Adsorption of poly(dimethyl siloxanes) from solution on silica: 1.

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The adsorption of a broad range of poly(dimethyl siloxanes) on silica, treated and untreated, has been studied. Three solvents, n-hexane, CCl_4, and benzene were employed. Adsorption was molecular weight dependent and more polymer adsorbed from n-C_6H_{14} than from CCl_4. Only negative adsorption from C_6H_6 solution was observed. The results are rationalized on the basis of the polymer–solvent interaction values (χ), the solvent–adsorbent and the solute–adsorbent adsorption energies. It is concluded that the loss in configurational entropy on adsorption of the macromolecules is a major factor in determining the adsorption isotherms.

INTRODUCTION

The adsorption behaviour of polymers at the solution/solid interface is of considerable technological importance, yet is not well understood due to the complexity of the adsorption process itself[1–8]. There are five pairwise energetic interactions to consider, i.e. polymer–adsorbent, solvent–adsorbent, polymer–solvent, solvent–solvent and polymer–polymer. Moreover, in addition to the entropic changes taking place during adsorption, there are conformational changes in both the polymer molecules in the bulk solution and those in the adsorbed phase. As a consequence of our inadequate understanding of the factors involved there is much scope for direct examination and measurement of the various energetic interactions, either separately or under actual adsorption conditions.

Studies concerned with the adsorption of poly(dimethyl siloxane) from solution onto glass and silica[9–11] have shown that the energies of interaction of the solvent molecules and the siloxane segments with the adsorbent are more similar than in most systems, and perhaps more complicated. The present investigation was therefore undertaken to establish clearly the effect of the various interactions on the adsorption behaviour of poly(dimethyl siloxane) at the solution/silica interface.

EXPERIMENTAL

Polymers

A summary of the polymers used (commercially available Silicone 200 Fluids, Dow-Corning Silicones Inter-America Ltd, Toronto, Ontario) with their viscosities (centistokes at 25°C), molecular weights and selected polydispersity ratios is given in *Table 1*. The number-average molecular weights ($\bar{M}_n$) were determined at 37°C in benzene using a vapour pressure osmometer. The polydispersity ratios ($\bar{M}_w/\bar{M}_n$) were obtained from gel permeation chromatography (g.p.c.) traces in tetrahydrofuran at 25°C.

Also employed in this study was the General Electric Co. (Waterford, NY) SE-76 dimethyl siloxane polymer. It was fractionated at a controlled temperature from dilute benzene solution using methanol as a non-solvent. The middle fraction was retained. The number-average molecular weight ($\bar{M}_n$), determined in toluene at 30°C with a membrane osmometer, was $\bar{M}_n$ = 520 000. The weight-average molecular weight ($\bar{M}_w$) as determined from light scattering measurements in toluene was $\bar{M}_w$ = 730 000 so that $\bar{M}_w/\bar{M}_n$ = 1.40.

Prior to characterization, the polymers were passed through alumina–silica gel columns to remove surfactant impurities. In the case of the SE-76 polymer this was done in a 10% n-hexane solution and the solvent later removed under high vacuum.

Hexamethyl disiloxane (MM) (General Electric Co., NY) was selected as the segment model compound for poly (dimethyl siloxane). As with the polymers, the MM was percolated through an alumina–silica gel column.

Solvents

The solvents for the adsorption experiments were spectroquality n-hexane, carbon tetrachloride and benzene. Each was allowed to stand over a molecular sieve for at least a month prior to use.

Adsorbents

Cab-O-Sil M5 (Cabot Corp., Boston, Mass.) with a reported surface area of 200 $m^2 g^{-1}$ was selected as the nonporous adsorbent and was used as received or after modifica-

Table 1 Polymeric adsorbates

Viscosity grade (cs)	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
2	385	–
5	684	–
10	1050	–
20	2080	1.10
50	3340	–
100	5620	1.32

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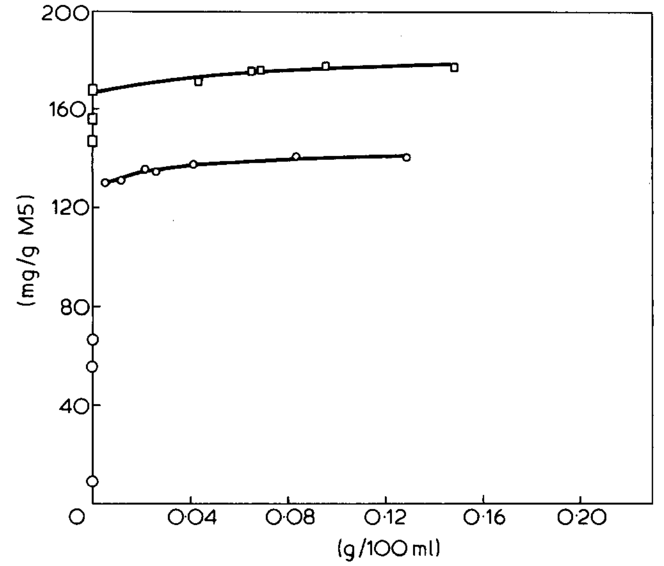

Figure 1 Adsorption of the $\bar{M}_n$ = 520 000 polymer from: □, n-hexane and ○, carbon tetrachloride onto untreated silica

tion with trimethylchlorosilane[12]. The surface coverages of the treated silicas were 0.53, 0.83, 1.28, 1.47 and 1.69 trimethylsilyl groups/100 Å ^{2}.

