydrogen-bonding to the PMS and because the molecules of this fit the Aerosil surface well, the total interaction is very strong.

Numerous infrared studies of adsorption from the gas phase on aerosils have been reported (Basila, 1968) but few infrared studies of adsorption from the liquid phase have been carried out. Two Russian workers (Tul'bovich & Priimak, 1969) studied the extent of adsorption on aerosils of a polydimethylsiloxane dissolved in n-hexane, but did not carry out an infrared investigation of the adsorption. We investigated the adsorption of the polydimethylsiloxane, dimethicone-1000 (PMS), by Aerosil-200 from the neat liquid, and compared the spectrum of the silica surface in the hydroxyl stretching frequency region ($3000\text{--}3800\text{ cm}^{-1}$) with the corresponding spectra in Nujol, hexachlorobutadiene, carbon tetrachloride, di-n-butyl ether, and hexamethyldisiloxane. The absorption bands due to the liquids were compensated wherever possible (see experimental section).

The spectra of the Aerosil suspended in Nujol (Fig. 1A), hexachlorobutadiene or carbon tetrachloride are similar to the spectra reported for aerosils alone, either as a powder, or pressed into a disc (McDonald, 1957; Tyler, Hambleton & Hockey, 1969). The sharp band at *ca* 3680 cm^{-1} is due to free hydroxyl groups on the silica surface, and the broad band at *ca* 3400 cm^{-1} to hydrogen-bonded hydroxyl groups and to physisorbed water (Hockey, 1965; Basila, 1968). The position of the former is perturbed from its position in Aerosil alone (3748 cm^{-1}); a similar effect has been observed for adsorption from the gas phase (McDonald, 1957, 1958). The Aerosil

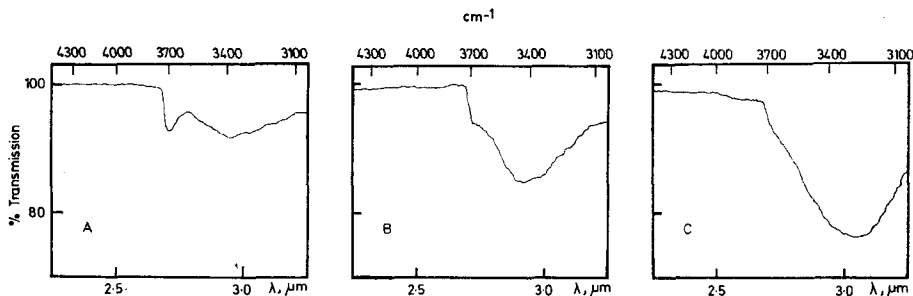


FIG. 1. A. Infrared spectrum of a 6.0% suspension of Aerosil-200 in Nujol.

B. Infrared spectrum of a 5.5% suspension of Aerosil-200 in PMS.

C. Infrared spectrum of a 5.3% suspension of Aerosil-200 in di-n-butyl ether. This spectrum is similar to those reported for the interaction between aerosils and dimethyl ether (McDonald, 1958) and diethylether and α -n-butylether (Davydov, Kiselev & Kuznetsov, 1965).

Table 1. Positions of the hydroxyl stretching bands of Aerosil-200 suspended in various liquids.

Liquid	Free-OH band (sharp) cm ⁻¹	Bonded-OH band (i)* (broad) cm ⁻¹	Bonded-OH band (ii) cm ⁻¹
none	3748	3430	3663
Nujol	3687	3380	—
Hexachlorobutadiene	3680	3400	—
CCl ₄	3679	3420	—
PMS	—	3420	3670 (sh)
Hexamethyldisiloxane	—	3370	3660 (sh)
Di-n-butyl ether	—	3290	3690 (sh)

* Extent of this band is *ca* 3000–3700 cm⁻¹ in all cases.

alone, as a powder between sodium chloride plates, showed a third band at 3663 cm⁻¹, fairly broad (*ca* 100 cm⁻¹), and weaker than the broad band at 3400 cm⁻¹. In Nujol, hexachlorobutadiene, and carbon tetrachloride, the sharp band due to free hydroxyl groups occurs in about the same position as the third band, and the latter is not apparent, except possibly as a broadening of the sharp band. The positions and assignments of the bands are shown in Table 1.

