JOURNAL OF MATERIALS SCIENCE 12 (1977) 2049–2055

XPS study of the adsorption of ethoxysilanes on iron

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The uptake by polished iron surfaces of two R–ethoxysilanes, used commercially as adhesion promoters, has been studied by XPS. It is concluded that the presence of an active group in the organic radical may influence uptake. However, the presence of unsuspected impurities in the solvent used in preparation of the test media also had an important effect. Subsidiary data on the adsorption of butylamine from the gas phase which yield values for the escape depth of electrons in organic materials are also reported.

1. Introduction

Coupling agents are used to improve the adhesion of organic polymer systems, i.e. paints, coatings or adhesives, to metals. The reagents frequently used for this purpose are ethoxysilanes which couple by elimination of ethylalcohol between the ethoxy group and the surface hydroxyl groups:

$$R \cdot Si(O\,Et)_3 + OH \ldots M =$$

$$R \cdot Si(O\,Et)_2 - O - M + C_2H_5OH$$

The radical, R, may be one of a whole range of radicals tailored to match different organic systems: an excellent review of those available has been given by Cassidy and Yager [1]. The radical may carry other substituent groups, i.e. amino, which permit improved coupling into a polymer system but which themselves are active towards certain metal surfaces.

In this paper we report the use of X-ray photoelectron analysis to compare the adsorption from methanolic solution of vinyl triethoxysilane $CH_2 = CH{-}Si(OCH_2CH_3)_3$ with γ-aminopropyltriethoxysilane, $NH_2CH_2CH_2CH_2Si(OCH_2CH_3)_3$, with the aim of detecting any change in adsorption behaviour attributable to the amino group. Both reagents are coupling agents of proven value marketed by Union Carbide under the designations A151 and A1100 respectively.

2. Experimental

Samples of pure iron (Johnson Matthey Ltd.) measuring 6 mm × 9 mm were cut from 1 mm sheet and metallographically polished to a final finish on 6 μm diamond paste. Samples were swabbed with lens tissue soaked in Analar methanol, immersed in distilled water for 200 sec, wiped with a lens tissue and then immediately immersed in a freshly prepared methanolic solution of the silane at appropriate strength. The purpose of the water dip was to ensure an adequate concentration of hydroxyl groups on the surface of the iron [2]. After immersion in the silane solution for 30 sec the samples were shaken free of drops, blotted on lens tissue rinsed in methanol and transferred to the X-ray photoelectron spectrometer (V.G. (Scientific) Ltd., England, ECSA 2) which has been described in several previous publications [3]. The spectrometer was coupled to a VG datasystem and this was used to measure the peak height and areas of the silicon, carbon and nitrogen peaks as a function of solution concentration. The position of the Fe_{2p} peak was monitored throughout the work.

To aid in interpretation of the orientation of the γ-aminopropyl triethoxysilane measurements were made on adsorbed butylamine molecules. In This work the iron surfaces were prepared by polishing to 6 μm diamond, and then argon-ion

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TABLE I The intensities measured from the photoelectron spectra of adsorbed silanes

Solvent	Coupling agent	Concentration (vol %)	Intensities (Counts sec^{-1})				Solution composition (Mole fraction)			Surface composition (at. %)		
			Si	N	Pb	Sn	Si	Pb	Sn*	Si	Pb	Sn
Industrial grade methanol	None	0	0	–	513	1788	0	0.18	0.82	0	18	82
	None	0.01	87	–	399	1584	0.02	0.18	0.80	49	14	36
	A151	0.1	81	–	135	606	0.13	0.16	0.72	71	7.5	21.5
	A151	1.0	132	–	126	495	0.59	0.07	0.39	82.5	5	12.5
Analar methanol	A151	0.01	44									
	A151	0.05	52									
	A151	0.1	161									
	A151	1.0	195									
	A151	10.0	282									
	A151	100	291									
	A1100	0.1	102	73								
	A1100	0.5	134	163								
	A1100	1.0	158	138								

*In the absence of analytical information for tin, the solution composition was assumed to be in equal ratio.
†The adsorption peaks obtained in the absence of silane.

etched within the spectrometer preparation chamber until the surfaces were oxide and contamination free. A capsule of butylamine was then broken in the preparation chamber and a pressure 10^{-1} torr maintained for 100 sec to give saturation coverage of the surface. The residue was then pumped away and the spectra obtained in the usual way.

