Adsorption of poly(dimethyl siloxanes) from solution on silica: 2.

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The adsorption energy ($\Delta\epsilon_s$), the change in energy on breaking a solvent–adsorbent bond and forming a segment–adsorbent bond, for poly(dimethyl siloxane) at the solution/silica interface has been measured under actual adsorption conditions. The effect of the adsorption energy on the extent of mass adsorption and on the conformation of the adsorbed polymer layer was evaluated. At low surface coverage, it is primarily the adsorption energy which determines the conformation of the adsorbed polymer layer as a function of the molecular weight. This effect is opposed by an entropy lowering, resulting from a restriction of the configuration of the adsorbed polymer molecules. At high surface coverage, lateral interactions between the adsorbed polymer molecules became an important factor causing a decrease in the fraction of directly adsorbed segments per molecule with increasing coverage.

INTRODUCTION

In a previous paper[1] the adsorption behaviour of a broad range of poly(dimethyl siloxanes) at the solution/silica interface was rationalized in terms of the polymer–solvent interaction values (χ), the solvent–adsorbent and the polymer–adsorbent adsorption energies. This was accomplished through the measurement of the energetics of each of the various interactions. It was demonstrated that the energetic interactions of the solvent molecules and the dimethyl siloxane segments with the silica largely determined the extent of adsorption. The solvent compatibilities with the polymer did not, however, give a correct prediction of the level of mass adsorption. The adsorption behaviour was qualitatively explained in terms of three contributions to the free energy change. These were:

(1) the free energy change associated with the breaking of solvent–adsorbent bonds and the formation of polymer–adsorbent bonds;

(2) the free energy change which occurred in response to the polymer and solvent molecules redistributing themselves between the surface and bulk phases;

(3) the free energy change incurred when restricting the configuration of the polymer molecules in the surface phase (an entropy lowering).

There has been little investigation of the relationship between polymer adsorption from solution and temperature, due in part to the fact that high precision in the adsorption isotherms is difficult to achieve[2]. The thermodynamic parameter of importance, of course, is the isosteric heat of adsorption at constant pressure. This is obtained by measuring the change in the equilibrium polymer concentration, at a constant quantity of adsorbed polymer at the interface, as a function of the change in temperature. The details of the analysis, however, are complex due to the five pairwise energetic interactions influencing the adsorption process, i.e. polymer–adsorbent; solvent–adsorbent; polymer–solvent; solvent–solvent; and polymer–polymer. Further complications arise because of the uncertainty that the isotherms are in thermodynamic equilibrium and, moreover, reversible[3]. Experimental work has also shown that the conformation which a particular polymer molecule assumes at an interface tends to differ from its conformation in the bulk solution and can vary with the degree of surface coverage[2,4,5]. Therefore, another factor that must be defined for a complete understanding of the system is the fraction of segments in the interfacial region that are actually adsorbed.

The present investigation is an attempt to measure the adsorption energy ($\Delta\varepsilon_s$), the energy change on breaking a solvent–silica bond and forming a siloxane–silica bond, under actual adsorption conditions. This was accomplished by studying the temperature dependence of the mass isotherms and then evaluating the effect of the adsorption energy on the extent of mass adsorption and the conformation of the adsorbed polymer layer.

EXPERIMENTAL

Polymers

Poly(dimethyl siloxanes) having the following number-average molecular weights ($\bar{M}_n$) and polydispersity ratios ($\bar{M}_w/\bar{M}_n$) were investigated: $\bar{M}_n = 2080$, $\bar{M}_w/\bar{M}_n = 1.10$; $\bar{M}_n = 5620$, $\bar{M}_w/\bar{M}_n = 1.32$; $\bar{M}_n = 520000$, $\bar{M}_w/\bar{M}_n = 1.40$. The characterization of these polymers has been discussed in greater detail elsewhere[1].

Solvents

The solvents for the adsorption experiments were spectroquality *n*-hexane and carbon tetrachloride.

Adsorbents

Cab-O-Sil M5 (Cabot Corp., Boston, Mass.) with a reported surface area of 200 m^2 g^{-1}, selected as the non-porous adsorbent, was used as received or after modification with trimethylchlorosilane[6]. The surface coverages

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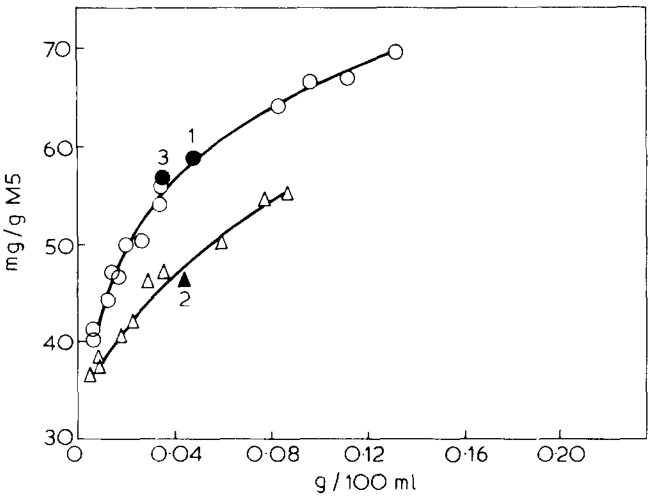

Figure 1 Adsorption of the $\bar{M}_n$ = 5620 silicone from CCl_4 onto untreated silica at 29.5° (○) and 44.6°C (△). The numbered data points correspond to samples cycled between these two temperatures

of the treated silicas were 0.53, 0.83, 1.28, 1.47, and 1.69 trimethylsilyl groups per 100 Å^2.

