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ELECTRON SPIN RESONANCE STUDIES OF SPIN-LABELLED POLYMERS—18

ADSORPTION OF SPIN-LABELLED POLY(VINYL ACETATE) ON SILICA SURFACES

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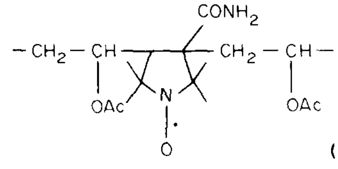
Abstract—The adsorption of spin-labelled poly(vinyl acetate) from dilute solutions in ethyl acetate, chloroform and toluene onto three silica adsorbents of different surface silanol contents was studied. The adsorption capacities of the three silica samples, which decreased with decreasing surface silanol content, were dependent on the nature of the solvent, being greatest in the poor solvent toluene and least in the good solvent ethyl acetate. The ESR spectra of the polymer adsorbed on the silica of highest silanol content suggested that the polymer had a relatively flat conformation when toluene or chloroform was solvent and a more looped conformation when ethyl acetate was solvent. With the silica of intermediate silanol content, the polymer adsorbed from chloroform solution also had a loopy conformation. The silica of lowest silanol content was prepared by treating the first silica absorbent with trimethylchlorosilane. The line-shapes in the ESR spectrum of the labelled polymer adsorbed on this modified silica indicated a change in mode of adsorption.

INTRODUCTION

In recent years ESR studies of spin-labelled polymers at solid–liquid interfaces have been conducted to complement the information available from other techniques [1–7]. Nitroxide radicals have invariably been the spin-labels of choice because of their outstanding stability and because their ESR spectra may be analysed to yield quantitative dynamic data. Provided the label cannot rotate independently of the polymer molecule, these data reflect the dynamics of the polymer chain to which the label is attached.

In this study, involving poly(vinyl acetate) (PVAc), the spin-labelled unit **I** satisfies this requirement because it constitutes part of the polymer backbone and rotation is possible only in cooperation with segmental motion. Our results provide an interesting comparison with an earlier, similar investigation which utilised PVAc labelled with a pendant nitroxide **II** capable of rotating independently of the main chain segments [5].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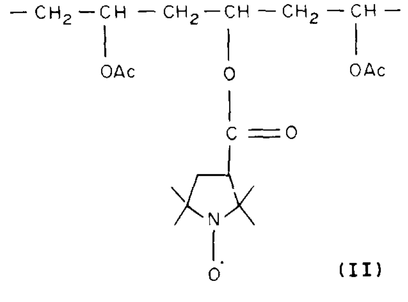
(II)

When a labelled polymer such as **I** is adsorbed at a solid–liquid interface, information on the extent of adsorption and on the chain conformation may be derived from the ESR spectrum. The affinity of a polymer for a solid surface and its conformation and segmental mobility when adsorbed depend upon the interplay of a number of factors including the relative energies of interaction of polymer segments and solvent molecules at surface sites, and the distribution of these sites on the surface. In the present study these factors were varied by changing the nature of the adsorbent and the solvent.

EXPERIMENTAL

Three silica-based adsorbents were used. Microsil GP (Crosfield) is a precipitated silica of surface area approx. 200 $m^2 g^{-1}$ as determined by N_2 adsorption; it contains a relatively high level of silanol groups, *ca* 6–8 per 100 $Å^2$. Cab-O-Sil M5 (Cabot) is a pyrogenic silica of similar surface area but with a lower content of silanol groups, *ca* 3–4 per 100 $Å^2$. A sample of surface-modified silica was prepared by treating Microsil GP with trimethylchlorosilane according to the published method [8, 9]; this treatment converts most of the silanols to trimethylsilyl groups but does not appear to alter the surface area [10].