Procedure

The silica samples were dried at 110°C and a pressure of less than 10^{-3} torr in ampoules fitted with Teflon stopcocks. The silica-filled ampoules were then cooled to room temperature, filled with dry nitrogen and transferred to a dry box for the pipetting of the polymer solutions.

The polymers were weighed into 100 ml volumetric flasks and made up to volume at 20°C in the dry box. The Teflon stopcocks were temporarily removed from the ampoules and 10 ml portions of solution were pipetted onto the powders (between 150 and 250 mg of silica). The ampoules were then resealed and equilibrated during agitation in a water-bath thermostatically controlled at 29.5° ± 0.1°C.

The usual equilibration time chosen for these experiments was of the order of 6 h, although some samples were analysed as early as 3 h after preparation. No differences were found as a result of this interval. In the case of the treated surfaces comparisons were made in the interval 6 to 9 h. Again no discernible differences could be found. To determine the polymer concentration, absorbance of the supernatant liquid was determined by infra-red spectrophotometry using the symmetric deformation of the methyl groups at 1261 cm^{-1}. Matched Irtran-2 cells of 1 mm path length were used with a Perkin–Elmer 521 Grating Infrared Spectrophotometer. Calibrations of the absorbance *versus* known concentrations of polymer in the solvent of interest were made and the unknown supernatant concentrations interpolated from them. Before analysis of the equilibrium solutions could be made, it was necessary to centrifuge the mixtures to ensure complete silica removal.

The amount of polymer adsorbed (Γ in mg/g.M5) was determined from:

$$\Gamma = (V/m)(c_i - c) \times 1000$$

where V is the volume (ml) of the polymer solution used; m is the weight of the silica (g); and c_i and c are the initial and equilibrium concentrations of polymer solution (g/100 ml), respectively. The Γ values were then plotted against their corresponding c values to construct the adsorption isotherm.

Adsorption and sorption from the vapour phase

The apparatus was based on the concept of McBain and Bakr[13] and has been described in detail elsewhere[14,15]. The heats of adsorption on silica were determined from adsorption isotherms using the Clausius–Clapeyron equation. The solution properties of the solvents were expressed in terms of the polymer–solvent interaction parameter, χ, and calculated by use of the Flory equation[16].

RESULTS AND DISCUSSION

Polymer adsorption isotherms and molecular weight dependence

Figures 1–3 show the mass isotherms for the SE-76 polymer and for the silicone fluids of different molecular weights adsorbed from carbon tetrachloride (CCl_4) and from n-hexane (n-C_6H_{14}) onto untreated silica. The adsorption of polymer from n-C_6H_{14} is greater than that from CCl_4 and for a given solvent the amount of polymer adsorbed increases with molecular weight. An interesting feature of the isotherms is that the adsorption at high surface coverage continues to increase slowly with concentration. The usual interpretation for this type of concentration dependence is a change in the organization of the adsorbed polymer layer owing to increased lateral interactions between the adsorbed polymer molecules as the concentration increases[17,18].

There was no preferential adsorption of any of the siloxanes from the benzene (C_6H_6) solvent. As shown in *Table 2,* when C_6H_6 solutions containing polysiloxanes of higher molecular weights are in contact with the adsorbent, an increase in polymer concentration in the liquid is observed. This is thermodynamically equivalent to preferential C_6H_6 adsorption on the solid. The degree of 'negative' adsorption is dependent on the molecular weight and suggests the centres of mass of the high molecular

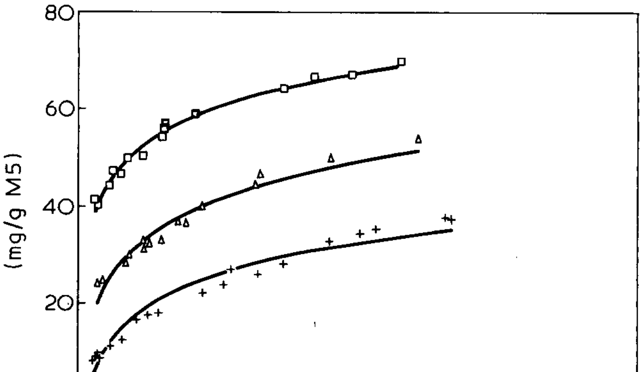

Figure 2 Adsorption of different molecular weight silicone fluids from carbon tetrachloride onto untreated silica. □, $\bar{M}_n$ = 5620; △, 3340; +, 2080 and ○, 162