Aerosil-200 suspended in PMS shows a broad band (Fig. 1B) whose intensity is approximately double that of the broad band observed in Nujol. Although the sharp band is absent, a shoulder is apparent at 3670 cm⁻¹. This spectrum is similar to those in hexamethyldisiloxane and in di-n-butyl ether: the broad band is even more intense, and for butyl ether its position is at an appreciably lower wave number (see Table 1) with the shoulder only just apparent (Fig. 1C).

McDonald, and later workers, have assigned the broad band to silanol groups hydrogen bonded to the ether oxygen. Basila (1961) suggested that the shoulder is due to weakly hydrogen-bonded silanol groups which are in cavities and which are not available for bonding with adsorbed molecules. The same assignment has been made for the 3663 cm⁻¹ band in aerosils alone (Basila, 1968). In the present work the appearance of this band as a common feature in all the spectra (except when it is obscured by the band due to free hydroxyl groups) is in accordance with the assignment.

The close similarities of the infrared spectra of the Aerosil in hexamethyldisiloxane, di-n-butyl ether, and PMS, and the resemblance to the spectra reported when ethers are adsorbed from the vapour phase, lead to the conclusion that the principal interaction between PMS and the silica surface is hydrogen-bonding between silanol groups on the latter and the oxygen atoms of PMS. Attempts to desorb the PMS from Aerosil with toluene, showed that, even after repeated washings, the PMS was not desorbed completely (see experimental). Estimates of the PMS remaining on the Aerosil surface were made from the intensity of the band at 2963 cm⁻¹ (due to the methyl groups of PMS) when each sample was suspended in carbon tetrachloride. The results are in Table 2. The findings on desorption agree with our observation that all the recovered Aerosil samples were hydrophobic, in contrast to the hydrophilic nature of the original Aerosil. Chemical combination between the Aerosil and the PMS would not be expected because the latter compound is free from silanol groups and both are free from acid catalysts, and the two compounds had been mixed by hand at ambient temperature (20°). A specimen of a commercial mixture of similar

Table 2. *Estimates of residual PMS on Aerosil after washing with toluene*

Approx. no. of times washed	Absorbance at 2963 cm ⁻¹ *	Residual PMS in mg per mg of Aerosil	No. of molecules of PMS per 10 ⁴ Å ² of surface
12	1.6	1.7	20
24	0.62	0.65	8
36	0.43	0.45	5.4
48	0.29	0.30	3.6
64	0.177	0.18	2.2

* For 1 mg of silica per ml of CCl₄ in a 1 cm cell.

proportions (*ca* 6% Aerosil), prepared by mixing the compounds at 50–70° for 20–30 min with a propeller at 800 rev min⁻¹ (Rhône-Poulenc), had an infrared spectrum identical with that of our mixture. The tenacity with which the PMS is held on the Aerosil surface obviously arises from the mode of adsorption and the fourth column of Table 2 shows the number of PMS molecules per 10⁴ Å² of the silica surface, calculated on the basis of a surface area of 200 m² g⁻¹ (Brünner, 1960). From work on the spreading of PMS on water (Noll, Steinbach & Sucker, 1963), the area occupied by one PMS molecule when parallel, uncoiled, chains are packed as closely as possible, is $n \times 13.47 \text{ \AA}^2$ where n is the number of monomer units per molecule. Our PMS had approximately 340 units, so the minimum area occupied by one molecule when the chains are uncoiled is 4600 Å², i.e. 2.2 molecules per 10⁴ Å². All of the results in Table 2, except the last, exceed this value, so we conclude that, in general, PMS adsorbed on Aerosil is partially coiled (it is well known that in the pure liquid or in solution PMS molecules are coiled into helices with the silicon-oxygen dipoles pointing inwards). Possibly at high surface coverages the PMS molecules are completely coiled and hydrogen-bonding takes place only at the ends of the helices which are oriented with their axes perpendicular to the surface. Such molecules would not be strongly held but, as the coverage is reduced by washing, some of them uncoil and interact more strongly with the surface in a manner analogous to the spreading of PMS on water. With the silicon-oxygen skeleton common to adsorbent and adsorbate, so the two would be expected to interact strongly via a large number of hydrogen bonds per PMS molecule (up to 340 in our case). On this basis it is possible to understand why it is so difficult to desorb the PMS completely, although there is no evidence for any chemical interaction with the silica.