The spin-labelled poly(vinyl acetate) PVAc I was prepared by radical copolymerisation of vinyl acetate with 2,2,5,5-tetramethylpyrroline-3-carboxyamide (TMPC) (prepared by the method of Rosantsev [11]) followed by oxidation of the copolymerised pyrroline units to the corre-

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sponding nitroxide. Vinyl acetate (40 ml, 0.44 mol), TMPC (1.22 g, 7.22 mmol) and AIBN (0.14 g, 0.85 mmol) were dissolved in dry benzene (40 ml) and sealed in a reaction vessel under N_2. Polymerisation was allowed to proceed for 3 hr at 70°C after which the cooled contents were poured into light petroleum (60–80) to precipitate the polymer. After drying, the polymer was dissolved in toluene (75 ml), and the solution filtered to remove the unreacted TMPC. The polymer was reprecipitated in light petroleum, filtered off and dried *in vacuo*. To oxidise copolymerised TMPC units to nitroxides, the polymer (6.4 g) and *m*-chloroperbenzoic acid (MCPA, 3.2 g) were each dissolved in benzene (100 ml). The MCPA solution was added dropwise with stirring to the polymer solution which developed a pale yellow colour after several minutes. The combined solutions were left to stand overnight then the product PVAc 1 was collected by precipitation in petroleum ether as before. At this stage the ESR spectrum of the product in toluene solution indicated that the labelled polymer was contaminated with a small-molecule nitroxide, presumably from residual free TMPC. It was removed by dissolving the PVAc 1 in methanol (2% w/v solution) and precipitating the polymer in a large volume of distilled water (in which the small nitroxide is soluble) containing $CaCl_2$ (*ca* 3% w/v) as coagulant. The filtered polymer was washed with distilled water to remove $CaCl_2$ and the dissolution–precipitation procedure was repeated twice more. The labelled polymer was finally washed with water and dried *in vacuo*. The ESR spectrum of the purified polymer in toluene solution showed no evidence of the presence of the small nitroxide contaminant. A sample of unlabelled poly(vinyl acetate) PVAc 3, was prepared in an identical manner but with the omission of TMPC.

The molecular weights of the two polymer samples were determined by gel permeation chromatography (GPC) in chloroform with a Waters Series 200 Instrument equipped with μ-Styragel columns of pore sizes 10^5, 10^4, 10^3 and 500 Å. The columns were calibrated with polystyrene standards and the data converted for use with PVAc samples by means of the universal calibration procedure [12]. The values of $\bar{M}_n$ thus obtained were 37,000 and 41,000 for PVAc 1 and PVAc 3 respectively. The GPC technique was also employed to study changes in the molecular weight distribution of dissolved polymer during adsorption. In this case, the solvent was THF.

The spin-concentration of PVAc 1 was approximately one spin per 20,000 monomer units. Details of the hyperfine coupling- and g-tensor values of PVAc samples labelled as in I above will be published elsewhere.

The adsorption isotherms of the polymers on the various substrates at room temperature were measured by ESR spectroscopy as described previously [2]. Solutions (10 ml) of various polymer concentrations were shaken vigorously with the solid adsorbent (0.2 g) to disperse the solid, then tumbled slowly over 24 hr to ensure that equilibrium had been reached [2]. The suspensions were then centrifuged at 2000 rpm and the ESR spectrum of the supernatant solution recorded. The peak-to-peak intensity of the central line in the spectrum, which is proportional to the concentration of labelled polymer, was measured and, by comparison with the intensity of the same peak in the original polymer solution, the amount of polymer adsorbed was determined. The ESR spectra of the adsorbed polymers were recorded from the concentrated solid suspensions after four washings with dry solvent. No free polymer was detected in these washings, indicating that desorption was negligible during the time scale of the experiment. All ESR spectra were recorded with a Varian E4 spectrometer.

To check the affinity of the nitroxide label for the substrates Microsil GP and surface-modified Microsil, the adsorption of the free nitroxide 3-carbamoyl-2,2,5,5-tetramethylpyrrolidine-1-oxyl (CTPO) in the presence of unlabelled PVAc 3 was examined. CTPO (2 mg) was dissolved in 25 ml solutions of PVAc 3 (1% w/v) in the various solvents under study. Each solution (10 ml) was mixed with the adsorbent (0.1 g) and shaken for 24 hr as before. The suspensions were treated as described for the experiments with labelled polymer and the ESR spectra recorded as before.