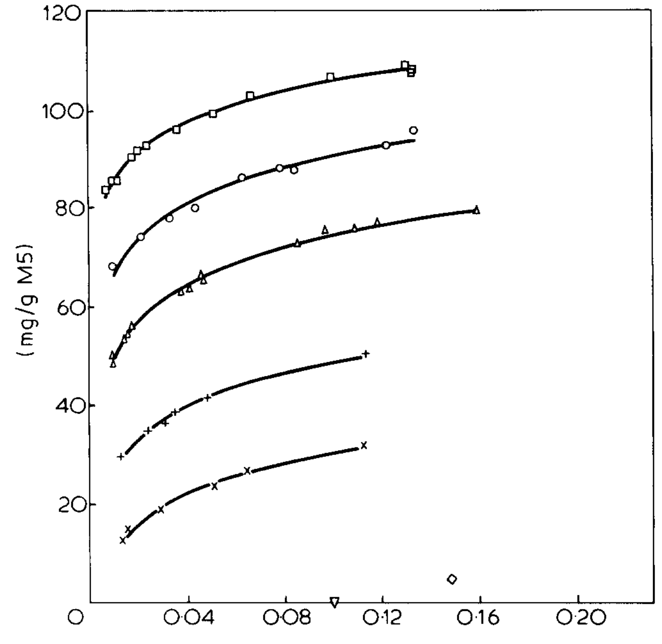

Figure 3 Adsorption of different molecular weight silicone fluids from n-hexane onto untreated silica. □, $\bar{M}_n$ = 5620; ○, 3340; △, 2080; +, 1050; X, 684; ◇, 385 and △, 162

Table 2 'Negative' adsorption of the polysiloxanes from benzene onto untreated silica

Polymer $\bar{M}_n$	Final concentration (g/100 ml)	Amount adsorbed (mg/g M5)
2080	0.166	0.0
5620	0.181	−1.5
520 000	0.144	−6.3

weight species are prevented from approaching the surface closer than approximately their root-mean-square radii of gyration[19].

An important feature of polymer adsorption, when the presence of the polymer in the surface phase is energetically favoured, is the increase in efficiency of the partitioning of the polymer between the surface and bulk phases with increasing molecular weight[6]. For a monomer to be preferentially adsorbed from a dilute solution, a strong bond must be formed between the monomer and the surface to overcome the increase in free energy which occurs in response to the monomer and solvent molecules redistributing themselves between the surface and bulk phases. For the adsorption of higher molecular weight oligomers, on the other hand, the formation of a strong bond between the repeating units and the surface sites is not as critical because of the increase in the number of potential energetic contacts with the surface on a per molecule basis. Moreover, since fewer polymer molecules, compared with an equivalent weight of monomeric material, have to be transported to the surface, the free energy increase due to desolvation is substantially diminished and increased mass adsorption is favoured. As shown in *Figures 2* and *3* there was no preferential adsorption of the dimer hexamethyl disiloxane (MM, $\bar{M}_n$ = 162) from either CCl_4 or n-C_6H_{14} in the concentration range investigated. As can be seen in *Figure 3*, however, it was possible to preferentially adsorb, to a small extent, the pentamer MD_3M ($\bar{M}_n$ = 385) from n-C_6H_{14} onto silica. For a given solvent a critical molecular weight is therefore needed before adsorption can be measured. Furthermore, because it was not possible to adsorb any of the polysiloxanes from the C_6H_6 solvent, a critical segment–solvent energetic exchange with the surface must be exceeded before preferential adsorption can occur at any molecular weight.

Figure 4 shows the mass adsorption at surface saturation from the n-C_6H_{14} and CCl_4 solutions on silica as a function of the molecular weight. The dependence of the amount of polymer adsorption in the plateau or pseudo-plateau region is generally expressed by the empirical relationship:

$$\Gamma_p = K(MW)^{\alpha}$$

where Γ_p is the mass adsorption at surface saturation; MW is the molecular weight; and K and α are *constants* for the system[7]. It is apparent that over the molecular weight range reported here the relationship between Γ_p and $\bar{M}_n$ is much more complex than is indicated by the empirical equation. Clearly, α decreases with increasing molecular weight and approaches a limiting value (*Table 3*) of about 0.1. In a review of polymer adsorption, Ash[7] has tabulated α values for adsorption on non-porous adsorbents and has pointed out that the α values for poly(dimethyl siloxane) on glass tend to be higher than average. The results reported here for the high molecular weight range are almost quantitatively comparable. For adsorption in the low molecular weight range, however, there are dramatic changes in the amount adsorbed with increasing molecular weight and hence larger α values. Evidently, adsorption as a function of

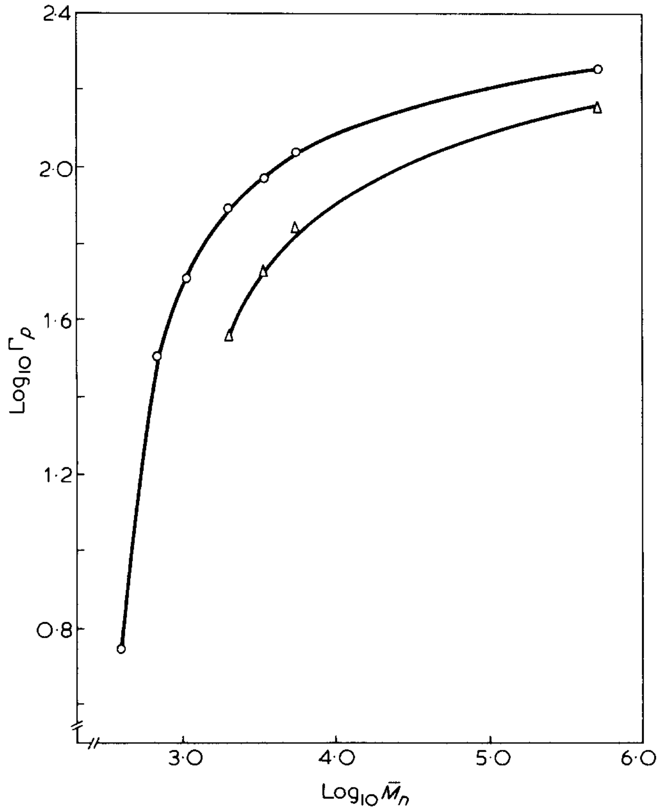

Figure 4 Effect of molecular weight on the adsorption of poly(dimethyl siloxane) from: ○, n-hexane and △, carbon tetrachloride onto untreated silica