From the intensity and position of the broad band (i), the hydrogen-bonding is stronger when the Aerosil is suspended in di-*n*-butyl ether. This is consistent with the smaller steric effect of the *n*-butyl groups compared with the geminal methyl groups in PMS, or with the trimethylsilyl groups in hexamethyldisiloxane. The Aerosil silanol groups can form shorter, stronger hydrogen bonds to the oxygen atoms of di-*n*-butyl ether molecules. When PMS is the adsorbate, the individual hydrogen bonds are weaker, but the large number of such bonds per molecule of PMS, and the way in which the molecule fits the Aerosil surface makes the total interaction very strong.

MATERIALS AND METHODS

Aerosil-200 was obtained from Degussa. It was not dried before use (some surface moisture was present, shown by a weight loss of 0.3% when the Aerosil was heated at 110–120° for 6 h). Active hydrogen determinations on the dried Aerosil gave 0.08%

(A. Bernhardt) and 0.049–0.053% (Dr. D. Thorburn Burns, Loughborough University) as a measure of the number of chemically accessible surface hydroxyl groups.

Polydimethylsiloxane [Dimethicone-1000 (*British Pharmaceutical Codex*, 1968)] was obtained from Société Rhône-Poulenc. Its viscosity is about 1000 centistokes corresponding to an average molecular weight of 25 000 (Meals & Lewis, 1959). The method of manufacture is designed to remove all reactive groups. Analyses for active hydrogen gave 0.00% (A. Bernhardt) and 0.010–0.015% (D. Thorburn Burns).

Nujol, hexachlorobutadiene, and carbon tetrachloride were Analar or Spectroscopic grade. Di-n-butyl ether was Laboratory Reagent grade, and the hexamethyldisiloxane was Pure grade (Koch-Light).

Infrared spectra. The spectra covered the range 2500–4000 cm^{-1} and were obtained on either a Grubb-Parsons Spectromaster or a Perkin-Elmer 157G. The spectrum of Aerosil-200 alone was obtained by packing it loosely between two NaCl plates separated by a 0.5 mm spacer. Loss of radiation by scattering was compensated by attenuating the reference beam.

The spectra of the suspensions in Nujol, hexachlorobutadiene, di-n-butyl ether, and hexamethyldisiloxane were obtained as follows. The suspensions were made up by weight (5–6% Aerosil) and stirred well to ensure homogeneity. Each suspension was transferred to a cell with NaCl windows and a 0.1 mm spacer. Absorption due to the liquid was compensated by a similar cell in the reference beam; careful adjustment of the pressure on the windows enabled perfect compensation to be achieved.

For the suspension in carbon tetrachloride, some Aerosil was stirred with 10 ml of the liquid and the coarser particles allowed to settle out. A syringe was used to transfer 2–3 ml of the suspension to a 1 cm silica cell (infrared grade) and 2.0 ml to a weighed beaker for analysis (the CCl_4 was allowed to evaporate and the beaker reweighed). The suspension in the cell was shaken and the spectrum obtained immediately (a tendency of the Aerosil to stick to the cell walls was noticed). A silica concentration of 1–2 mg per ml gave a good quality spectrum.

Desorption of PMS. A sample of the suspension of Aerosil in PMS was stirred with toluene and centrifuged (see *British Veterinary Codex*, 1965). The supernatant liquid was discarded and the procedure repeated about 40 times. After the final treatment with toluene, the Aerosil was washed with light petroleum (b.p. 40–60°) and allowed to dry in the air at room temperature. The spectrum of the recovered Aerosil, suspended in CCl_4 , showed a broad band at 3676 cm^{-1} which merged into a broader band at 3420 cm^{-1} . The presence of a distinct band at 3676 cm^{-1} probably indicates that some of the silanol groups on the silica surface were free from interaction with PMS, and were only perturbed by CCl_4 (compare with the suspension of the original aerosil in CCl_4 which shows a relatively sharp band at 3679 cm^{-1}). The suspension of the recovered Aerosil in CCl_4 was stable and the silica did not stick to the cell walls. The absorbance of the band at 2963 cm^{-1} , due to PMS, was converted into that standard absorbance which would be given by 1 mg of the Aerosil suspended in 1 ml of CCl_4 in a 1 cm cell (second column of Table 2). The spectrum of a solution of PMS in CCl_4 gave an absorbance of 0.96 at 2963 cm^{-1} for 1 mg ml^{-1} cm^{-1} .

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