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Report

Estimation of Surface Polarity of Silicas by Absorption Spectroscopy of Glycerin Suspensions of Adsorbed 6-Nitrobenzoindolinopyran

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The title compound (6-NO_2-BIPS) is adsorptiochromic, becoming colored upon adsorption to a polar surface. Powders of 6-NO_2-BIPS adsorbed to silica gel or silicic acid are suspended in glycerin, and the absorption spectrum of the adsorbate is recorded by conventional absorption spectroscopy. The wave number of maximum absorption is related to the effective surface polarity by $\nu^*/\text{cm}^{-1} = 90.85\,Z + 11{,}571$, where Z is the Kosower polarity measure. Silica surface polarity corresponds to $Z = 86–89$.

KEY WORDS: adsorptiochromism; spiropyrans; silica surface polarity; suspension spectra; solvatochromism.

INTRODUCTION

The ability of a solid surface to adsorb molecules from solution is related to the "polarity" of the surface. The concept of surface polarity cannot be unambiguously defined, but it is analogous to the notion of solvent polarity. Quantitative measures of surface polarity can be useful guides in selecting adsorbents for practical applications, and they may provide insight into the mechanism of adsorption. Fowkes (1) has reviewed chemical techniques for the study of surface properties. In the present paper we describe an improved method for the measurement of the surface polarity of silicas by absorption spectroscopic observation of suspensions.

Measurement of the absorption spectrum of an adsorbate species bound to a solid is possible if the adsorbate–adsorbent power is suspended in a liquid having a refractive index very close to that of the solid. Several investigators have used this technique. For the study of species bound to silicas (refractive index, 1.420), cyclohexane (1.426) has served as a suspending liquid (2–5).

The purpose of the matching of the refractive indices of solid and liquid is to minimize scattering of the incident beam by the suspended particles, whose role is essentially to provide a uniform distribution of adsorbate molecules in the cuvette space. Absorption spectra obtained in this way show resolution and spectral features characteristic of solution spectra. A drawback of the method (aside from its limitation to a few solids) is the instability of the suspensions in cyclohexane.

In this report, we describe the use of the suspension spectroscopy technique in which we employ glycerin as the suspending medium, together with a photochromic substance, 6-nitrobenzoindolinopyran (6-NO_2-BIPS), as the adsorbate. 6-NO_2-BIPS is also adsorptiochromic; that is, it changes color upon adsorption (6,7). The structural basis of this photochromism and adsorptiochromism is the equilibrium between the colorless spiropyran form and the colored "open" form capable of extensive electron delocalization (Fig. 1). A more polar environment favors the colored form. deMayo *et al.* (8) made use of this principle in their study of silica surface polarity by direct absorption spectroscopy of a dry powder consisting of a spiropyran adsorbed on a silica, but no spectra were shown, and the experimental procedure is evidently difficult. We have combined the features of the adsorptiochromic phenomenon and the glycerin suspension to give a convenient technique for the estimation of surface polarities of silicic acid and silica gel.

EXPERIMENTAL

Materials

6-Nitrobenzoindolinopyran was synthesized by the method of Przystal *et al.* (9). Equimolar amounts of Fischer's base and 5-nitrosalicylaldehyde (both from Eastman) were refluxed in isopropyl alcohol for 4 hr. The precipitate was recrystallized from 90% ethanol in water, giving a final 87% yield; mp, 177.5–178.0°C [lit. mp, 179–180°C (10)]. The mass spectrum was consistent with the structure. Glycerin (J. T. Baker, anhydrous ACS reagent) was used directly. Solvents were the best commercial grades. Silica gel (surface area, 500 m^2/g; Analtech) and si-

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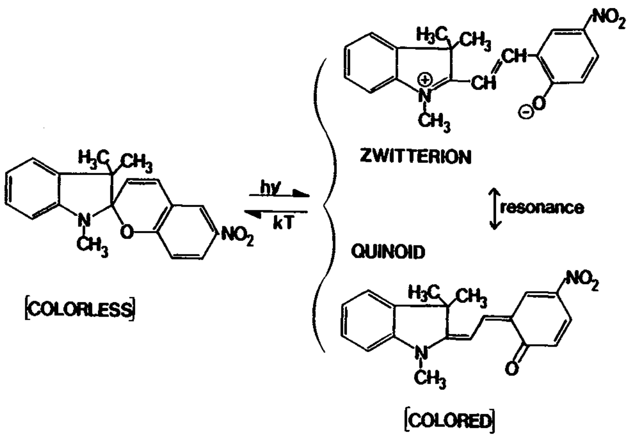