During adsorption of polymer molecules from solution, the molecular weight distribution of the unadsorbed polymer may change with extent of adsorption. To examine this fractionating effect more closely, the molecular weight distribution of PVAc 3 dissolved in toluene was determined before and after adsorption on Microsil GP. Five solutions of PVAc 3 in toluene covering the concentration range 0.04–0.20 g PVAc 3 per 100 ml of toluene were prepared. These concentrations were chosen to produce 50–80% adsorption of the total polymer at equilibrium when Microsil GP (0.1 g) was shaken with 5 ml aliquots over 24 hr. After centrifugation at 2000 rpm for 15 min, the supernatant solution was removed by decantation and the toluene removed by evaporation. The polymer residue was then dissolved in THF, and the GPC trace recorded. The GPC calibration and experimental data were processed to yield values of $\bar{M}_w$ and $\bar{M}_n$ by a Spectra-Physics SP4100 Data System with programs developed for GPC.

The three solvents toluene, chloroform and ethyl acetate used in this work were "Analar" grade and were dried over calcium sulphate before use.

RESULTS AND DISCUSSION

Adsorption isotherms

The adsorption isotherms for labelled PVAc 1 from toluene, chloroform and ethyl acetate onto Microsil GP are shown in Fig. 1 which indicates that the solvent has a strong influence on the affinity of the polymer for the surface. With ethyl acetate, a thermodynamically good solvent for PVAc, relatively low amounts of polymer are required to saturate the surface. The adsorption capacity of the surface is greater when chloroform, which is also a good solvent, is employed and there is a less pronounced tendency to reach a plateau. The capacity of the surface is greatest when the polymer is adsorbed from toluene, a thermodynamically poor solvent for PVAc, and here the surface shows no indications of approaching saturation over the concentration range studied. The tendency for the adsorption capacity of surfaces to vary with solvent quality in this manner has been observed in other systems and has been explained on the basis of the differences in

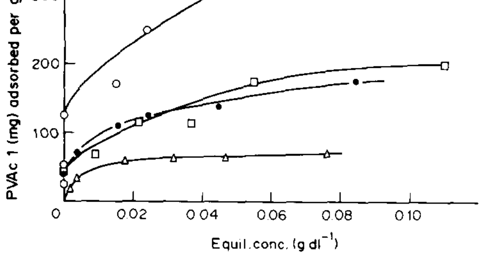

Fig. 1. Adsorption isotherms at ambient temperature for spin-labelled PVAc 1 from toluene (○), chloroform (□) and ethyl acetate (△) on Microsil GP, and from chloroform (●) on Cab-O-Sil M5.

polymer–surface, solvent–surface and polymer–solvent interactions [13]. It is believed that the adsorption of PVAc on silica surfaces results mainly from hydrogen bonding between silanol groups and the ester carbonyl groups on the polymer [14]. Therefore, with ethyl acetate as solvent, the ester groups of the solvent compete strongly with those on the polymer for available surface sites. The thermodynamically favourable polymer–solvent interactions in ethyl acetate also mitigate against adsorption. With toluene, on the other hand, adsorption of the PVAc is more favoured because the solvent is less strongly adsorbed and also because preferential adsorption of the polymer leads to a diminution in polymer–solvent interactions which are unfavourable in a poor solvent. Adsorption of PVAc from chloroform lies between these extremes.

