

Infrared Study of the Adsorption of Propionitrile on Silica Immersed in Liquid Hydrocarbons

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Infrared spectra have been recorded of silica which had been evacuated at 423 K and subsequently immersed in solutions of propionitrile in toluene, 2,2,4-trimethylpentane and toluene+2,2,4-trimethylpentane mixtures. The adsorption process involved the formation of hydrogen bonds between surface hydroxyl groups and the cyano groups of propionitrile molecules. The adsorption of propionitrile on silica was impeded by strong lateral interactions between adjacent surface silanol groups. Only isolated hydroxyl groups and weakly interacting hydroxyl groups acted as adsorption sites. Increasing strength of interaction between the predominant (hydrocarbon) components of the liquid phase and surface silanol groups decreased the surface concentration of propionitrile molecules for a particular equilibrium concentration in solution.

An infrared study of silica immersed in solutions of cyclohexanone in 2,2,4-trimethylpentane established that both isolated and adjacent interacting surface hydroxyl groups acted as sites for the adsorption of cyclohexanone molecules.¹ Absorbance data taken from the infrared spectra allowed estimates to be made of the relative numbers of cyclohexanone molecules adsorbed by interactions with single hydroxyl groups and with pairs of adjacent hydroxyl groups. The analysis was possible because distinguishable infrared bands due to CO-stretching vibrations were observed for carbonyl groups perturbed either by a single hydrogen-bonding interaction or by the simultaneous acceptance of two hydrogen bonds from a pair of adjacent hydroxyl groups.²⁻⁴ Propionitrile interacts with isolated hydroxyl groups on the silica surface to give an hydrogen-bonded complex of 1:1 stoichiometry in which the cyano group in each adsorbed molecule acts as the acceptor of a single hydrogen bond.^{5,6} Acceptance of two hydrogen bonds by a single cyano group is unlikely and therefore the modes of adsorption of propionitrile and cyclohexanone on adjacent surface hydroxyl groups must differ. The present work was aimed at testing whether infrared spectroscopy could be used to identify the adsorption of propionitrile on to adjacent hydroxyl group sites and, if so, whether the fractions of the total surface concentrations of propionitrile which were adsorbed on to different types of hydroxyl group could be separately estimated. The hydrocarbon components of the liquid phase 2,2,4-trimethylpentane, toluene and a 2,2,4-trimethylpentane+toluene mixture were chosen because the same liquids were used in a corresponding infrared study of propionitrile adsorbed on to a silica surface which did not contain any adjacent interacting hydroxyl groups.⁶

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EXPERIMENTAL

Experimental procedures were identical to those used before⁶ except that the aerosil silica ($176 \text{ m}^2 \text{ g}^{-1}$) discs, after heat treatment in air, were exposed to saturated water vapour at room temperature and finally heated for 24 h at 423 K in vacuum. Liquids in contact with silica discs during spectroscopic examination were at $25 \pm 0.2^\circ \text{C}$.

RESULTS

Spectra of silica in vacuum contained infrared bands at 3750, 3725(sh), 3665 and 3550(sh) cm^{-1} [fig. 1(a)]. The shoulder at 3725 cm^{-1} was weaker than in previous spectra and the shoulder at 3550 cm^{-1} corresponded to a more intense maximum