Fig. 1. Structural basis of photochromism and adsorptiochromism in 6-NO_2-BIPS.

licic acid (Mallinckrodt) were dried to a constant weight in 2 hr at 110°C. The surface area of the silicic acid, measured by the BET method, was 360 m^2/g. Cab-O-Sil M-5 (Cabot Corp.) is a fumed silica; its surface area was 200 m^2/g.

Procedures

Spectroscopy of Suspensions. The adsorbate–adsorbent system was prepared by adding 0.2–1.0 g of dried adsorbent to 50 ml of solutions of 6-NO_2-BIPS (2×10^{-4} to 8×10^{-3} *M*) in cyclohexane. The stoppered vessels were placed in a constant-temperature shaker bath at 25°C until equilibrated. The contents were filtered through Gelman 25-mm filter holders equipped with GA-8 Metricel cellulose triacetate filters of 0.2-μm pore size, and the solid phase was air-dried. Spectrophotometric measurement of the 6-NO_2-BIPS remaining in the filtrate allowed calculation of the amount of adsorbate adsorbed per gram of adsorbent.

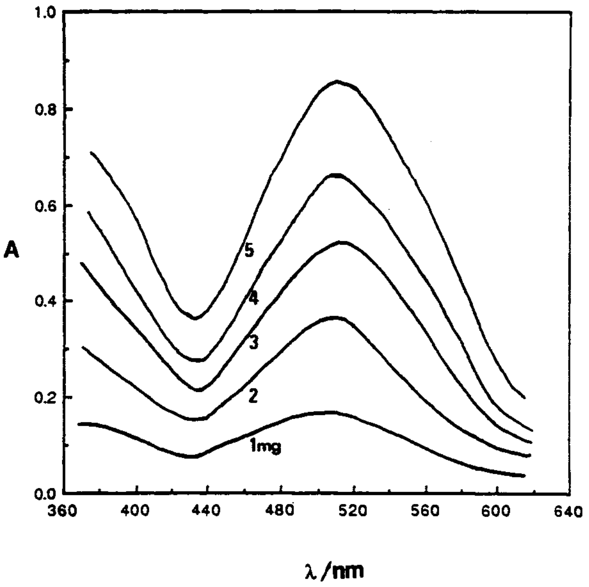

Fig. 2. Glycerin suspension spectra of 214.6 mg/g of 6-NO_2-BIPS on silica gel. Twenty milliliters of glycerin was used to disperse (bottom to top) 1, 2, 3, 4, and 5 mg of powder.

A suspension was prepared by levigating 25–150 mg of the spiropyran/adsorbent dried powder preparation with a small amount of glycerin, and this was diluted with glycerin; a total volume of 20 ml of glycerin was used. This suspension was placed in a standard 1-cm spectrophotometer cell, and the visible spectrum was recorded against a reference suspension of the pure adsorbent in glycerin. A Perkin–Elmer 559 spectrophotometer was used.

Solvatochromic Measurements. The visible absorption spectrum of 6-NO_2-BIPS was recorded in most of the solvents in the usual manner, although sonication was sometimes used to increase the dissolution rate. The very low solubility in water, however, prevented a direct spectral measurement from being made in water. The following extraction procedure was developed to solve this problem. To a 10^{-3} *M* solution of 6-NO_2-BIPS in cyclohexane contained in a separatory funnel, an equal volume of water was added. The funnel was irradiated with long-wavelength (366-nm) UV light in a UV light cabinet for 1 min, whereupon some of the colored form of 6-NO_2-BIPS (blue in cyclohexane solution) was produced, as in Fig. 1. Shaking of the funnel transferred some of this polar form to the aqueous phase, giving an orange solution, whose spectrum was quickly recorded.