Differences in the conformation of the adsorbed PVAc molecules may also be expected when the solvent is changed. When the affinity of the polymer for the surface is relatively weak, the adsorbed molecules are likely to be held rather loosely and experience considerable motional freedom; this conformation is generally described as consisting of "loops" and "tails". On the other hand, when the solvent is thermodynamically poor, the adsorbed chains are held more strongly on the surface. The resulting motionally restricted conformations are believed to be relatively flat and are referred to as "trains". Such conformational differences are apparent in the ESR spectra of the adsorbed, labelled PVAc. The spectra from the polymer adsorbed on Microsil GP from toluene and chloroform solutions (Fig. 2a and b) are virtually identical and have broad lines characteristic of a slowly tumbling nitroxide, suggesting a relatively flat conformation. The spectra of labelled polymer adsorbed from ethyl acetate, however, are composites of broad and motionally-narrowed lines (Fig. 2c) indicating that some of the segments at the surface are located in loops or tails which are relatively freer and more mobile. The spectra did not change on increasing the polymer

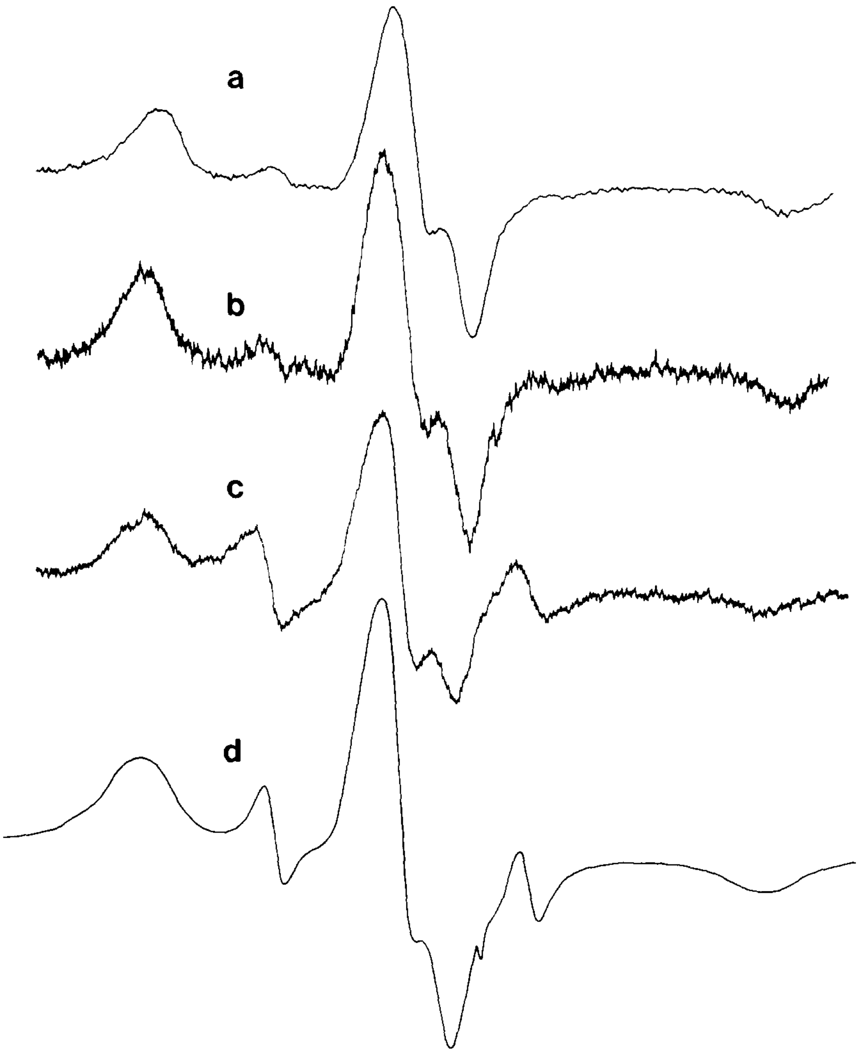

Fig. 2. ESR spectra of PVAc 1 (a, b and c) and CTPO (d) adsorbed on Microsil GP: (a) from toluene solution, equilibrium conc. 0.077 g dl^{-1}; (b) from chloroform solution, equilibrium conc. 0.110 g dl^{-1}; (c) from ethyl acetate solution, equilibrium conc. 0.076 g dl^{-1}; (d) from toluene solution.