Table 3 Values of α for adsorption from n-hexane and carbon tetrachloride

$\bar{M}_n$	$\alpha_{n-C_6H_{14}}$	α_{CCl_4}
385		
684	3.06	
1050	1.06	
2080	0.61	
3340	0.40	0.80
5620	0.28	0.53
520 000	0.11	0.16

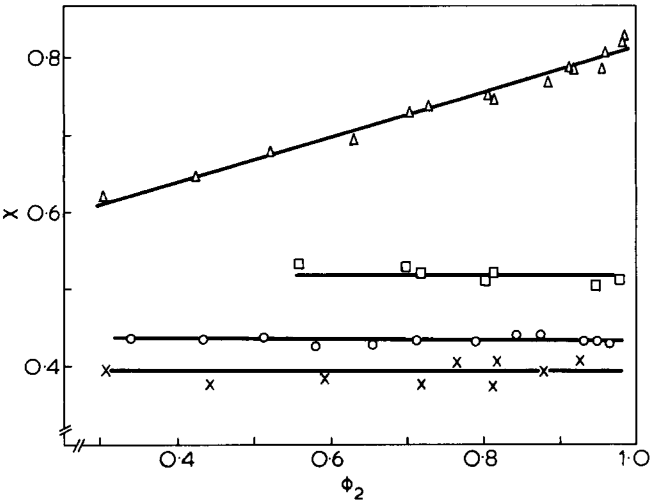

Figure 5 χ parameter *versus* the polymer volume fraction (ϕ_2) at 20.0°C for: △, benzene; □, carbon tetrachloride; ○, n-heptane and X, n-pentane [15]

molecular weight, after this low molecular weight range has been exceeded, is not strongly affected by the free energy increase due to bringing the polysiloxanes to the interface. This view is strengthened when it is noted in *Figure 1* that at low polymer coverages, where the supernatant polymer concentrations were experimentally inaccessible, the adsorbed macromolecules are in equilibrium with an infinitely dilute solution.

The limiting behaviour in the change in mass adsorption with increasing molecular weight can be interpreted in terms of the polymer coils in the solution being adsorbed in either a flat configuration or as impenetrable spheres on the adsorbent surface[7]. Although it is difficult to assess which of the two models is more realistic, it would appear from the isotherm data, which indicate changes in the organization of the adsorbed polymer layer with concentration, that the final configuration is a compromise between the two.

Polymer–solvent interactions

When a polymer segment is adsorbed from a dilute solution there is a reduction in the number of polymer–solvent contacts in the bulk solution and an increase in the number of solvent–solvent contacts. If the solvent is a poor one, the polymer–solvent contacts are not energetically favoured relative to the solvent–solvent or polymer–polymer contacts. Hence, a poor solvent would shift the equilibrium in favour of increased polymer adsorption. Moreover, the polymer coils would not be as expanded as they would be in a good solvent thereby causing more of the polymer to be accommodated at the interface.

Previous work in this laboratory[14,15] (*Figure 5*), involving measurement of the polymer–solvent interaction parameter, χ, for the SE-76 siloxane polymer and various solvents has shown that n-C_6H_{14} is a better solvent than CCl_4, which in turn is better than C_6H_6. Adsorption of poly (dimethyl siloxane) on untreated silica follows the same pattern, i.e. adsorption is greatest from the n-C_6H_{14} solution followed by that from CCl_4. Poly(dimethyl siloxane) could not be adsorbed on untreated silica from the C_6H_6 solution. This adsorption ranking is completely the reverse of what would be expected. Since the solvent compatibilities with the polymer do not give a correct prediction of the level of adsorption, it is apparent that the energies of interaction of the solvent molecules and the polymer segments with the adsorbent are the predominant energetic interactions to consider in this system.

Polymer– and solvent–adsorbent interactions

To determine the importance of the polymer–adsorbent and solvent–adsorbent energetic interactions, the following program was undertaken. First, the energetic interactions of the solvents and MM with untreated and Me_3SiCl modified silicas were obtained by determining the isosteric heats of adsorption from the vapour phase as a function of surface coverage. In this way it was possible separately to characterize the interactions of the various compounds with the surface properties of the silica. Secondly, having a knowledge of these interactions with untreated and treated silica, it was possible to alter the surface energy of the silica systematically and relate the extent of mass adsorption to the polymer–adsorbent interactions.

Figures 6–9 show the isosteric heats of adsorption of n-C_6H_{14}, CCl_4, C_6H_6 and MM plotted against surface coverage for the untreated and 1.69 trimethylsilyl/100 Å^2 treated silicas. The horizontal dashed lines correspond to ΔL_v, the heat of condensation of the adsorbates, and the vertical dashed lines correspond to $\theta = 0.50$, the half-monolayer capacity on the untreated silica.