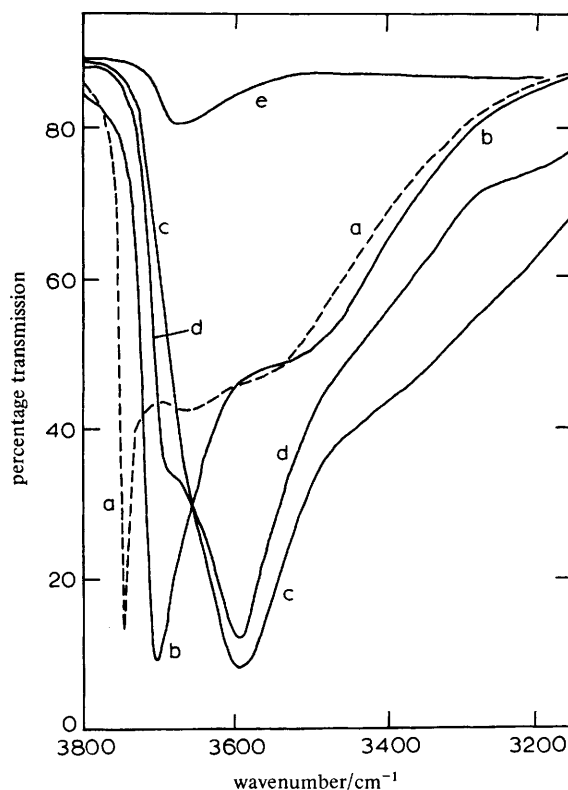


FIG. 1.—Spectra of silica after (a) evacuation at 423 K and subsequent immersion in (b) 2,2,4-trimethylpentane, (c) toluene and (d) a 2,2,4-trimethylpentane + toluene mixture with a mole fraction ratio (x_T/x_M) of (3.22/1). (e) Spectrum of the empty infrared cell.

observed before at 3535 cm^{-1} and ascribed to laterally interacting hydroxyl groups.¹ The greater extent of dehydroxylation in the present work reflected the longer time used here for the treatment of silica discs at 423 K, and also the marginally lower dynamic vacuum attainable in the glassblown infrared cell⁶ rather than in the cell containing several O-ring seals and adhesive joints.⁴ The maximum at 3665 cm^{-1} was composed of two components, a band at 3680 cm^{-1} [fig. 1(e)] due to bulk hydroxyl groups in the optical windows of the infrared cell,⁶ and a band at 3650 cm^{-1} which

may be ascribed to adjacent laterally interacting hydroxyl groups on the surface planes of silica.¹ The band at 3680 cm^{-1} made a constant contribution to all the spectra reported here.

Spectra of silica immersed in 2,2,4-trimethylpentane [fig. 1(b)] and toluene [fig. 1(c)] exhibited maxima at 3705 and 3595 cm^{-1} due to isolated surface hydroxyl groups which were perturbed by interactions with adsorbed 2,2,4-trimethylpentane and toluene molecules, respectively.^{4,6} A shoulder at 3500 cm^{-1} for silica in 2,2,4-trimethylpentane and a broad increase in absorption intensity in the range $3100\text{--}3500\text{ cm}^{-1}$ for silica in toluene may be ascribed to laterally interacting surface hydroxyl groups which gave the band at 3550 cm^{-1} for silica in vacuum and were further perturbed by interactions with adsorbed hydrocarbon species. A shoulder at *ca.* $3640\text{--}3675\text{ cm}^{-1}$ for silica in 2,2,4-trimethylpentane was primarily due to surface hydroxyl groups¹ and not to the band at 3680 cm^{-1} in the spectrum of the infrared cell alone.

Spectra of silica immersed in a 2,2,4-trimethylpentane + toluene mixture containing a mole fraction $x_M = 0.237$ of toluene contained combined features of the spectra of silica immersed in the separate liquids [fig. 1(d)]. The relative intensities of the maximum at 3595 cm^{-1} and the shoulder at 3705 cm^{-1} were in accordance with corresponding results for silica which had been preheated at 873 K and for which 62% of the isolated surface hydroxyl groups were perturbed by interaction with adsorbed