Procedure

The adsorption isotherms were obtained as described previously[1]. In this study, isotherms were determined at four temperatures, specifically 14.5°, 29.5°, 44.6°, and 59.4°C. Since the equilibrium polymer concentrations were analysed at ambient temperature, they were corrected for solution expansion or contraction during equilibration using the volume expansion coefficients for the solvents. The enthalpies of adsorption were calculated from the temperature dependence of the mass isotherms.

Of the polymer molecules bound to the surface, not all the segments are physically adsorbed. The fraction of segments physically adsorbed, the bound fraction (p), was measured by an experimental technique devised by Rupprecht and Liebl[7] and Joppien[8]. The infra-red transmittance of the peaks corresponding to the isolated hydroxyls on the silica surface, which act as adsorption sites, was monitored as the polysiloxanes were adsorbed from CCl_4. The present investigation of bound fractions was limited to this solvent because it alone had the same refractive index as Cab-O-Sil. The silica gels, with adsorbed polymer, were centrifuged from the supernatant solutions and then uniformly spread between NaCl windows of 1 mm pathlength. The gels were scanned in the 2800–4000 cm^{-1} region using a Perkin–Elmer 521 Grating Infra-red Spectrophotometer. The isolated hydroxyl peak at 3685 cm^{-1} was perturbed from 3747 cm^{-1} by the CCl_4. With the adsorption of the polysiloxanes the 3685 cm^{-1} peak height decreased and strongly hydrogen-bonded silanols which absorbed at 3450 cm^{-1} were created. The adsorbed polysiloxane segments thus caused a shift ($\Delta\nu_{OH}$) in the isolated hydroxyl band of approximately 300 cm^{-1}. A calibration of the peak heights at 3685 cm^{-1} *versus* the number of isolated hydroxyls per 100 Å^2 of untreated silica was made using silicas having 0.53 and 0.83 chemisorbed trimethylsilyl (TMS) groups per 100 Å^2. It was not possible to continue lowering the concentration of the isolated hydroxyl groups using the higher silanized surfaces because the 3685 cm^{-1} peak began to shift to higher frequencies as the TMS concentration increased. A linear relationship, i.e. absorbance *versus* TMS group concentration, was obtained which extrapolated to 1.7 TMS groups per 100 Å^2 of silica at zero absorbance. This value is identical to the one estimated by Hair and Hertl[9] for the total isolated hydroxyl group concentration per 100 Å^2 of Cab-O-Sil.

The bound fractions were calculated assuming one dimethyl siloxane repeating unit interacted with one isolated hydroxyl. At a particular surface coverage:

$$p = \frac{(\text{no. of OH})\,(A)\,M_s)}{(MG)\,(N_A)}$$

where (no. of OH) is the number of isolated hydroxyls per 100 Å^2 interacting with the polysiloxanes as determined through infra-red transmittance; A is the surface area of the silica which was 199.7 m^2/g M5; M_s is the molecular weight of the repeating units which is 74.2; MG is the number of milligrams of polymer adsorbed per gram of silica; and N_A is Avogadro's number.

RESULTS AND DISCUSSION

Equilibrium and reversibility

In *Figure 1* adsorption of the $\bar{M}_n = 5620$ polymer from CCl_4 onto untreated silica is plotted as a function of the equilibrium polymer concentration at 29.5° and 44.6°C. The results were obtained from samples that had been directly equilibrated at either of these two temperatures over a 6 h period. The 3 numbered data points, however, correspond to samples that were cycled between these two temperatures. All 3 samples were first equilibrated at 29.5°C, one of the samples (1) then being analysed. The two remaining samples were re-equilibrated at 44.6°C, after which a second sample (2) was analysed, followed by re-equilibration and analysis of the last sample (3) at 29.5°C. Each re-equilibration was allowed 6 h. It is clear that the data for the 'cycled' samples closely match those determined directly at the one temperature. The above results indicate that equilibrated values can be realized within a 6 h period and that the adsorption is reversible as a function of the temperature.