For n-C_6H_{14} and CCl_4 (*Figures 6* and *7*, respectively) the heats of adsorption gradually decrease with increasing surface coverage and show minimal differences between the

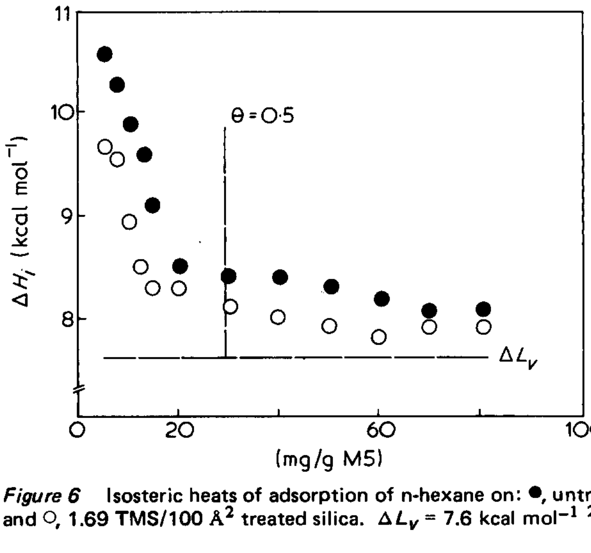

Figure 6 Isosteric heats of adsorption of n-hexane on: ●, untreated and ○, 1.69 TMS/100 Å^2 treated silica. ΔL_v = 7.6 kcal mol^{-1} [27]

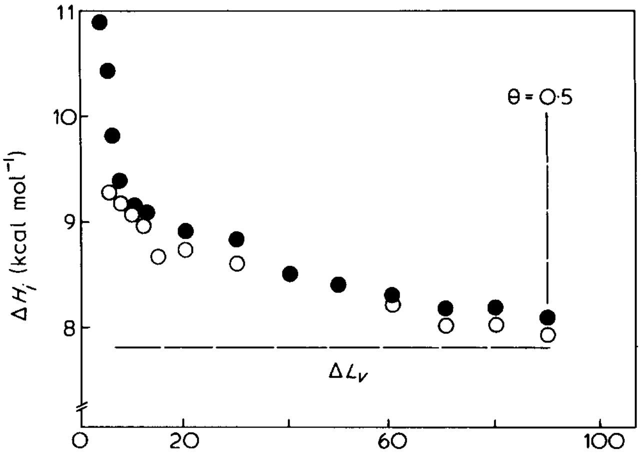

Figure 7 Isosteric heats of adsorption of carbon tetrachloride on: ●, untreated and ○, 1.69 TMS/100 Å^2 treated silica. ΔL_v = 7.8 kcal mol^{-1} [27]

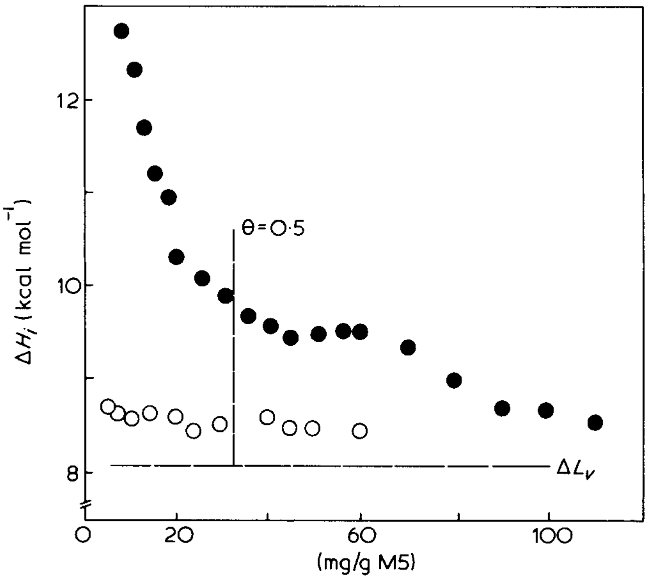

Figure 8 Isosteric heats of adsorption of benzene on: ●, untreated and ○, 1.69 TMS/100 Å^2 treated silica[14]. ΔL_v = 8.1 kcal mol^{-1} [27]

untreated and chemically-modified silica. For C_6H_6 and MM on untreated silica (*Figures 8* and *9*, respectively) the heats of adsorption are strongly dependent on surface coverage. As the first layer of adsorbed molecules is filled up, a sharp decrease in the heat of adsorption is observed on changing to predominantly filling the second layer. This indicates that the adsorbate–surface interactions are quite strong up to monolayer coverages. However, for the treated surface, the interaction energy of MM is greatly diminished to the extent that the maximum value of the heat of adsorption of MM on the chemically treated silica corresponds roughly to the value obtained on the untreated silica at the completion of a monolayer (θ = 1.0, *Figure 9*). For C_6H_6 adsorption on the treated surface, the heats of adsorption with increasing surface coverage remain relatively constant and close to the heat of condensation.