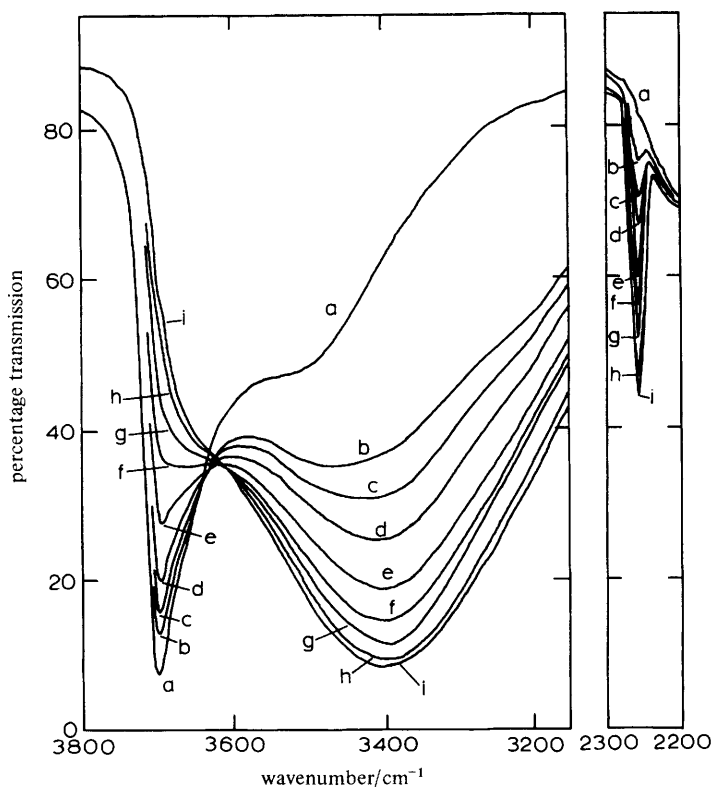


FIG. 2.—Spectra of silica in (a) 2,2,4-trimethylpentane, (b)–(i) propionitrile + 2,2,4-trimethylpentane mixtures with mole fractions, x_P , of propionitrile given by $10^3 x_P$ equal to (b) 0.056, (c), 0.11, (d) 0.28, (e) 0.60, (f) 1.29, (g) 2.74, (h) 5.31 and (i) 8.66.

toluene molecules.⁶ The conclusion that isolated surface silanol groups interacted more strongly with toluene than with 2,2,4-trimethylpentane molecules is also consistent with the relative magnitudes of the shifts $\Delta\nu_{\text{OH}}$ from 3750 to 3595 and 3705 cm^{-1} , respectively, in the position of the infrared band assigned to the OH-stretching vibration of the isolated silanol groups.

The immersion of silica in 2,2,4-trimethylpentane containing increasing concentrations of propionitrile resulted in decreases in the intensity of the infrared band at 3705 cm^{-1} and the concomitant appearance of a broader maximum at 3395 cm^{-1} (fig. 2). The linearity of the relationship between absorbance values at 3705 and 3395 cm^{-1} [fig. 3(a)] was in marked contrast with the corresponding result for the

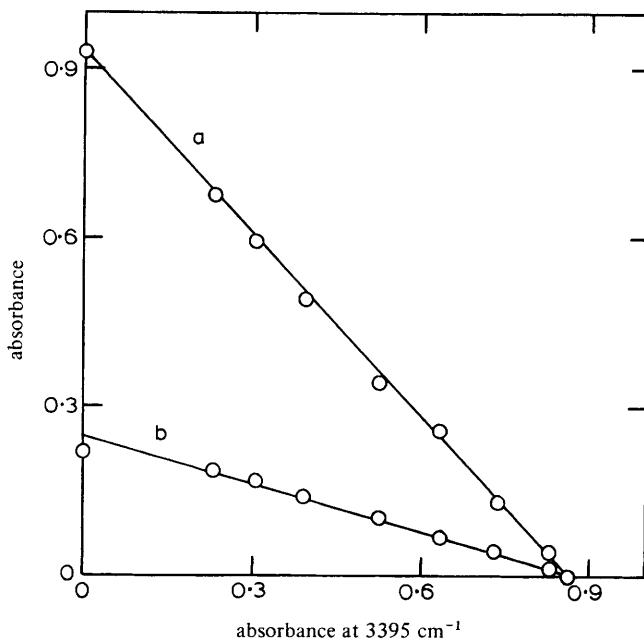


FIG. 3.—Correlations between the growth of the maximum at 3395 cm^{-1} and the decreases in absorption intensities at (a) 3705 and (b) 3660 cm^{-1} for the adsorption of propionitrile on silica immersed in 2,2,4-trimethylpentane.

adsorption of cyclohexanone.¹ Hydrogen-bonding interactions between isolated silanol groups and the cyano groups of adsorbed molecules gave a surface-adsorbate complex for which the infrared band due to the OH-stretching vibration of the perturbed silanol groups was at 3395 cm^{-1} . An infrared band due to the CN-stretching vibrations of perturbed cyano groups in the complex was present in spectra at 2260 cm^{-1} (fig. 2). Unperturbed cyano groups gave a maximum at 2248 cm^{-1} in spectra of propionitrile in 2,2,4-trimethylpentane. Solution concentrations were too low for the latter band to make an appreciable contribution to the spectra in fig. 2. The intensities of the maxima at 3395 and 2260 cm^{-1} due to perturbed hydroxyl and cyano group, respectively, were not only directly proportional to each other but also conformed to the same relationship as that previously reported⁶ for silica which had been preheated at 873 K before immersion in propionitrile + 2,2,4-trimethylpentane mixtures (fig. 4).