RESULTS AND DISCUSSION

Spectra of Suspensions in Glycerin. Figure 2 shows absorption spectra of glycerin suspensions of a colored powder consisting of 6-NO_2-BIPS adsorbed on silica gel. This powder is dark red, and the spectrum is consistent with the visual appearance. Reproducibility of the technique was established by preparing six identical suspensions and measuring their spectra; the mean absorbance at the maximum for these samples was 0.261, with a standard deviation of 0.031. With some care to avoid the excessive presence of air bubbles, the glycerin suspension technique provides a simple means for measuring adsorbate spectra on silica surfaces. The technique is successful because the refractive index of glycerin (1.473) is reasonably close to that of silica and because glycerin's high viscosity provides a good suspension stability.

The spectral observations receive no important contribution from desorbed 6-NO_2-BIPS in solution; the equilibrium solubility and the rate of desorption are both too low for this to be a significant factor.

In this work the adsorbate–adsorbent powders were prepared quantitatively and the cyclohexane solutions were analyzed for their equilibrium concentration of 6-NO_2-BIPS, in order to study the method and to compare its spectral results with those for the adsorption isotherm. For measuring the polarity of the surface, however, it is not necessary to know the amount of adsorbate per gram of adsorbent; all that is needed is to have sufficient adsorbate present to provide a spectrophotometric response.

Figure 3 shows that the absorbance of the suspension varies linearly with the suspension concentration. The "saturation" effect at high surface coverage should be noted; the adsorption isotherm revealed that the adsorptiochromism reaches its maximal effect at lower adsorbate surface coverages than are required for complete adsorption.

Three adsorptiochromic spiropyrans besides 6-NO_2-

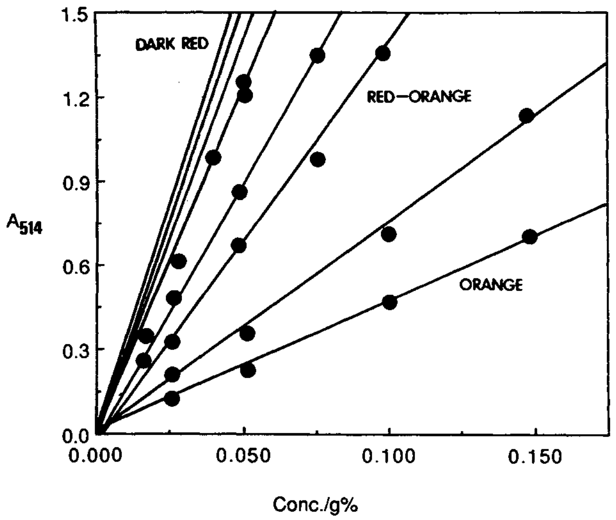

Fig. 3. Plots analogous to Beer's law plots for glycerin suspensions of 6-NO_2-BIPS on silica gel. The absorbance at λ_{max} is plotted against the suspension concentration as gram percentage. Steeper slopes correspond to higher surface coverages.

BIPS were tested for their suitability in this method, but the 6-NO_2-BIPS spectrum was the simplest to interpret for this purpose (11). The suspensions of 6-NO_2-BIPS/silica lose their color in 30–45 min if left exposed to room light. This "photobleaching" effect is reduced by protecting them from light.

Solvatochromism of 6-NO_2-BIPS. In order to transform a spectral measurement of adsorbed 6-NO_2-BIPS to a surface polarity, a working curve is required. This was generated by measuring the spectrum of 6-NO_2-BIPS in a set of solvents whose effective polarities are known. Table I lists the results, with both the wavelength of maximum absorption (nm) and the corresponding wave number (cm^{-1}) being given. (The apparent molar absorptivities are not included because they are poorly reproducible owing to the photobleaching effect and its reverse; values were of the order $\epsilon \approx 10^2$ l/mol-cm.) Table I also gives Kosower's Z value for these solvents; Z is a solvatochromic measure of solvent polarity (12).