To expand further on the above findings it is necessary to comment on the chemical nature of the Cab-O-Sil surface. Infra-red investigations have shown that the major adsorption sites on the silica surface are hydroxyl groups[20]. However, physical adsorption and chemical reactivity studies indicate that these are composed of two major types. There are OH groups located at relatively large interhydroxyl spacings (Type A or 'isolated hydroxyls') and other OH groups located in such a way as to promote interhydroxyl bonding (Type B or 'vicinal hydroxyls'). The adsorption properties of each type of group are widely different. For example, compounds with lone-pair electrons or proton-accepting power will adsorb preferentially on the isolated hydroxyls which are highly protonized[21]. Investigations have shown that the physical interactions of the compounds studied here occur primarily with the isolated hydroxyl groups, since the vicinal hydroxyls prefer to remain hydrogen-bonded[22–24]. These interactions can be quantified as described below.

Basila[21] and McDonald[20] have shown that polar and non-polar molecules have a perturbation action on the stretching frequency (3747 cm^{-1}) of the isolated hydroxyl groups. With adsorption the hydroxyl frequency is shifted to lower wavenumbers. Kiselev *et al.*[25,26] have reported that the extent of this perturbation represents the degree of the specific interaction between the adsorbate molecules and the adsorbent surface. They have also shown that a direct relationship exists between the frequency shift of the hydroxyl group and the net heat of adsorption. The net ΔH_{ads} was defined as the difference between the heat of adsorption of a compound on a fully hydroxylated surface and that on a dehydroxylated surface, i.e.:

$$\text{net } \Delta H_{ads} = \Delta H_{hydr} - \Delta H_{dehydr}$$

Since the isosteric heat is a function of the extent of the surface coverage, values are usually taken at half-monolayer capacity.

In this study, data were not obtained on a strongly dehydroxylated surface. However, it has also been shown[27] to a good approximation that the net energy of interaction of the adsorbate molecules with a hydroxylated silica surface may be evaluated from the following equation:

$$\text{net } \Delta H_{ads} = \Delta H_{hydr} - \Delta L_v$$

The net heats of adsorption at half-monolayer capacity for the four adsorbates on untreated silica are given in *Table 4*,

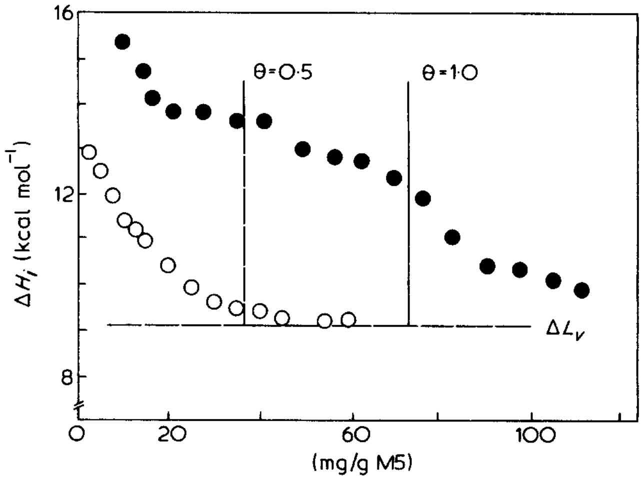

Figure 9 Isosteric heats of adsorption of hexamethyl disiloxane on: ●, untreated and ○, 1.69 TMS/100 Å^2 treated silica[14]. ΔL_v = 9.2 kcal mol^{-1} [12]

Table 4 Net heats of adsorption at $\theta = 0.5$ and infra-red frequency shifts of various vapours on untreated silica

Adsorbate	Net ΔH_{ads} (kcal mol^{-1})	$\Delta\nu_{OH}$ (cm^{-1})
n-Hexane	0.8	40[a]
Carbon tetrachloride	0.4	51[a]
Benzene	1.7	127[a]
Hexamethyl disiloxane	4.5	360–480[b]

[a] Curthoys *et al.*[27]
[b] Hertl and Hair[24]

together with published values for the frequency shifts of the isolated hydroxyl band. The non-specific interaction of n-C_6H_{14} and CCl_4, which possess only σ-bonds, with untreated silica is reflected in the small shifts in the isolated hydroxyl band and net heats of adsorption. It is not clear why CCl_4 has a smaller net heat of adsorption and yet a somewhat larger frequency shift of the isolated hydroxyl band. It should be pointed out, however, that the differences between the net heats of adsorption may not be significant from the point of view of the experimental error (±0.2 kcal mol^{-1}). In this regard, it is also interesting to note that the interactions of these two compounds with the untreated and treated silicas are not significantly different, yet Hair and Hertl[28] have demonstrated that trimethylchlorosilane reacts primarily with the isolated hydroxyl groups and on a 1:1 basis to give this chemisorbed trimethylsilylated surface. Furthermore, in a separate paper[22], they have estimated the total isolated hydroxyl group concentration per 100 Å^2 of Cab-O-Sil to be 1.7, a value almost identical to the number of trimethylsilyl groups on the treated silica employed here.