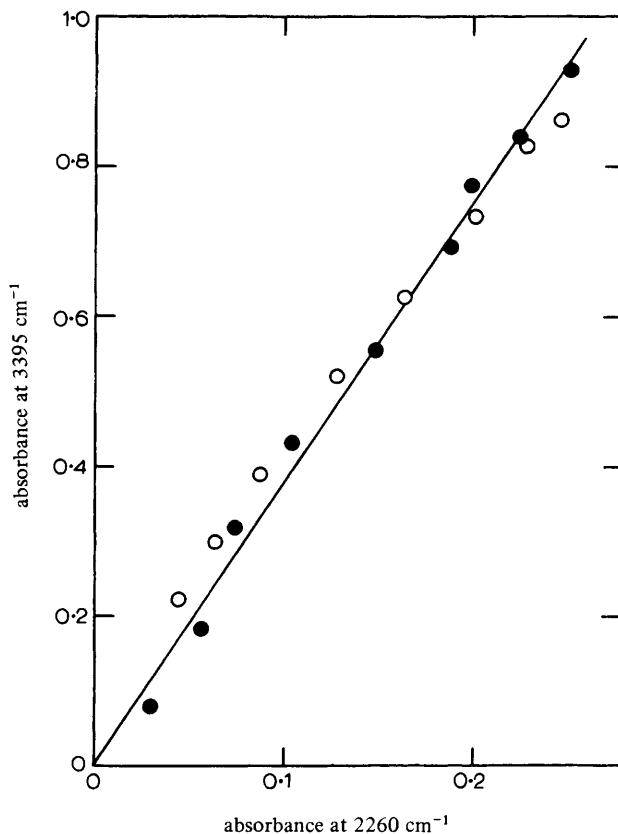


Fig. 4.—Relationship between absorbance values at 3395 and 2260 cm^{-1} for the adsorption of propionitrile immersed in 2,2,4-trimethylpentane after heat treatment at \circ , 423 and \bullet , 873 K.

Comparison of the spectra in fig. 2 with the corresponding spectra⁶ for silica which had been preheated at 873 K suggests that surface hydroxyl groups other than isolated silanol groups responsible for the band at 3705 cm^{-1} also provided sites for the adsorption of propionitrile. Previous spectra exhibited a well defined isosbestic point at 3660 cm^{-1} .⁶ Here (fig. 2) the isosbestic point was not as well defined and was shifted to *ca.* 3625 cm^{-1} . Decreases in absorption intensity at 3660 cm^{-1} were linearly related to the growth in intensity of the broad maximum at 3395 cm^{-1} [fig. 3(b)]. Adjacent interacting silanol groups, responsible for the shoulder at *ca.* 3640–3675 cm^{-1} ,¹ were perturbed by the formation of hydrogen bonds with cyano groups in propionitrile molecules. Absorption of radiation by the resulting hydrogen-bonded complex must have contributed to the total intensities of the maxima at 3395 and 2260 cm^{-1} . Similar results have been reported for the adsorption of cyclohexanone on silica,¹ although in that case the absorbance losses at 3660 cm^{-1} did not conform over the full surface coverage range to a single linear relationship with the growth of the infrared band (at 3370 cm^{-1}) due to perturbed hydroxyl groups. At high surface coverages of silica by cyclohexanone all the available surface silanol groups were probably perturbed by interaction with cyclohexanone molecules.¹ Infrared spectra for high coverages of silica which had been heated at 423 K¹ were closely similar to corresponding spectra

for silica preheated at 1073 K.⁴ In contrast, propionitrile was less effective at disrupting lateral hydrogen-bonding interactions between adjacent surface silanol groups. At the higher concentrations of propionitrile studied, absorption intensities in the range 3450–3680 cm^{-1} were appreciably higher for silica which had been preheated at 423 K [fig. 2(h) and (i)] than for silica preheated at 873 K.⁶ A residual concentration of adjacent hydroxyl groups remained unperturbed by propionitrile molecules even when the coverage of isolated silanol group adsorption sites was virtually complete.