Table 1. Changes in molecular weight distribution of PVAc 3 in toluene solution on adsorption on Microsil GP

Sample	Initial conc. of solution (g dl^{-1})	$\bar{M}_w \times 10^{-3}$*	$\bar{M}_n \times 10^{-3}$*	$\bar{M}_w/\bar{M}_n$	% Polymer† adsorbed
Parent	—	107	41	2.61	—
1	0.20	73	33.5	2.18	51
2	0.16	68	30	2.27	54
3	0.10	76.5	36.5	2.10	59
4	0.06	38	23	1.65	68
5	0.04	20	15	1.33	82

*From GPC of supernatant solution. †Estimated from adsorption isotherm for PVAc 1 in Fig. 1a.

concentration in any of these solvents showing that, over the range of concentrations examined, the conformation of adsorbed PVAc is relatively insensitive to the amount of polymer adsorbed.

The experiments with the free label CTPO revealed that the nitroxide is adsorbed on Microsil GP to a detectable extent from toluene solution only. The ESR spectrum of the adsorbed CTPO (Fig. 2d) is a composite of broad-line and motionally-narrowed spectra. The nitrogen hyperfine coupling constant from the latter is 14.2 G, identical to the value of the free nitroxide in toluene solution, and so it is likely

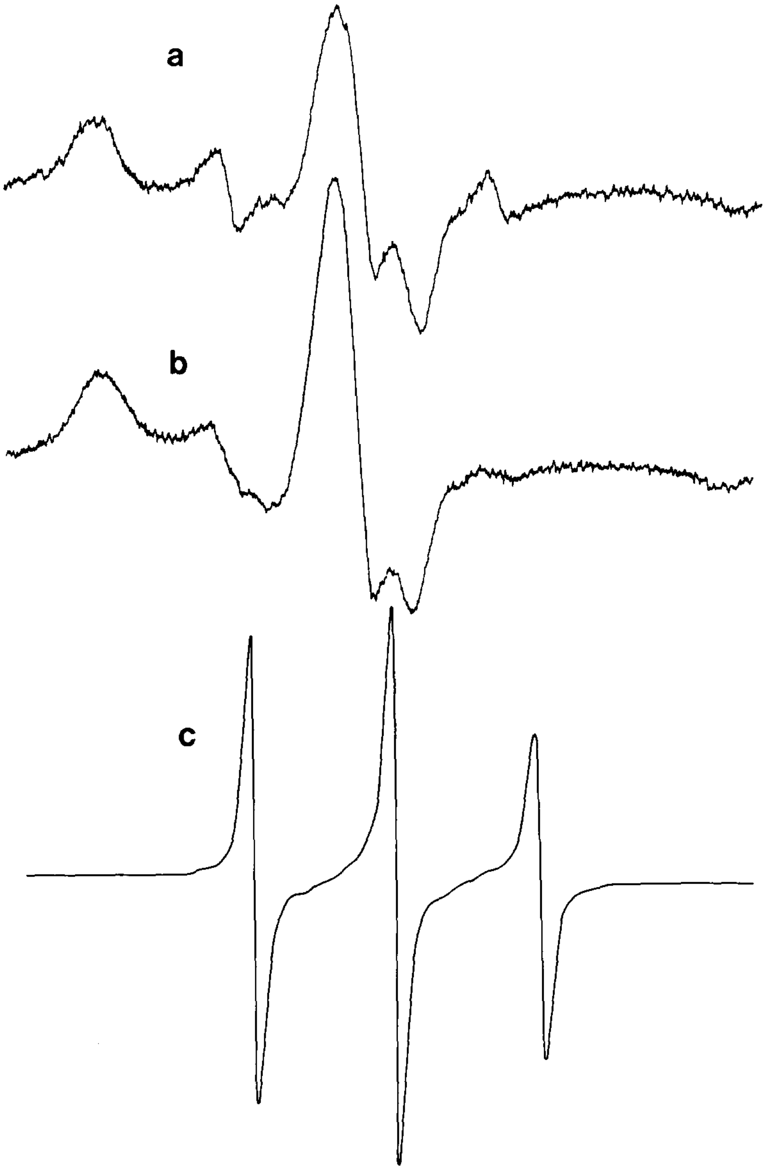

Fig. 3. ESR spectra of adsorbed PVAc 1 (a and b) and CTPO (c). (a) On Cab-O-Sil M5 from chloroform solution, equilibrium conc. 0.085 g dl^{-1}. (b) On trimethylsilylated Microsil GP from toluene solution, equilibrium conc. 0.084 g dl^{-1}. (c) On trimethylsilylated Microsil GP from toluene solution.

that the motionally-narrowed spectrum arises from a small amount of desorbed CTPO. This signifies that only in toluene solution does the nitroxide label compete significantly with PVAc for surface sites and that, from the other two solvents, adsorption through label–surface interactions is negligible. The adsorption of CTPO on to Microsil GP from toluene probably arises from its low solubility in that solvent. Although the concentration of nitroxide labels in PVAc 1 is very low, the affinity of this group for the silica surface in toluene will contribute to the adsorption of polymer from toluene.

Changes in the molecular weight and the molecular weight distribution of free PVAc (in this case the unlabelled sample PVAc 3) in contact with Microsil GP in toluene solution were obtained by GPC; the relevant data are summarised in Table 1. These show that the largest molecules of PVAc are adsorbed preferentially and that this selectivity apparently diminishes as the surface coverage increases. This type of behaviour has been observed during the adsorption of a number of polydisperse nonionic polymers [15–17] and has been shown to be consistent with reversible adsorption [18]. The smaller polymers, by virtue of their higher diffusion coefficients, may be adsorbed preferentially in the initial stages but, because of the higher energies of adsorption of the larger polymers, they will in time displace the smaller ones already adsorbed. At low surface coverage this exchange process can occur fairly readily but at higher coverages the polymer molecules already on the surface retard the exchange. The fractionating effect of the surface is therefore most marked at relatively low surface coverage.