Table I. Visible Absorption Spectral Data for 6-NO_2-BIPS in 13 Solvents

Solvent	λ_{max} (nm)	ν^* (cm^{-1})	Z^a
Chloroform	578	17,301	63.2
Methylene chloride	575	17,391	64.2
Acetone	564	17,730	65.7
Dimethylformamide	559	17,889	68.5
Dimethylsulfoxide	555.5	18,002	71.1
Acetonitrile	556	17,986	71.3
1-Octanol	547	18,282	—
Benzyl alcohol	540	18,519	—
Amyl alcohol	542	18,450	—
Isopropyl alcohol	543.5	18,399	76.3
Ethanol	537	18,622	79.6
Methanol	523	19,120	83.6
Water	492	20,325	94.6

[a] From Ref. 12.

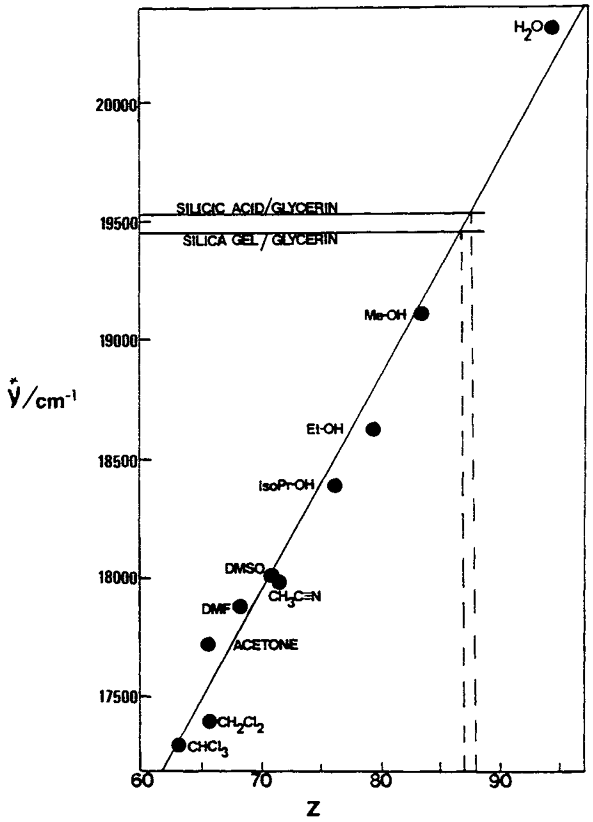

Fig. 4. Plot of spectral data for 6-NO_2-BIPS against solvent Z values; data from Table I. The spectral results for 6-NO_2-BIPS adsorbed to silicic acid and to silica gel are also shown.

Figure 4 is a plot of the wave number of maximum absorption of 6-NO_2-BIPS against the Z value. The line is satisfactorily linear, having a correlation coefficient $r = 0.992$, with the equation

$$\nu^* = 90.85\, Z + 11{,}571 \tag{1}$$

where ν^* is the wave number (cm^{-1}) and Z is Kosower's polarity measure (12). Note that the point for water, obtained by the irradiation extraction technique, falls reasonably close to the line. [It may incidentally be noted that Eq. (1) and the data in Table I allow Z values to be estimated for 1-octanol, benzyl alcohol, and amyl alcohol.]

Polarity of the Surface. The wavelength of maximum absorption of 6-NO_2-BIPS adsorbed to silica gel, examined by the glycerin suspension technique, was 514 nm (ν^* = 19,455 cm^{-1}); silicic acid yielded a broader absorption band centered at 512 nm (ν^* = 19,531). Cab-O-Sil gave a λ_{max} of 514 nm. From Eq. (1) or Fig. 4 the effective surface Z values are 86 (silica gel) and 89 (silicic acid). Kosower (12) found that a solution of 70% (v/v) ethanol in water had a value of 86.4. Thus these Z estimates for silica surfaces provide quantitative measures of polarity that can be related to an equivalent solvent polarity. That these estimates are reasonable is confirmed by the results of deMayo *et al.* (8) by their related but independent method, in which they expressed silica polarity in terms of methanol–water mixture compositions, finding that silica pretreatment to alter its polarity led to corresponding changes in the absorption spectrum. The method described in the present paper offers the same capability as the spectroscopic methods of deMayo *et al.* (8) and Leersmaker and co-workers (3–5), but it is simpler to apply experimentally.

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