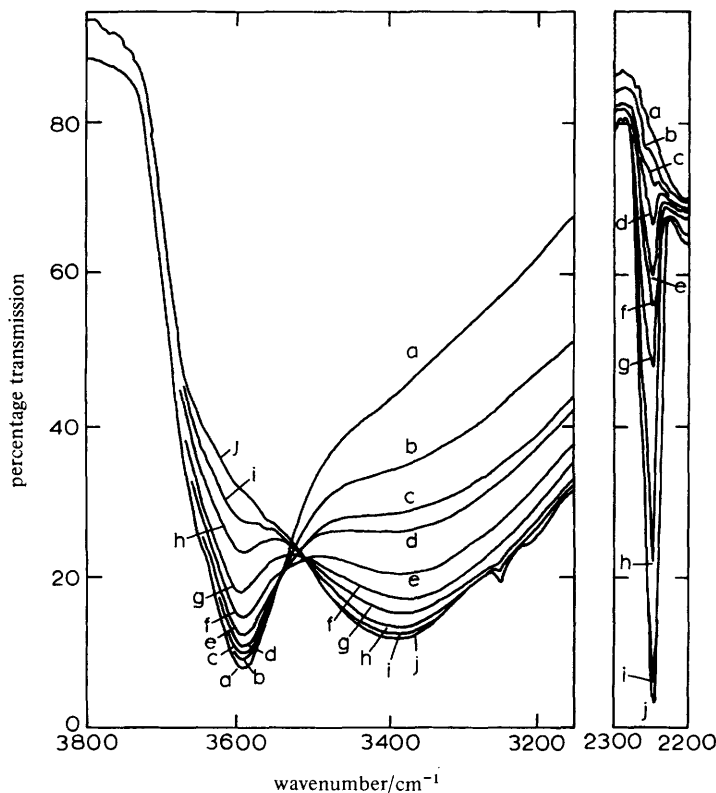


FIG. 5.—Spectra of silica in (a) toluene, (b)–(j) propionitrile + toluene mixtures with 10^3x_p equal to (b) 0.098, (c) 0.34, (d) 1.35, (e) 3.21, (f) 7.52, (g) 14.8, (h) 47.8, (i) 104 and (j) 200.

Spectra (fig. 5) of silica immersed in solutions of propionitrile in toluene exhibited similar features to the results for systems in which 2,2,4-trimethylpentane was the predominant component of the liquid phase. With increasing propionitrile concentrations the maximum at 3595 cm^{-1} was progressively replaced by a broader band at 3395 cm^{-1} although higher concentrations were necessary to produce the same surface coverages in toluene as in 2,2,4-trimethylpentane. The maximum at 2260 cm^{-1} was therefore obscured by a strong band at 2248 cm^{-1} (fig. 5) due to propionitrile in solution. The sharp isosbestic point at 3550 cm^{-1} in spectra of silica preheated at 873 K before immersion in propionitrile + toluene mixtures⁶ became less well-defined and was centred at *ca.* 3520 cm^{-1} for silica preheated at 423 K. A proportion of the adjacent interacting silanol groups on the silica surface was perturbed by hydrogen-

bonding interactions with propionitrile molecules. This conclusion was further substantiated by the decreases in intensity of a shoulder at 3645 cm^{-1} in the spectrum of silica immersed in toluene [fig. 5(a)]. The shoulder was absent from spectra of silica heated at 873 K before immersion in toluene⁶ and may be ascribed to weakly interacting adjacent silanol groups.¹ A high proportion of these groups formed hydrogen bonds with adsorbed propionitrile molecules but were not appreciably perturbed by the adsorption of toluene. However, absorption intensities in the spectral range $3100\text{--}3500\text{ cm}^{-1}$ for silica discs in contact with solutions containing high concentrations of propionitrile in toluene were greater for silica preheated at 423 K [fig. 5(j)] than at 873 K .⁶ The intensity differences were compatible with the retention of strongly interacting adjacent hydroxyl groups at the silica-toluene interface in the presence of 0.2 mole fraction of propionitrile. Adjacent hydroxyl groups, responsible for the infrared band at *ca.* 3550 cm^{-1} [fig. 1(a)] for silica in vacuum, were weakly perturbed by toluene molecules at the silica-liquid interface, but the majority of the lateral hydrogen bonds were not disrupted by the adsorption of either toluene or propionitrile.