The findings of Perkel and Ullman[10] were at variance with these observations. They reported that adsorption of a high molecular weight poly(dimethyl-siloxane) ($\bar{M}_n$ = 536000) was not reversible when desorption studies were attempted from a glass substrate in the presence of n-C_7H_{16} or CCl_4. However, desorption may be a function of the polymer molecular weight. The work by Stromberg *et al.*[11] supports this position. They proposed that the rate of desorption for lower molecular weight polystyrene from a chrome surface was faster than for higher molecular weights owing to fewer attachments per molecule. A similar conclusion regarding desorption as a function of molecular weight was reached by Gilliland and Gutoff[12]. Thus, for a high molecular weight polysiloxane on glass, and silica, the apparent irreversibility may be ascribed to the multiplicity of adsorbing sites per molecule energetically favouring adsorption. This results in small desorption rate constants. In view of the above experimental data, only the low molecular weight dimethyl siloxanes were deemed suitable for thermodynamic evaluation. On this basis the $\bar{M}_n$ = 2080 and 5620 silicones were studied in detail.

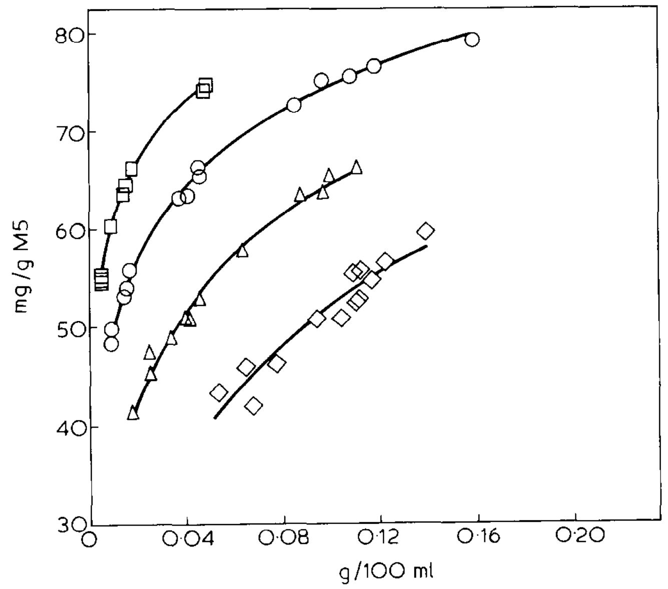

Figure 2 Adsorption of the $\bar{M}_n$ = 2080 silicone from n—C_6H_{14} onto untreated silica at 14.5° (□); 29.5° (○); 44.6° (△); and 59.4°C (◇)

Heats of adsorption

The enthalpy change during adsorption may be calculated from the temperature dependence of the mass isotherm by[13]:

$$\left(\frac{\partial \ln(a/a_s)}{\partial(1/T)}\right)_P=\frac{\Delta H}{R}$$

where a and a_s are the activities of the polymer in the solution and on the surface, respectively; P is the pressure; T is the absolute temperature (K); R is the ideal gas constant (8.314 J K^{-1} mol^{-1}); and ΔH is the difference in the partial molar enthalpy of the polymer on the surface and in the solution (J mol^{-1}). To apply this equation, two assumptions have to be made: (1) the polymer solution is dilute so that a is proportional to the concentration c; and (2) the activity of the polymer at the surface, a_s, remains constant when the amount adsorbed, Γ, is kept constant. The isosteric heat of adsorption is then calculated using:

$$\left(\frac{\partial \ln c}{\partial(1/T)}\right)_{P,\Gamma}=\frac{\Delta H}{R}$$

The slope of the straight line, ln c *versus* $1/T$, gives the change in enthalpy for the reversible transformation.

Figure 2 shows mass isotherms at four temperatures for the adsorption of the $\bar{M}_n = 2080$ polymer onto untreated silica from n-C_6H_{14}. The semilog plot of the equilibrium polymer concentration as a function of the reciprocal of the absolute temperature at selected surface coverages, shown in *Figure 3*, indicates a linear relationship at all coverages. This gives further evidence that the thermodynamic treatment employed here applies over the temperature range investigated. The exothermic heats decrease progressively with increasing coverage. Temperature dependence studies were conducted using two partly silanized silica surfaces (i.e. 0.53 and 0.83 TMS/100 Å^2) with the $\bar{M}_n = 2080$ silicone in n-C_6H_{14}. It had been previously shown for this system[1] that adsorption was predominantly onto unreacted isolated hydroxyl sites.

The isosteric heats of adsorption, for both the $\bar{M}_n = 2080$ and 5620 polymers, are plotted against surface coverage, *Figure 4*. Since these heats are being measured at relatively high surface coverage, only small changes with coverage would be expected. However, they are seen to decrease rapidly with surface coverage with the curves running parallel to one another. The rapid decrease in the isosteric heats may be interpreted in terms of a decrease in the bound fraction of polysiloxane molecules with coverage. Killmann and Eckart[5] have also proposed decreasing bound fractions to explain the heats of adsorption of poly(ethylene glycol) on silica. The parallel decrease in the isosteric heats indicates that they primarily reflect the interaction of only those siloxane segments which replace n-C_6H_{14} molecules in direct contact with the surface isolated hydroxyls. Consequently, the decrease in the isosteric heats, which are expressed per mole of polymer adsorbed and not per mole of siloxane segments adsorbed, results from a decrease in the bound fraction at high surface coverages.