3. Results

Table I gives the count rate obtained from the silicon $2p$ peak at various solutions strength of the vinyl triethoxysilane and the data for both the nitrogen and silicon peaks for the γ-amino propyl triethoxysilane. The former data are shown in Fig. 1 against a curve of the form I_{Si} versus log [Si] showing that they conform of the Temkin isotherm [4]. The fit of the Langmuir and Freundlich isotherms was very poor. The silicon intensity from the aminopropylsilane was lower than that of the vinylsilane at all concentrations. The nitrogen intensities were similar to those for silicon. The nitrogen intensity for the absorbed butylamine was very much less than those obtained with the aminopropylsilane. The relevant data for this experiment are given in Table II. The binding

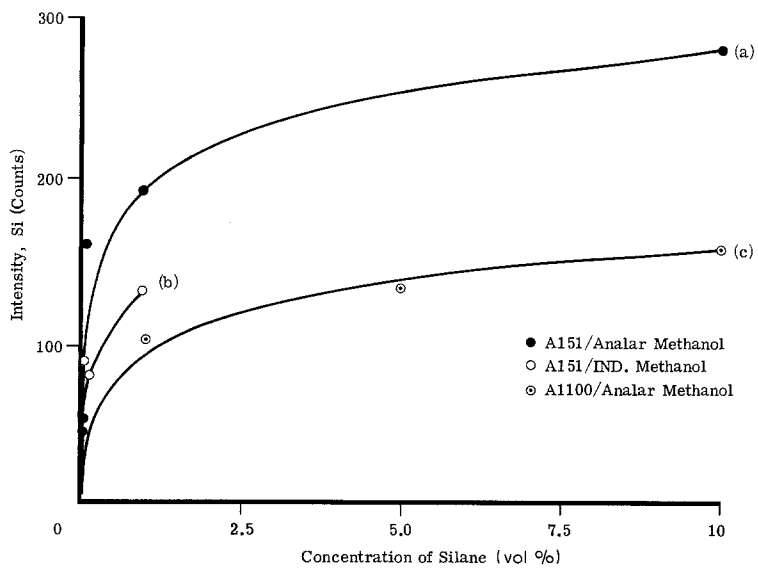

Figure 1 Adsorption of silanes, measured as the intensity of the Si_{2p} photoelectron, as a function of solution concentration. (a) and (b) A151, (c) A1100.

TABLE II Intensities measured from the spectrum of adsorbed butylamine

Treatment	Intensities (Counts sec^{-1})		
	C_{1s}	M_{1s}	Fe_{2p}
Before adsorption	324	0	5033
After adsorption	812	84	4233
Apiezon grease	4703	–	–

energies of all elements were measured for the absorbed layers of A1100 and butylamine respectively, and are given in Table III: the oxygen spectra (Fig. 2) showed peaks at 529 and 531 eV.

4. Discussion

The uptake of the vinyl silane has the high initial coverage typical of chemisorption and fits the Temkin isotherm [4], $x = k \ln c$, where x is the uptake, measured as the intensity of the Si_{2p} peak. Since the measurement made by XPS is true adsorption and not apparent adsorption, as is usually measured in adsorption from solution, gas phase isotherms such as the Temkin should be directly applicable to the results. The observation of a chemisorption isotherm is in line with the manufacturer's recommendation of a 1% addition of the silane to primer and adhesive formulations. The uptake at this concentration corresponds to 67% of that achieved in a 100% solution and represented 10 at.% of Si in the surface film. It is in contrast to the findings of Gettings *et al.* [5] who did not detect chemisorption of a similar silane from aqueous solution unless an amine was also included to catalyse its surface polymerization. The surface concentration which they then measured was 5 at.% but since their organic radical, γ-glycidoxypropyl, was longer than that used in the present work the silicon peak would be expected to have a lower intensity for the same surface coverage of molecules; this point is returned to below.