Previous infrared studies of silica immersed in three-component liquid mixtures involved discs which had been preheated to high enough temperatures for adjacent interacting silanol groups to have been completely removed from the oxide surface.^{4, 6, 7}

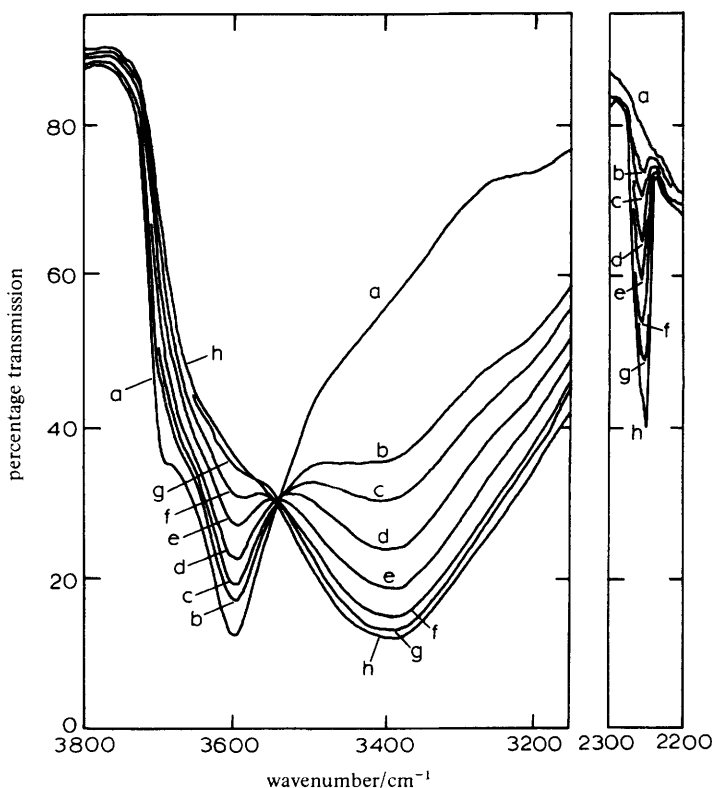


FIG. 6.—Spectra of silica in propionitrile + 2,2,4-trimethylpentane + toluene mixtures with a constant mole fraction ratio (x_T/x_M) of (3.22/1) and mole fractions of propionitrile given by 10^3x_P equal to (a) 0, (b) 0.46, (c) 0.92, (d) 2.04, (e) 4.52, (f) 9.05, (g) 17.7 and (h) 31.8.

Only isolated surface silanol groups remained and the fraction of groups interacting with each component of the liquid mixtures could be quantitatively estimated using absorbance data taken from the spectra.⁴ Spectra of silica heated at 423 K before immersion in propionitrile + toluene + 2,2,4-trimethylpentane mixtures (fig. 6) confirm that the combination of four types of surface hydroxyl group¹ and three adsorbates precludes reliable quantitative analysis of surface coverages of specific sites by individual components of the liquid mixtures. Comparison with corresponding spectra for silica preheated at 873 K⁶ showed that the maxima at 3705 and 3595 cm^{-1} were less clearly defined [fig. 6(a)] because of overlap with underlying bands due to vibrations of adjacent interacting hydroxyl groups.