The theoretical interpretation for a decreasing bound fraction is that it results from a change in the organization of the adsorbed polymer layer as a result of lateral interactions between the adsorbed polymer molecules[14,15]. These unfavourable polymer–polymer interactions would arise from an excluded volume effect.

The difference in the mass adsorption of the $\bar{M}_n = 2080$ and 5620 silicones on untreated silica (*Figure 4*) must necessarily reflect a difference in the number of contact points per polymer molecule with the silica. Indeed, the bound fraction for the $\bar{M}_n = 5620$ silicone would have to be smaller at high coverage. Support for this interpretation has been indicated in several other studies[4,5,11,16].

For the adsorption of the $\bar{M}_n = 2080$ silicone onto the untreated and the two partly treated silicas, the differences

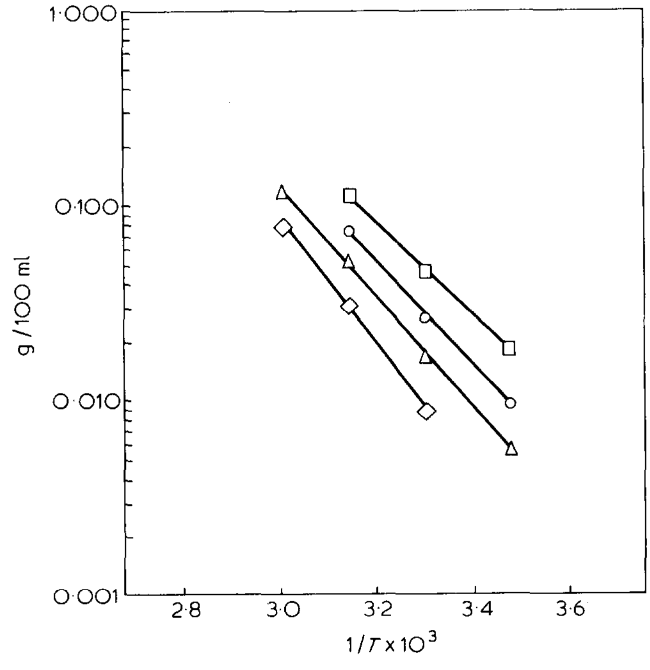

Figure 3 Semilog plot of the equilibrium concentration of the $\bar{M}_n$ = 2080 silicone in n—C_6H_{14} *versus* the reciprocal of the absolute temperature for given surface coverages on untreated silica.
□, 66.0 mg/g M5, ΔH = −45.4 kJ mol^{-1}; ○, 60.0 mg/g M5, ΔH = −51.0 kJ mol^{-1}; △, 55.0 mg/g M5, ΔH = −54.4 kJ mol^{-1}; ◇, 48.0 mg/g M5, ΔH = −61.3 kJ mol^{-1}

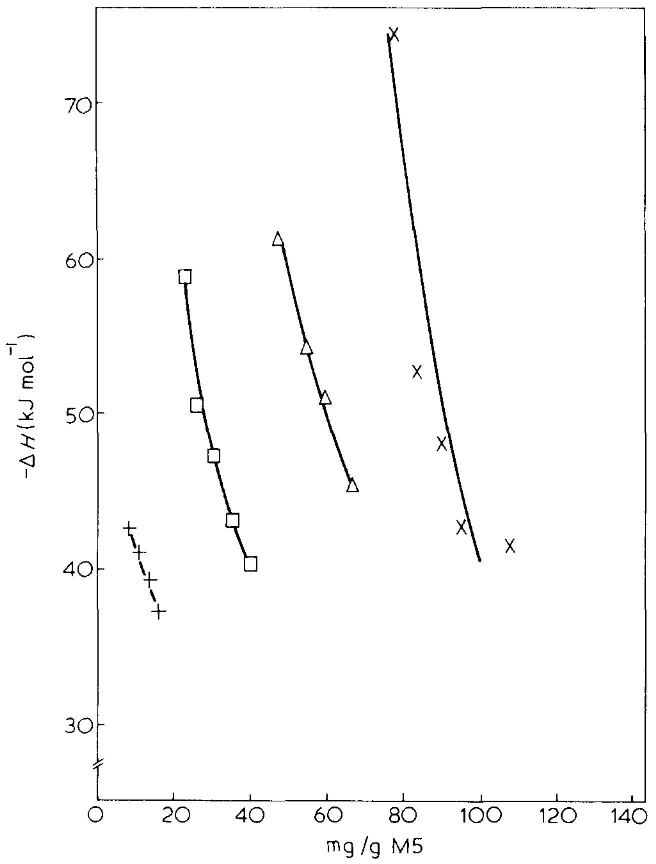

Figure 4 Heats of adsorption of the $\bar{M}_n$ = 2080 and 5620 silicones from n—C_6H_{14} onto untreated and partly trimethylsilylated silicas. x, 5620 – untreated; △, 2080 – untreated; □, 2080 – 0.53 TMS/100 Å^2; +, 2080 – 0.83 TMS/100 Å^2

in the mass adsorption can be directly correlated with the number of isolated hydroxyls present on each surface (ref 1).