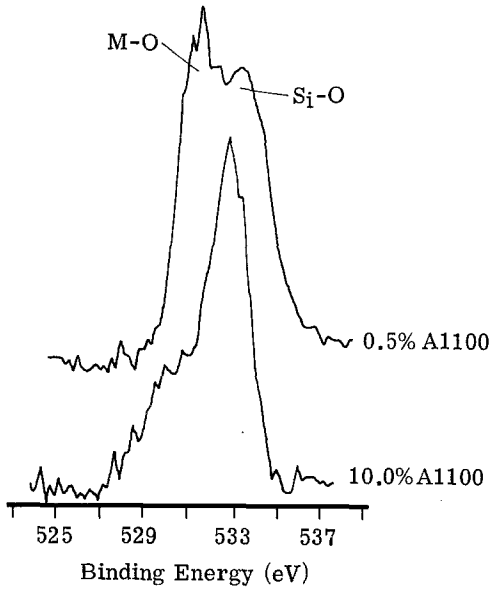

Figure 2 The oxygen photoelectron peak at two levels of adsorption.

The Temkin isotherm is based on the assumption that the heat of adsorption falls linearly with increasing coverage. By change, the results of some preliminary experiments in which industrial menthanol was used as a solvent for the vinylsilane gave the opportunity to investigate the possibility that the heat of adsorption was dependent on coverage. The industrial methanol was found to contain substantial concentrations of lead and tin (Pb = 0.04 wt%, Sn ≃ 0.1 wt%) presumably arising from solder contamination in the steel containers. The spectrum (a) in Fig. 3 shows the unexpectedly high adsorption of these elements on a sample of pure iron dipped in the industrial

TABLE III Peak positions from spectra of adsorbed molecules and reference compounds

	Si_{2p}	N_{1s}	O_{1s}	Fe_{2p}	C–N	Si–O	Fe–O
Si*	98	–	–	–	–	–	–
SiO_2*	101.4	–	531.2	–	–	429.8	–
A1100 (10%)	101.4	398.3	(529.2) 531.6	709.4	114.3	430.2	180.2
A1100 (0.5%)	101.2	399	(529.2) 530.9	709.2	115.0	429.7	180.0
$CH_3(CH_2)_3NH_2$	–	398.2	–	–	114.2	–	–
$CH_3(CH_2)_3NH_2$†	–	398.1	–	–	114.1	–	–
Fe_2O_3*	–	–	529.8	710.7	–	–	180.9
$Fe_3O_4(Fe^{2+})$*	–	–	529.8	708.5	–	–	178.7

*Reference data from this laboratory.
†Reference data, Seigbahn *et al.* [10].

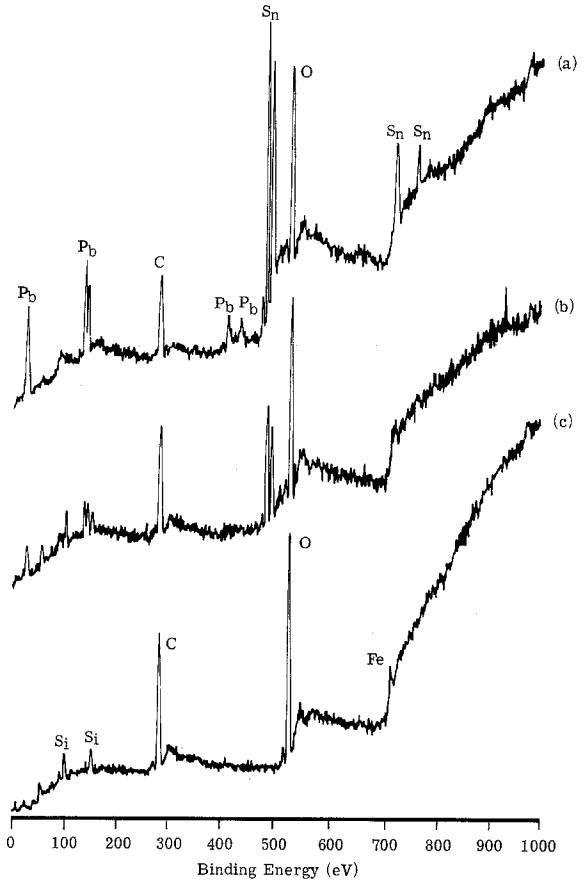

Figure 3 XPS spectra of pure iron (a) after immersion in industrial methanol; (b) after immersion in 1% vinyl silane in industrial methanol; (c) after immersion in 1% vinyl silane in analar methanol.