The general spectroscopic changes associated with the adsorption of propionitrile on silica in toluene + 2,2,4-trimethylpentane mixtures were similar to the corresponding changes for adsorption from the separate hydrocarbon liquids. The amounts of propionitrile which were adsorbed for a particular solution concentration were, in terms of the hydrocarbon components of the liquid phase, in the sequence 2,2,4-trimethylpentane > toluene + 2,2,4-trimethylpentane > toluene (fig. 7). The absorbance at 2260 cm^{-1} (fig. 7) may be taken as a measure of the total concentration of

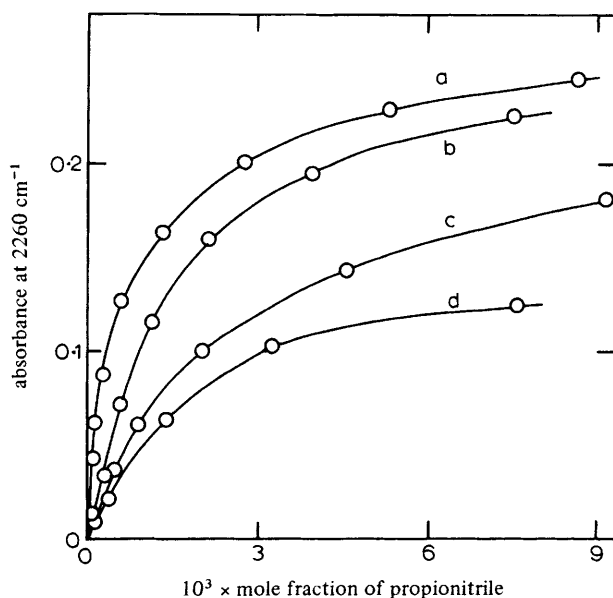


FIG. 7.—Intensity of the infrared band due to perturbed cyano groups in propionitrile molecules adsorbed onto silica immersed in (pretreatment temperatures of the silica in brackets) (a) 2,2,4-trimethylpentane (423 K), (b) 2,2,4-trimethylpentane (873 K), (c) 2,2,4-trimethylpentane + toluene [(x_T/x_M) of (3.22/1)] (423 K), (d) toluene (423 K).

propionitrile molecules containing cyano groups which were perturbed by hydrogen-bonding interactions with surface hydroxyl groups. The curves in fig. 7 are for silica discs of equal weight. Contributions to the absorbance at 2260 cm^{-1} due to the band at 2248 cm^{-1} for propionitrile in solution were negligible for low propionitrile concentrations.

DISCUSSION

Quantitative coverages of isolated silanol group sites by propionitrile, 2,2,4-trimethylpentane and toluene molecules were previously evaluated for silica which had been preheated at 873 K from the intensities of infrared bands due to OH-stretching vibrations of the silanol groups.⁶ A similar analysis was not possible for silica preheated at 423 K because of overlap between infrared bands due to different types of surface hydroxyl group. Fractional coverages of isolated and adjacent interacting hydroxyl groups by cyclohexanone were separately estimated from the intensities of two distinguishable infrared bands due to CO-stretching vibrations of adsorbed cyclohexanone molecules.¹ A comparable method of analysis was also impossible for propionitrile because only one infrared band at 2260 cm^{-1} resulted from CN-stretching vibrations of propionitrile molecules perturbed by hydrogen-bonding interactions with hydroxyl groups. However, the spectroscopic changes associated with the adsorption of propionitrile on silica do give a qualitative indication of the relative extents to which different types of surface hydroxyl group acted as adsorption sites. The general features of the spectroscopic changes were independent of whether toluene, 2,2,4-trimethylpentane or a toluene + 2,2,4-trimethylpentane mixture constituted the hydrocarbon liquid from which adsorption took place. As before,⁶ the propionitrile concentration ranges over which the spectral changes occurred were influenced (fig. 7) by the strengths of interaction between surface hydroxyl groups and hydrocarbon molecules.

The losses in absorption intensity at 3705 (fig. 2), 3595 (fig. 5) and $3705 + 3595\text{ cm}^{-1}$ (fig. 6) as a function of propionitrile concentration in solution were similar for silica which had been preheated either at 873 K ⁶ or at 423 K . Adsorption of propionitrile, as for cyclohexanone,¹ on to isolated silanol group sites was not influenced by other types of hydroxyl group on the silica surface. At high propionitrile concentrations all isolated silanol groups were perturbed by hydrogen-bonding interactions with cyano groups.