Clearly, the isosteric heat data does not provide a clear picture as to why there is less polymer adsorption from CCl_4 [a poorer solvent for poly(dimethyl siloxane)] than from n-C_6H_{14}. By using binary solvent mixtures of n-C_6H_{14} and CCl_4, however, it is possible to demonstrate whether one solvent is more strongly adsorbed relative to the other. *Figure 10* shows data for the adsorption of the $\bar{M}_n = 2080$ silicone polymer onto untreated silica from n-C_6H_{14} and CCl_4. The filled data points correspond to 10% by vol solutions of one solvent in the other. It is noted that whereas the presence of 10% n-C_6H_{14} in CCl_4 had a negligible effect on the amount of polymer adsorbed as compared to the CCl_4 isotherm, 10% CCl_4 in n-C_6H_{14} resulted in a marked decrease in the amount of adsorbed polymer when compared with the n-C_6H_{14} isotherm. The results indicate that the CCl_4 molecules compete very effectively with the siloxane segments and the n-C_6H_{14} molecules for the surface sites. To support this conclusion it should be mentioned that Clark-Monks and Ellis[29] have observed specific adsorption of chlorinated compounds on Cab-O-Sil and proposed that it was not possible to describe this silica only in terms of Type A and B sites, but that it was also necessary to postulate the presence of an anomalous site. They estimated the site concentration to be 0.31 to 0.34 sites per 100 Å^2 of silica and advanced the argument that these sites are highly polarizable due to surface steps or kinks. It is likely that these anomalous sites account for the above observation.

As may be ascertained from *Table 4*, the unexpected adsorption ranking for the poly(dimethyl siloxane)–C_6H_6–silica system is more clearly defined and may be ascribed to that solvent's affinity for isolated hydroxyl groups. Kiselev[30] has attributed this specific interaction to the formation of a π complex between the proton of the SiOH group and the C_6H_6 molecule. Siloxane compounds also possess π-bonding character involving the ultimate $d\pi$ and $p\pi$ orbitals in the silicon and oxygen atoms, respectively[31], and this is reflected in the correspondingly larger net heat of adsorption and shift of the isolated hydroxyl band. However, for adsorption on the treated silica, where the isolated hydroxyls have been replaced with trimethylsilyl groups, the heats of adsorption are significantly reduced as would be expected.

It was reported that MM could not be adsorbed from n-C_6H_{14}, CCl_4 or C_6H_6 onto untreated silica at low concentration. It is evident from *Table 4* that MM is capable of a much stronger interaction with the isolated hydroxyls than any of these three solvents. Therefore, even though solvent desorption from the surface would be an endothermic process, a larger exothermic contribution due to MM adsorption should be favourable to its adsorption. However, as discussed earlier, an MM molecule will only be preferentially adsorbed if this net energetic exchange with the silica overcomes the increase in free energy which would accompany the removal of an MM molecule from the bulk solution. With higher molecular weight polysiloxanes in n-C_6H_{14} and CCl_4, however, there is preferential adsorption in the low concentration range owing to the greater number of energetic contacts with the surface on a per molecule basis (in the form of $(CH_3)_2SiO$ linkages). The question arises as to why there is not preferential adsorption of these higher molecular weight species in the presence of C_6H_6 considering that MM is capable of a much stronger interaction with the isolated hydroxyls. A possible explanation is that the contribution of the energetic interaction of the $(CH_3)_2SiO$ linkages with the isolated hydroxyls is considerably less than that for MM. This is borne out by the experimental results of Chahal and St-Pierre[12]. However, bound fraction studies for the adsorption of these same polysiloxanes from CCl_4 onto untreated silica showed a shift in the isolated hydroxyl band of approximately 300 cm^{-1} (ref 32). This shift of 300 cm^{-1}

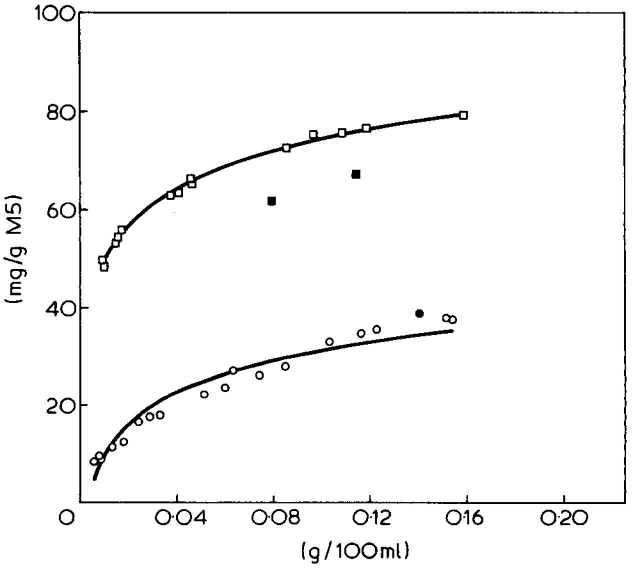

Figure 10 Adsorption of the $\bar{M}_n = 2080$ silicone fluid from: □, n-hexane; ○, carbon tetrachloride; ■, 10% carbon tetrachloride in n-hexane; and ●, 10% n-hexane in carbon tetrachloride onto untreated silica