methanol for 200 sec. Samples which had either not been exposed to the impure methanol, or which had been dipped in Analar methanol showed no trace of these elements. Spectra for 0.01%, 0.1% and 1% solutions of silane showed that the silane and the unknown lead and tin compounds were in direct competition for surface sites. Fig. 3b is a typical spectrum of the mixed coverage while Fig. 3c is that for the analar solution. The effect is shown by Fig. 4 which shows the at.% of silicon and its competitors as a function of the approximate mole fraction: 0.01% of silane gives a 50 at.% coverage but further reduction of impurity adsorption is much more difficult to achieve. This is better illustrated by considering the net exchange reaction

$$2Si_{soln} + Sn_{ads} + Pb_{ads} = 2Si_{ads} + Sn_{soln} + Pb_{soln}.$$

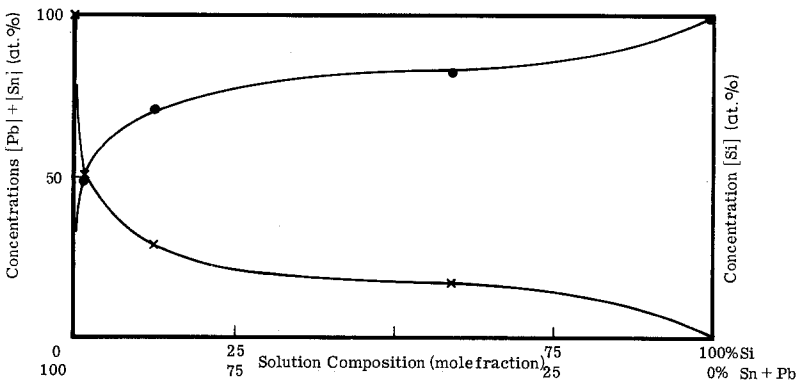

Figure 4 Surface composition as a function of mole fraction of impure solutions.

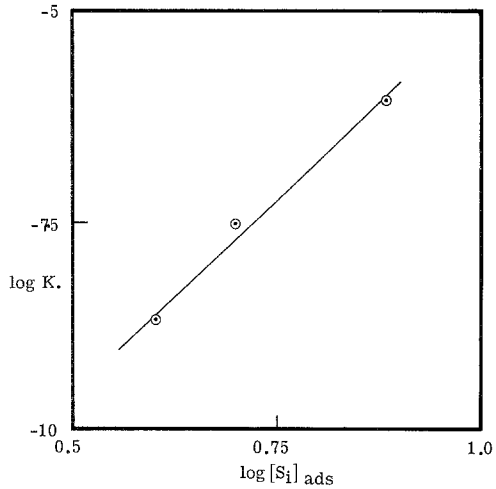

Figure 5 Coefficient of exchange between adsorbed impurities and silane as a function of silane adsorption.

Since throughout the work Sn and Pb were at a nearly constant concentration in the methanol used to prepare the solutions, and since the surface area exposed was very small compared with the volume of solution we may write

$$k = (\mathrm{Pb})_{\mathrm{ads}}(\mathrm{Sn})_{\mathrm{ads}}(\mathrm{Si})^2_{\mathrm{soln}}/(\mathrm{Si})^2_{\mathrm{ads}}.$$

Fig. 5 shows that the exchange equilibrium constant increases rapidly with the extent of silicon adsorption, and this may be taken as an indication that the surface sites are far from identical in their heats of adsorption. From the point of view of the potential user, the important point is the reduction in capacity of the surfaces for silane, as shown by the curve b in Fig. 1.