The effect of solvent on the adsorption of the $\bar{M}_n = 2080$ and 5620 silicones has also been investigated. In *Figure 5*, isosteric heats for the two silicones adsorbed from n-C_6H_{14} and CCl_4 onto untreated silica are compared. With respect to the molecular weight, the isosteric heats are significantly less at comparable coverage in the presence of the CCl_4 solvent and, furthermore, maxima are observed. At high surface coverage, maxima are normally attributed to lateral interactions between adsorbed molecules. However, such maxima were not observed in the study with the n-C_6H_{14} solvent, although they could possibly occur at lower surface coverages than those which were experimentally accessible. An alternative explanation for the presence of the maxima in CCl_4 could be a specific endothermic contribution due to the desorption of the solvent at lower coverages. It was previously shown[1] that CCl_4 had a specific interaction with a small number of active sites on the silica surface. This specific interaction was also rationalized on the basis that CCl_4 is a poorer solvent for poly(dimethyl siloxane) than n-C_6H_{14} and thus greater mass adsorption would be predicted. A further account for the maxima would first require a quantitative measure of the bound fractions of these molecules with coverage.

Bound fractions

The diminution of the 3685 cm^{-1} infra-red peak with the adsorption of the $\bar{M}_n = 2080$, 5620 and 520000 polysiloxanes is presented in *Figure 6* where the absorbance is plotted as a function of the mass adsorption at 29.5°C. The broken lines emanating from the experimental curves serve to illustrate the divergence from linearity of the absorbance with increasing polymer adsorption. This divergence diminishes with increasing molecular weight and indicates that there are dramatic differences in

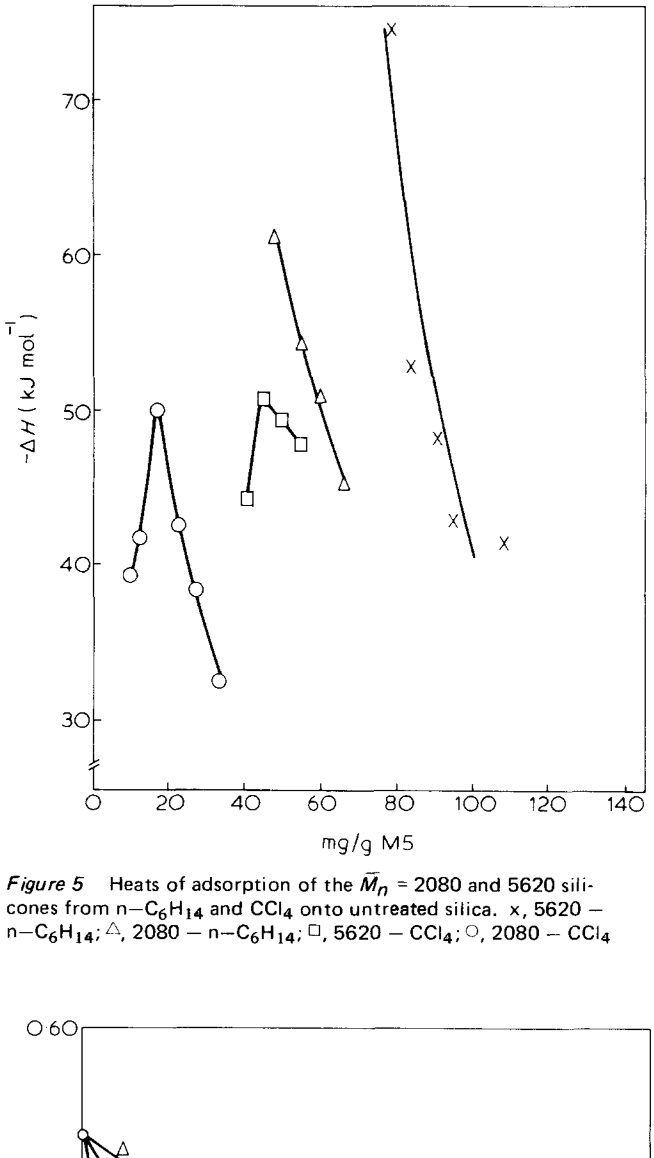

Figure 5 Heats of adsorption of the $\bar{M}_n$ = 2080 and 5620 silicones from n—C_6H_{14} and CCl_4 onto untreated silica. x, 5620 – n—C_6H_{14}; △, 2080 – n—C_6H_{14}; □, 5620 – CCl_4; ○, 2080 – CCl_4