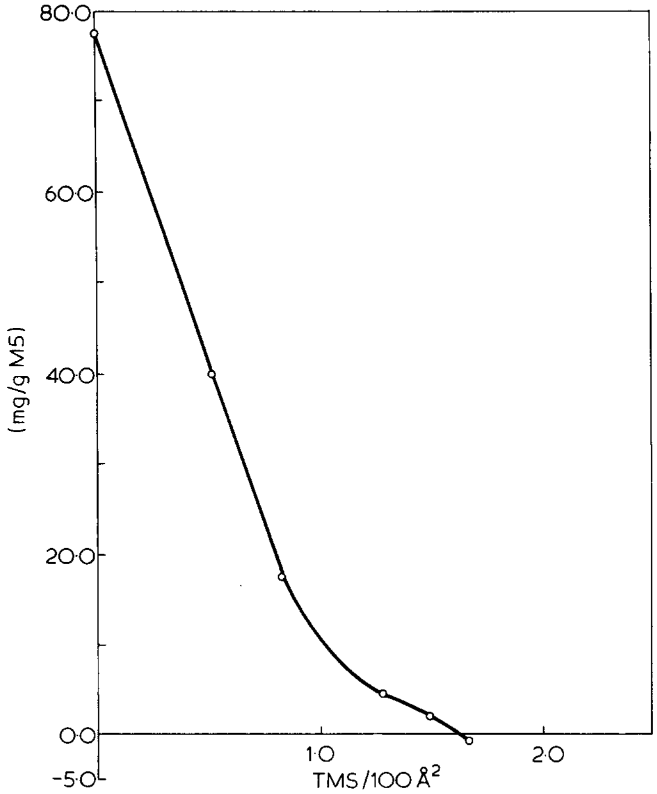

Figure 11 Adsorption of the $\bar{M}_n$ = 2080 silicone fluid at surface saturation from n-hexane as a function of the number of TMS groups per 100 Å² of silica

is still considerably greater than the 127 cm^{-1} shift reported for C_6H_6. Thus, the reason for the lack of adsorption from C_6H_6 cannot be completely accounted for on the basis of adsorption energies. It is interesting to note that other investigators[9,11] have reported that poly(dimethyl siloxane) can be adsorbed from this solvent onto glass. However, these glass adsorbents were outgassed at approximately 280°–300°C. The concentration of vicinal hydroxyls is dependent on temperature *in vacuo*[33]. The groups start to condense and eliminate water at 170°C resulting in the formation of siloxane bridges which would provide surface sites for siloxane adsorption from C_6H_6 [9]. In the present study, the silica was outgassed at 110°C in order to remove only the physisorbed water.

Since it is possible to alter the energy of silica surfaces with trimethylsilyl (TMS) groups, it should be possible to relate the extent of polymer adsorption in terms of the polymer–adsorbent interaction energy. As discussed, solvent–adsorbent interactions can be extremely important factors in determining polymer adsorption. In order, therefore, to measure the importance of the polymer–adsorbent interaction energy, the solvent–adsorbent interaction effects should be completely eliminated. Such is indeed the case when n-C_6H_{14} is employed as the solvent, the interactions with untreated and chemically-modified silica being essentially the same.

The decrease in the extent of mass adsorption with an increase in the treatment of the silica should be the result of the following:

(a) a decrease in the number of available isolated hydroxyls on the silica surface; and

(b) a diminishing polymer–adsorbent interaction due to the TMS groups sterically shielding the remaining isolated hydroxyl sites.

Table 5 'Negative' adsorption of the polysiloxanes from n-hexane onto 1.69 TMS/100 Å² treated silica

Polymer $\bar{M}_n$	Final concentration (g/100 ml)	Amount adsorbed (mg/g M5)
2080	0.129	–0.1
5620	0.138	–1.4
520 000	0.161	–3.4

These two effects, (a) and (b) above, are illustrated in *Figure 11*, where the mass adsorption values in the pseudo-plateau region for the $\bar{M}_n$ = 2080 polymer in n-C_6H_{14} are plotted against the number of TMS groups per 100 Å² of silica. There is a sharp linear decrease in the mass adsorption with increasing treatment of the silica followed by an inflection at approximately 1 TMS group per 100 Å² of silica, adsorption then being almost insignificant. When studying the vapour phase interaction of MM with these same surfaces, Brender[34] determined that the heats of adsorption of MM at low coverage decreased somewhat with increasing silanization of the silica, but that after 1 TMS group per 100 Å² of silica the decrease was much more pronounced. He ascribed this abrupt change to a critical concentration of chemisorbed TMS beyond which the remaining isolated hydroxyl sites become shielded. An identical effect, in terms of the amount of polymer adsorbed, is found here.

It is apparent that the polysiloxanes adsorb from solution primarily on the isolated hydroxyls, as evidenced by the initial linear decrease in the adsorbed amount with increased silanization of the silica. A reduction in this polymer–adsorbent interaction results in an insignificant amount of polymer being adsorbed, the segment–solvent–surface energetic exchange becoming insufficient to overcome the increase in free energy due to bringing the polysiloxane to the surface. However, inspection of *Figure 11* also reveals that the adsorption becomes 'negative' at, or near, the coverage of 1.7 TMS groups per 100 Å² of silica. Furthermore, with increasing molecular weight the degree of 'negative' adsorption increases, as shown in *Table 5*. A parallel situation was found when attempts were made to adsorb these same polysiloxanes from C_6H_6 onto untreated silica (*Table 2*). Since, in both cases, the degree of 'negative' adsorption reflects the size of the random coil of the polysiloxanes in the presence of these solvents, it is apparent that for the higher molecular weight species the unfavourable energetics are also insufficient to overcome the loss in configurational entropy that accompanies the flattening of the polymer coils on the adsorbent. Indeed, the limiting behaviour in the extent of adsorption of the polysiloxanes as a function of molecular weight in n-C_6H_{14} and CCl_4 on untreated silica could well be ascribed to the formation of compressed coils at the interface.

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