Figure 1 includes an isotherm (d) for the adsorption of labelled PVAc 1 onto Cab-O-Sil M5 from chloroform solution. The initial part of this isotherm lies very close to the curve for Microsil GP, but the Cab-O-Sil isotherm reaches a plateau with a significantly lower amount of polymer. This is consistent with the lower surface silanol content of the Cab-O-Sil. The spectra of adsorbed PVAc 1 on Cab-O-Sil M5 (Fig. 3a) show that a small proportion of the labels are in an environment which permits motion in the fast regime (i.e. correlation time $< \sim 3 \times 10^{-9}$ sec). The proportion of rapidly tumbling nitroxide labels was estimated as 1 to 2% which, although small, contrasts with the behaviour of the polymer adsorbed onto Microsil GP from chloroform where the spectra contained no evidence of rapidly tumbling label. This variation with adsorbence is consistent with their differing silanol concentrations. Because the Cab-O-Sil surface carries fewer active sites, adsorbed polymer molecules are likely to be attached by fewer points along the change permitting more segments to be located in loops or tails. Liang *et al.* [5] have studied the adsorption of PVAc labelled with nitroxide **II** from chloroform solution onto Cab-O-Sil M5 and the typical ESR spectrum from their work is of the motionally-narrowed type (see Fig. 4E of Ref. 5) in contrast to the superposition of narrowed and broad-line spectra in Fig. 3a. Clearly the label **II** experiences much more motional freedom in the adsorbed polymer than does label **I** under identical circumstances. This is almost certainly a consequence of the fact that the label **I** is capable of rotation only in cooperation with segmental motion of the backbone whilst label **II** is able to rotate about the pendant —C—O—CO—C< sequence of bonds. The label **II** may also experience greater spatial freedom, since it is located at some distance from the backbone. The contrast in behaviour between these labels shows that there are distinct advantages to be gained by having the label located within the backbone where it is more sensitive to the environment of the polymer molecule. The superior sensitivity of in-chain over side-chain labels has been revealed earlier in a study of polyethylene. The spectra of a xylene solution of polyethylene labelled in the backbone changed abruptly from the motionally-narrowed to the broad-line form when cooled to *ca* 333 K where precipitation took place. No such change occurred on precipitation, under the same conditions, of polyethylene samples labelled at pendant groups and in this case the Arrhenius plots of correlation times for tumbling of the label above and below the precipitation temperature were colinear [19–21]. The greater motional freedom of label **II** over **I** is reflected in the correlation times τ_c for the two polymers in chloroform and toluene solutions; in chloroform at room temperature τ_c values for **I** [22] and **II** [23] are 0.6 and 0.04 nsec respectively, and in toluene solution the corresponding figures are 0.8 and 0.06 nsec respectively.