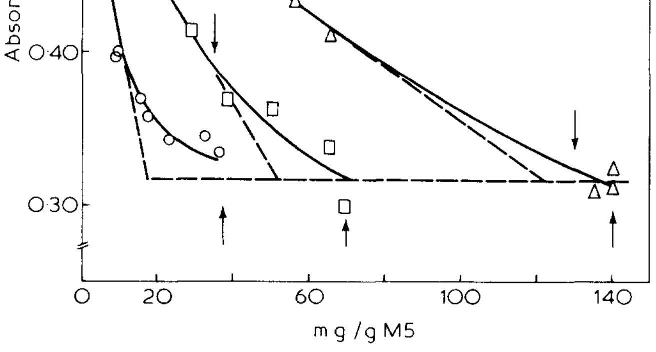

Figure 6 Absorbance of the 3685 cm^{-1} peak as a function of the mass adsorption of the polysiloxanes from CCl_4 onto untreated silica at 29.5°C. △, $\bar{M}_n$ = 520000; □, 5620; ○, 2080

Table 1 Bound fractions (p) for the polysiloxanes adsorbed from CCl_4 on untreated silica at 29.5°C

$\bar{M}_n$ = 2080		$\bar{M}_n$ = 5620		$\bar{M}_n$ = 520 000	
Amount adsorbed (mg/g.M5)	p	Amount adsorbed (mg/g.M5)	p	Amount adsorbed (mg/g.M5)	p
10	0.93	10	0.33	10	0.13
13	0.92	30	0.32	30	0.13
18	0.75	50	0.27	70	0.13
23	0.63	70	0.24	140	0.12
28	0.54				
33	0.47				

the manner in which the various polysiloxanes adsorb at the interface, i.e. the greater the divergence, the greater the change in the bound fraction (p) with change in surface coverage. The arrows in the direction of the abscissa correspond to the quantity of polymer adsorbed at the minimum equilibrium concentrations that were experimentally accessible. The arrows pointing away from the abscissa indicate the amount of polymer adsorbed in the region of the pseudo-plateaux.

It is clear from *Figure 6* that the pseudo-plateaux values for each polysiloxane correspond to approximately the same absorbance value, as is indicated by the horizontal broken line. Irrespective of the molecular weight, therefore, adsorption of the segments in the surface layer reaches a common limiting value. Accordingly, with increasing molecular weight there has to be an increasing volume of polymer that is situated in unadsorbed structures (surface protruding loops and tails).

The bound fractions at various surface coverages for each of the polysiloxanes are given in *Table 1*. It is evident that at low surface coverage, where p approaches unity, the $\bar{M}_n = 2080$ polymer adsorbed in an almost flat conformation onto the silica surface. This suggests that the polymer molecules adsorbed independently of one another, allowing the polymer chains to unfold onto the surface to yield a relatively flat conformation and thereby maximize the energetic contacts between their segments and the surface. With increase in the concentration of polymer in solution, the bound fraction decreased as there was a restriction on the unfolding of the polymer chains due to increasing lateral interactions between the adsorbed molecules. Hence, a new equilibrium conformation was formed with fewer of the segments attached to the surface and more sequences of segments extending out into the solution. Finally, in the region of surface saturation, some limiting conformation was attained with roughly half of the segments in actual contact with the adsorbent.

The bound fraction data for the $\bar{M}_n = 5620$ polymer show that only a third of its segments are in direct contact with the silica even at low surface coverage. As the polymer chains would be adsorbing independently of one another at low coverage, it is apparent that the restriction on the unfolding of the polymer chains cannot be attributed to repulsive lateral interactions. Indeed, these interactions appear to become operative only at higher coverages as indicated by the diminishing bound fraction. For the $\bar{M}_n = 520\,000$ polymer, however, the bound fraction was even smaller (0.13) and almost independent of surface coverage.

Adsorption at low surface coverage

At low surface coverage, the above results clearly show that at an intermediate molecular weight, between $\bar{M}_n = 2080$ and 5620, the conformation of poly(dimethyl) siloxane) in the interfacial region changes from one that is flat in the surface layer to one with a looped or coiled structure. At higher surface coverages, however, there is a reorientation of the polymer molecules which is only significant for the lower molecular weight species.