The intensity of the silicon peak measured after adsorption of γ-amino-propyl triethoxysilane by the procedure used for the vinyl-triethoxysilane was only about half that found for the vinyl-silane. The values are plotted in Fig. 1c together with an isotherm of the same family as that derived for the vinyl compound. The fact that the values show a similar behaviour suggests that a chemisorption process is operating and that the reduced intensity may, as in the results of Gettings *et al.*, be a function of the longer length of the organic radical which scatters a larger proportion of the photoelectrons. In the limit, assuming the axis of the molecule to be perpendicular to the surface, the reduction in intensity would be $\exp(-l/\lambda \sin\theta)$ where l is increased length of the organic radical, i.e. N–C–C, say 0.2 nm, λ is the "escape depth" of the Si_{1s} electron in an organic matrix and θ is the collection angle for the XPS spectrometer (45°). The conventional value for λ would be $\simeq 18$ Å giving an intensity ratio, $R = 0.85$ for Si_{2p} in A1100 to that in A151, which is much less attenuation than that observed ($R = 0.56$ at 10% concentration). There is, however, evidence that the correct escape depths for organic matrices are greater than those derived for inorganic or metallic coatings [6]. A figure of ~ 50 Å has been quoted for amide slip coatings on polymeric materials [7] which would imply virtually no difference in the silicon signal from the two molecules used in this work (or from that used by Gettings) when at equal coverage ($R = 0.94$). To establish the correct escape depths to use with absorbed organic molecules, the subsidiary experiment involving adsorption of butylamide on ion-etched (oxide-free) subtrates was undertaken. At high coverages this molecule would be expected to bond, nitorgen to iron, with the molecule perpendicular the surface. Thus since the adsorption was carried out *in situ* under UHV clean conditions, the attenuation of the iron substrate and the intensity of the carbon (relative to a standard from a thick hydrocarbon layer) should provide interpretable and complementary results. In addition the attenuation of an atomic layer of nitrogen by four layers of carbon can be determined. The data obtained are given in Table II and were interpreted according to the following relationships:

$$\lambda_{1200} = l_{4\mathrm{C}}/\sin\theta \ln(1 - I_{4\mathrm{C}}/I_{\infty\mathrm{C}}), \qquad (1)$$

where $l_{4\mathrm{C}}$ is the length of the butyl radical (0.36 nm) and $I_{4\mathrm{C}}$ the intensity of the carbon signal from the butyl radical. $I_{\infty\mathrm{C}}$ is the signal from carbon in Apiezon grease used as a standard.

$$\lambda_{750} = l_5/\sin\theta \ln(I_{\mathrm{Fe}}/I_{\mathrm{Fe}_0}) \qquad (2)$$

where l_5 is the length of the complete molecule (0.45 nm) I_{Fe_0} is the intensity from the clean iron and I_{Fe} is the intensity with the adsorbed amine. The values thus obtained are $\lambda_{1200} = 4.6$ nm and $\lambda_{750} = 3.7$ nm. These values are consistent with each other, showing a square root dependence on energy, and with the few literature values for organic compounds. Thus the lower silicon signal from adsorbed A1100 silane in this work and from A187 in the work of Gettings *et al.* is attributable to a lower coverage. Steric hindrance is unlikely to be a problem and it seems most likely that the presence of the electro-negative amino and glycidoxyl groups has modified the chemisorption

behaviour of the molecule. The good agreement between the carbon signal from the adsorbed amine and the reduction in intensity of the iron substrate suggests that the molecule had adsorbed perpendicularly and that the surface was therefore covered in a molecular stack, 5 atoms thick, of which the lower sheet consisted of nitrogen atoms. Thus a relationship for the relative intensities of the carbon and nitrogen peaks can be constructed [8] using established emission and adsorption equations in the following way: The signal from a fifth layer of carbon atoms is given by

$$I_{5C} - I_{4C} = (\exp[-l_4/\lambda \sin\theta] - \exp[-l_5/\lambda \sin\theta])I_\infty,$$

or, since the fifth layer is nitrogen

$$I_N = (\exp[-l_4/\lambda \sin\theta] - \exp[-l_5/\lambda \sin\theta])I_\infty (FN/FC),$$

where FN, FC are the sensitivity factors for carbon and nitrogen respectively. Taking FN/FC = 1.48 [9], and $I_C = I_{4C} = (\exp[-l_4/\lambda \sin\theta])I_\infty$ where I_∞ is the signal from an infinitely thick layer of carbon molecules, we obtain

$$\frac{I_N}{I_C} \simeq 33\% \text{ for } \lambda = 4.6\,\text{nm and } 30\% \text{ for } \lambda = 1.8\,\text{nm}$$

Thus the nitrogen/carbon ratio for adsorbed butylamine is virtually independent of the escape depth. The value found however was only 17% (Table II). There is no obvious reason for this low value. Any deviation from perpendicular, nitrogen group down, adsorption should give a greater rather than a lesser figure for the N/C ratio and no difficulty was found in observing the nitrogen signal from the absorbed aminopropylsilane which was very strong. It may be that, by virtue of the type of adsorption site, the nitrogen atom is shielded by the surface iron atoms.