Isotherms for the adsorption of labelled PVAc 1 onto trimethylsilylated Microsil GP from toluene and chloroform solutions are shown in Fig. 4. Again, the adsorption capacity is greater when the polymer is adsorbed from toluene than from chloroform, but the adsorption capacity of the modified Microsil is markedly lower than that of the other two adsorbents (compare Figs 1 and 4). The modified Microsil has the lowest content of surface silanol groups of the three substrates and this observation is consistent with the view that these groups constitute the principal sites of adsorption. The ESR spectra of PVAc 1 adsorbed on modified Microsil from toluene solution (Fig. 3b) are of the slow-motion type but the overall shape is quite distinct from the slow-motion spectra recorded with PVAc 1 adsorbed from toluene or chloroform solutions on unmodified Microsil GP or Cab-O-Sil M5. No spectra of PVAc 1 adsorbed from chloroform onto modified Microsil could be obtained because the silica suspension proved to be

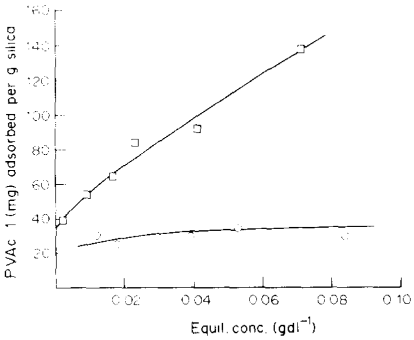

Fig. 4. Adsorption isotherms at ambient temperature for spin-labelled PVAc 1 on trimethylsilylated Microsil GP from toluene (□) and chloroform (○) solutions.

stable to centrifugation; such behaviour has been observed by other authors [10]. These observations set the modified Microsil apart from the other two adsorbents and may indicate that the mode of adsorption at the trimethylsilylated surface is fundamentally different. Whilst in the absence of more pertinent data we are unable to speculate further, it is noteworthy that the ESR spectrum of the small nitroxide CTPO adsorbed on the modified Microsil from toluene solution (Fig. 3c) is quite different from its spectrum when adsorbed on unmodified Microsil GP (Fig. 2d). With the modified Microsil the spectrum is of the motionally-narrowed type with no evidence of the slow-motion component which is apparent in Fig. 2d. The CTPO molecules appear to be less tightly bound to the trimethylsilylated surface. The spectrum in Fig. 3c resembles that of a small rapidly-tumbling nitroxide in dilute solution but closer examination reveals that it is not identical with the spectrum of CTPO in dilute toluene solution. Thus, the nitrogen hyperfine coupling constant, a_N, increases from 14.2 to 15.5 G on going from the free solution to the adsorbed state, suggesting that the nitroxide molecule is in a more polar environment when associated with the surface of modified Microsil. Although the reasons underlying this observation are not entirely clear, it is apparent that there is a subtle difference in the adsorption behaviour of the modified and unmodified surfaces.

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