To account for the conformational dependence on the molecular weight at low surface coverage, adsorption energies were determined as a function of surface coverage. *Figure 7* is a plot of the averaged energy difference between the segment–surface and the solvent–surface bond, represented by $-\Delta\varepsilon_s/kT$, as a function of the surface coverage for the $\bar{M}_n = 2080$ and 5620 silicones in CCl_4 on untreated silica at 29.5°C. The mean $\Delta\varepsilon_s$ values were calculated using the isosteric heat data in *Figure 5* and dividing by the number of segment–silica contacts per molecule (the product of the corresponding bound fractions and the degrees of polymerization). It is noted that as the surface coverage increases the adsorption energy, $\Delta\varepsilon_s$, initially increases and then finally becomes almost independent of coverage. Since the bound fractions for the $\bar{M}_n = 2080$ polymer are greater than 0.90 at low coverage, where the molecules were adsorbing independently of one another, the mean $\Delta\varepsilon_s$ must be smaller due to a relatively strong endothermic contribution from the desorption of the CCl_4 molecules from a small number of active surface sites, a contribution which diminishes with increasing coverage. This specific endothermic contribution would provide an explanation for the maxima observed for the two silicones in *Figure 5*. After the maxima, however, the decreasing isosteric heats in *Figure 5* are directly proportional to a decreasing bound fraction as $\Delta\varepsilon_s$ is now relatively constant. In this regard, it should be pointed out that polymer segments which replace previously adsorbed segments during this rearrangement produce no additional contribution to the enthalpy of adsorption[5].

In a paper by Lal and Stepto[17], the adsorbed configurational behaviour of low molecular weight polymers

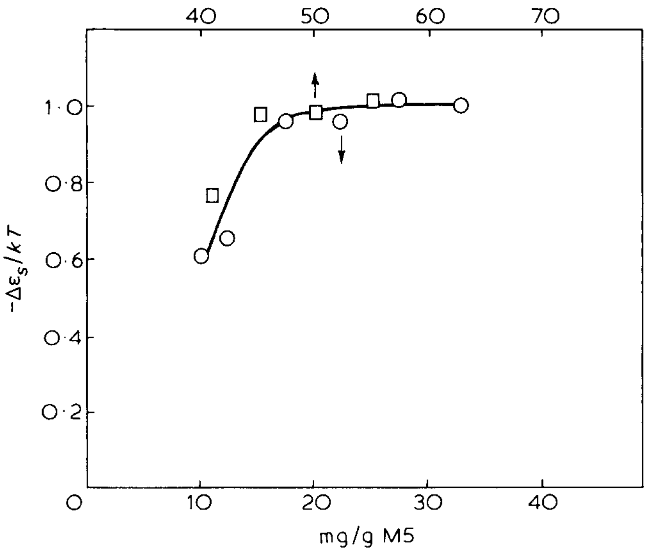

Figure 7 Adsorption energies for the $\bar{M}_n$ = 2080 and 5620 silicones from CCl_4 onto untreated silica as a function of the surface coverage at 29.5°C. ○, $\bar{M}_n$ = 2080 – bottom axis; □, 5620 – top axis

at two adsorption energies was investigated, assuming freely rotating chains adsorbed from an athermal solution. While the numerical results for the bound fractions are not quantitatively comparable with those obtained here, the general predictions are useful in rationalizing the present results. Their model predicts that for weak adsorption energies, e.g. $-\Delta\varepsilon_s/kT=0.5$, the thickness of the adsorbed polymer layer is dominated by the unadsorbed tail sections of the molecule, the length of which increases with molecular weight. However, the chain lengths of the adsorbed segments and unadsorbed loops change little with molecular weight. For stronger adsorption energies, however, e.g. $-\Delta\varepsilon_s/kT=0.9$, there is a tendency for polymers of increasing molecular weight to assume a more flattened conformation in the surface layer. It is probable that the decrease in the bound fraction in going from the $\bar{M}_n=2080$ to the 5620 polymer in the region of low surface coverage can be attributed to the weak adsorption energy in this range, as shown quantitatively in *Figure 7*. This would also mean that this adsorption energy could not completely overcome the entropy lowering resulting from a restriction on the configuration of the $\bar{M}_n=5620$ molecule, a free energy increase readily exceeded in the case of the smaller $\bar{M}_n=2080$ molecule. The free energy change occurring in response to the polymer and solvent molecules redistributing themselves between the surface and bulk phases may be considered to be a small contribution as both adsorbed molecules were in equilibrium with infinitely dilute solutions at low coverage (*Figure 6*). Similar conclusions could also be drawn for the $\bar{M}_n=520\,000$ polymer in the presence of CCl_4.

Support for the above interpretations may be found in a prior study[1] where attempts were made to adsorb preferentially these same polysiloxanes from n-C_6H_{14} onto a highly trimethylsilylated silica (i.e. 1.69 TMS/100 $Å^2$). 'Negative' adsorption, i.e. preferential solvent adsorption, was observed which increased with polymer molecular weight. Since the degree of 'negative' adsorption reflected the size of the polymer molecules in the presence of this solvent, it was concluded that a weak or unfavourable $\Delta\varepsilon_s$ could not overcome the loss in configurational entropy which would accompany the adsorption of these polysiloxanes. This same rationale was used to explain the 'negative' adsorption results of these polysiloxanes in the presence of benzene on untreated silica.