The oxygen spectrum, Fig. 2, shows a gradual change on adsorption, from a peak at 529 eV to one at 531 eV. The peak at 529 eV may be identified by its position relative to the iron peak (Table III) as that from oxygen in a surface oxide (in the ferric state). That which replaces it at 531 may be identified by comparison with the data for SiO_2 as an Si–O bond. It is not yet clear whether it will be possible to distinguish the Si–O–M linkage from either Si–O–H or Si–O–Si. However, adsorbed problems in which adhesives are displaced by water should be amenable to study in this way.

The position of the N_{1s} peak in the absorbed aminopropyl silane is the same as that given by Siegbahn [10] for unadsorbed butylamine which suggests that no strong inductive effect occurs in the molecule on adsorption. The fact that the nitrogen binding energy in adsorbed butylamine is also the same as that found by Siegbahn is surprising. This molecule is generally believed to adsorb strongly on iron by electron donation from the amine group into the '*d*' band of iron [11]. Our results give no evidence for this.

5. Conclusions

(a) Vinyl triethoxysilane is chemisorbed from methanolic solution onto a hydrated metal surface with an isotherm which is of the Temkin type. This is indicative of a non uniform heat of adsorption.

(b) The silane is displaced by impurities which might be widely encountered in industrial grade solvents supplied in metal drums. The exchange coefficient is non linearly dependent on intake of silane.

(c) γ-amino-propyl triethoxysilane is less strongly adsorbed than vinyl triethoxysilane.

(d) The escape depth of electrons in organic matrices is greater than in inorganic materials. Values of 4.6 nm for 1200 eV electron and 3.7 nm for 750 eV electrons were found.

Acknowledgements

The authors are grateful to the Union Carbide Corporation for the gift of sample quantities of adhesion promoters, the Science Research Council for part purchase of the spectrometer and to Professor M. B. Waldron for provision of departmental facilities.

References

1. P. E. CASSIDY and B. J. YAGER, *J. Macromol. Sci.* DI (1971) 1.
2. J. C. BOLGER and A. S. MICHAELS, "Interface Conversion for Polymer Coatings", edited P. Weiss and G. D. Cheever. (Elsevier, New York, 1968) p. 3.
3. J. E. CASTLE and M. J. DURBIN, *Carbon* 13 (1975) 23.
4. S. J. GREGG, "The Surface Chemistry of Solids", 2nd edition (Chapman and Hall, London, 1961).
5. M. GETTINGS, J. P. COAD, F. S. BAKER, A. J. KINLOCH, *J. Appl. Polymer Sci.* (1977) To be published September 1977, or available as *AERE* Report R.8289.

6. C. J. POWELL, *Surface Science* **44** (1974) 29.
7. W. M. RIGGS, Application Data Bulletin ES-0008, Dupont Instruments, Wilmington, USA (1975).
8. C. R. BRUNDLE, *J. Vac. Sci. Tech.* **11** (1974) 212.
9. C. K. JORGENSEN and H. BERTHAU, *Disc. Farad. Soc.* **54** (1972) 269.
10. K. SIEGBAHN, C. NORDLING, A. FAHLMAN, R. NORDBERG, K. HAMRIN, J. HEDMAN, G. JOHANSSON, T. BERGMARK, S. KARLSSON, I. LINDGREN and B. LINDBERG, "ESCA, Atomic, Molecular and Solid State Structure Studies by means of Electron Spectrometry", (Almquist and Wiksells, Uppsala, 1967).
11. R. R. ANNAND, R. M. HURD and M. HACKERMAN, *J. Electrochem. Soc.* **112** (1965) 138.

Received 14 December 1976 and accepted 28 January 1977.