The spectroscopic changes at *ca.* $3640\text{--}3675\text{ cm}^{-1}$ (fig. 2), monitored by absorbance data at 3660 cm^{-1} [fig. 3(b)], for silica immersed in 2,2,4-trimethylpentane and the behaviour of the shoulder at 3645 cm^{-1} [fig. 5(a)] for silica in toluene are ascribed to the perturbation by adsorbed propionitrile molecules of hydroxyl groups responsible for the bands at 3725 and 3650 cm^{-1} in spectra of silica in vacuum. Surface hydroxyl groups which were perturbed by weak lateral interactions with adjacent groups were sites for the adsorption of propionitrile but not the adsorption of 2,2,4-trimethylpentane or toluene. At high propionitrile concentrations the majority of the total available sites were covered. In contrast, lateral interactions between hydroxyl groups responsible for the band at 3550 cm^{-1} in spectra of silica in vacuum largely retained their integrity in the presence of high concentrations of propionitrile. Increasing strengths of interaction between hydroxyl groups and solvent molecules or of lateral interaction between adjacent hydroxyl groups therefore decreased the ability of surface hydroxyl groups to act as sites for the adsorption of propionitrile on silica.

The contrast between the linearity of the plots in fig. 3 and the non-linearity of corresponding plots for the adsorption of cyclohexanone¹ suggest there was a significant difference between the modes of adsorption of cyclohexanone and propionitrile on to adjacent surface hydroxyl groups. Pairs of hydroxyl groups formed two hydrogen bonds to the carbonyl groups of single cyclohexanone molecules. This mode of adsorption depended on the existence of two lone pairs of electrons on each carbonyl oxygen atom and was stronger than the interaction between an isolated silanol group and a single cyclohexanone molecule. Adsorption on paired hydroxyl

group sites predominated at low total coverages of the silica surface. The linearity of the plots in fig. 3 suggests that the ratio of surface populations of propionitrile molecules adsorbed on to isolated hydroxyl groups and on to pairs of adjacent hydroxyl groups was approximately independent of total surface coverage. Together with the existence in spectra of a single band at 2260 cm^{-1} due to perturbed cyano groups the data are compatible with the conclusion that the adjacent interacting hydroxyl groups each formed one hydrogen bond to a single propionitrile molecule. The existence of only one lone pair of electrons on the nitrogen atom of the cyano group led to the acceptance of only one hydrogen bond per cyano group and precluded the formation of a surface-adsorbate complex involving two hydrogen bonds for each adsorbed molecule.

The differing modes of adsorption of propionitrile and cyclohexanone on to adjacent hydroxyl groups was also reflected in the relative extents to which adsorption involving strongly interacting silanol groups took place. All hydroxyl groups on silica which had been preheated at 423 K constituted sites for the adsorption of cyclohexanone from solution in 2,2,4-trimethylpentane.¹ Estimated hydroxyl group concentrations were $n_{\text{OH}} \approx 2\text{ nm}^{-2}$ for isolated groups⁸ and $n_{\text{OH}} \approx 2.5\text{ nm}^{-2}$ for adjacent groups.¹ Comparison of the spectroscopic isotherms in fig. 7(a) and (b) shows that the lower temperature of pretreatment of silica enhanced the amount of propionitrile adsorbed by only ca. 10-30%. Despite the large error in this estimate it is safe to conclude that a high proportion (76-92%) of the total surface population of adjacent silanol groups was unaffected by the adsorption process. The ratio (0.28/1) of the slopes of the lines in fig. 7 will give a very approximate indication of the relative numbers of weakly interacting adjacent hydroxyl groups and isolated hydroxyl groups which formed hydrogen bonds with adsorbed propionitrile molecules. The ratio is compatible with the enhanced uptake of propionitrile for silica which had been preheated at 423 K (fig. 7). The data therefore support the conclusion that weakly interacting hydroxyl groups responsible for the maxima at 3725 and 3650 cm^{-1} for silica in vacuum formed hydrogen bonds with adsorbed propionitrile molecules. Strongly interacting hydroxyl groups (3550 cm^{-1} for silica in vacuum) constituted sites for the adsorption of cyclohexanone but not propionitrile.

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