It is noted in *Figure 5* that the isosteric heats of adsorption for the $\bar{M}_n=5620$ silicone in n-C_6H_{14} decrease much more rapidly with coverage than those in CCl_4 (after the maximum in the case of adsorption from CCl_4). In fact, the decrease is comparable with that for the $\bar{M}_n=2080$ silicone in the presence of CCl_4 where the bound fraction was diminishing rapidly. It is suggested, therefore, that the $\bar{M}_n=5620$ silicone has assumed a relatively flat conformation in the surface layer at low surface coverage in n-C_6H_{14}, owing to a strong energetic interaction with the silica. Hence, for a given solvent, the adsorption energy, $\Delta\varepsilon_s$, largely determines the conformation of the adsorbed polymer layer as a function of the molecular weight. It is unfortunate that this cannot be confirmed experimentally with bound fraction data in the presence of n-C_6H_{14}.

Adsorption at high surface coverage

In the region of high surface coverage, unfavourable polymer–polymer interactions in the surface layer become an important factor. A decrease in the value of the bound fraction would relieve this force, but as adsorption increases and more adjacent sites become occupied a limiting value would eventually be reached. It is proposed that this contribution primarily accounts for the three polysiloxanes having the same number of segments in the surface layer at surface saturation in CCl_4. This view is strengthened when adsorption from both CCl_4 and n-C_6H_{14} are compared. There is considerably more polymer adsorbed from n-C_6H_{14} in the pseudo-plateau region compared with that from CCl_4. As shown in a previous study[1], adsorption of the $\bar{M}_n=2080$ polymer from n-C_6H_{14} became 'negative' at, or near, a coverage of 1.7 TMS groups per 100 $Å^2$ of silica, the TMS groups having reacted on a 1:1 basis with the isolated hydroxyls. This would imply that the polysiloxane can interact with a comparable number of isolated hydroxyls on the untreated silica. Using the calibration plot derived from the CCl_4–trimethylsilylated silica gels, the absorbance corresponding to the pseudo-plateau values for the three polysiloxanes in CCl_4 (*Figure 6*) converts to an average of 0.7 hydroxyls per 100 $Å^2$ of Cab-O-Sil. Clearly, there are more than twice the number of siloxane segments in direct contact with the silica at surface saturation when adsorption occurs from n-C_6H_{14}. It seems reasonable to assume that the stronger energetic interaction with the silica, as shown quantitatively in *Figure 5*, overcomes any effect that the unfavourable polymer–polymer interactions may have on the fraction of surface occupied. Moreover, n-C_6H_{14} is a better solvent than CCl_4 for poly(dimethyl siloxane)[1] and thus the adsorbed polymer molecules would experience even greater repulsive interactions in the surface phase, i.e. a better solvent makes polymer–solvent contacts energetically more favourable relative to polymer–polymer contacts.

CONCLUSIONS

The adsorption behaviour of poly(dimethyl siloxane) onto silica from solution may be explained in terms of four main contributions to the free energy change occurring during adsorption:

(1) the contact energy per molecule;

(2) the free energy change accompanying the removal of the polymers from the bulk solution;

(3) the free energy change due to the lowering of the entropy of the surface-phase polymers owing to a restriction on their configurations; and

(4) the free energy change arising from the repulsive polymer–polymer interactions in the interfacial region at high surface coverage.

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REFERENCES

1 Brebner, K. I., Chahal, R. S. and St-Pierre, L. E. *Polymer* 1980, **21**, 533
2 Ash, S. G. 'Colloid Science', Chemical Society, London, 1973, Vol. 1, Ch 3
3 Ullman, R., 'Encyclopedia of Polymer Science and Technology', Wiley, New York, 1970, Vol. 1
4 Stromberg, R. R., Tutas, D. J. and Passaglia, E. *J. Phys. Chem.* 1965, **69**, 3955

5 Killmann, E. and Eckart, R. *Makromol. Chem.* 1971, **144**, 45
6 Chahal, R. S. and St-Pierre, L. E. Macromolecules 1968, **1**, 152
7 Rupprecht, H. and Liebl, H. *Kolloid. Zh.* 1970, **239**, 685
8 Joppien, G. *Makromol. Chem.* 1974, **175**, 1931
9 Hertl, W. and Hair, M. L. *J. Phys. Chem.* 1969, **73**, 4269
10 Perkel, R. and Ullman, R. *J. Polym. Sci.* 1961, **54**, 127
11 Stromberg, R. R., Grant, W. H. and Passaglia, E. *J. Res. Nat. Bur. Stand. (A)* 1964, **68**, 391
12 Gilliland, E. R. and Gutoff, E. B. *J. Appl. Polym. Sci.* 1960, **3**, 26
13 Koral, J., Ullman, R. and Eirich, F. R. *J. Phys. Chem.* 1958, **62**, 541
14 Hoeve, C. A. J. *J. Polym. Sci. (C)* 1970, **30**, 361
15 Hoeve, C. A. J. *J. Polym. Sci. (C)* 1971, **34**, 1
16 Robb, I. D. and Smith, *R. Eur. Polym. J* 1974, **10**, 1005
17 Lal, M. and Stepto, R. F. T. *J. Polym. Sci.* 1977, **61**, 401