Infrared Spectrum of Acetic Acid adsorbed at the Alumina/Water Interface

William Neagle and Colin H. Rochester*

Chemistry Department, The University, Dundee DD1 4HN, U.K.

I.r. spectra of alumina dispersed in solutions of acetic acid in deuterium oxide exhibit bands characteristic of adsorbed acetate anions and illustrate the use of i.r. spectroscopy for the study of surface species *in situ* at the solid/water interface.

The use of i.r. spectroscopy for the study of adsorption at the solid/liquid interface has primarily involved systems in which carbon tetrachloride or a hydrocarbon was the predominant component of the liquid phase.[1,2] I.r. studies of adsorption from aqueous solution have been accomplished by separation of the solid and liquid phases before spectroscopic examination of solid plus surface species.[1] However it is unsatisfactory to interpret the spectra of the separated solid as giving unambiguous information about adsorption phenomena *in situ* at the solid/aqueous solution interface. The present work was designed to test whether, despite the strong absorption of i.r. radiation by liquid water, direct examination of aqueous dispersions of powdered solids would enable spectra of adsorbed species to be recorded. Dispersions of alumina in aqueous acetic acid were chosen for study because the surface acetate, a possible product of adsorption,[3—5] would be expected to give an i.r. spectrum distinguishable from that of undissociated acetic acid. Deuterium oxide was used as the dispersion medium since the intense maximum at 1645 cm^{-1} in spectra of protium oxide would have obscured part of the spectral region of interest.

Alon fumed alumina (Cabot Corporation) of surface area 120 $m^2 g^{-1}$ was agitated with deuterium oxide to form a homogeneous gel which was placed on one of the fluorite windows of a demounted variable path length i.r. cell. The cell was reassembled and the gel was sandwiched between the windows by adjusting the path length to 0.02 mm. The i.r. spectrum, recorded using a Perkin Elmer 681 spectrometer, exhibited a broad absorption maximum at 2300—2700 cm^{-1} and a band at 1215 cm^{-1} due to stretching and bending vibrations, respectively, of deuterium oxide molecules.[6] In addition, bands at 3400 and 1455 cm^{-1} [Figure 1(a)] were due to stretching and bending vibrations of HDO[7] which resulted from H/D-exchange between D_2O and surface hydroxy groups or H_2O

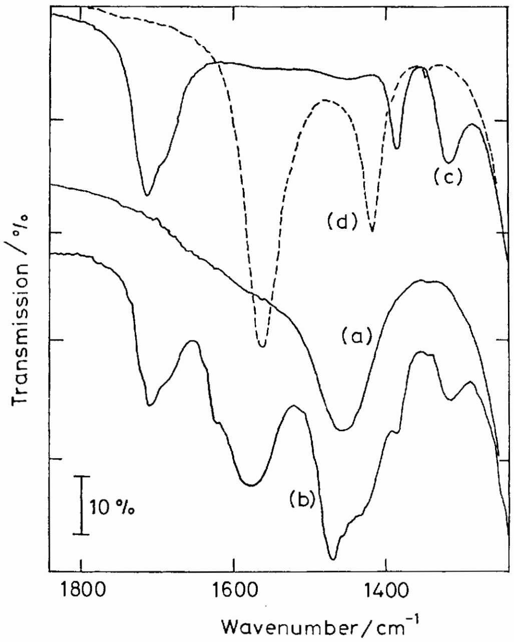

Figure 1. I.r. spectra of (a) alumina dispersed in D_2O, (b) alumina dispersed in a solution of acetic acid in D_2O, (c) acetic acid (1.01 mol kg^{-1}) in D_2O, and (d) sodium acetate (1.03 mol kg^{-1}) in D_2O. Spectra are staggered vertically for clarity; all samples gave 70—80% transmission at 1800 cm^{-1}.

present on the alumina surface before immersion in deuterium oxide.

Figure 1(b) shows the spectrum of alumina (0.26 g) immersed in a solution (0.57 g) of acetic acid (1.01 mol kg^{-1}) in deuterium oxide. The ratio of alumina to solution was adjusted to give the same intensities of the band at 3400 cm^{-1}, and hence also of the band at 1455 cm^{-1}, in the absence and presence of acetic acid. Only a small contribution [Figure 1(c)] to the band at 1455 cm^{-1} resulted from exchange between D_2O and CO_2H groups. Spectra of the gel [Figure 1(b)] contained maxima at 1712, 1386, and 1318 cm^{-1} which corresponded to similar maxima in spectra of acetic acid in D_2O [Figure 1(c)]. However, bands at 1622(sh), 1575, 1468, and 1350 cm^{-1} were not present in spectra (a) or (c) (Figure 1) and may be assigned to vibrations of adsorbed acetate anions on the alumina surface.[8,9] Superposition of spectra (a) and (b) also revealed a band which was present as a shoulder at 1425 cm^{-1} in spectra of the gel. Spectrum (d) enables a comparison to be made between the spectra of acetate anions in solution (bands at 1561, 1418, and 1350 cm^{-1}) and adsorbed at the alumina/solution interface. The spectra of adsorbed acetate resembled corresponding spectra for alumina exposed to acetic acid vapour[3,4] or immersed in solutions of acetic acid in carbon tetrachloride.[5] Filtration of gels containing H_2O established that some contribution to the bands assigned to adsorbed acetate was due to soluble aluminium acetate species formed by dissolution of alumina in the acid solution. However, spectra of separated alumina, after washing and drying, confirmed the presence of adsorbed acetate.

The present results exemplify the ease with which spectra of adsorbed species at the oxide/water interface may be recorded. Sols gave negligible radiation scattering effects and attenuation of the blank beam of the spectrometer was not necessary. The results in Figure 1 accurately reflect the low noise levels in the spectral traces. The availability of either H_2O (intense bands at 2900—3700 and 1645 cm^{-1}) or D_2O (2300—2700 and 1215 cm^{-1}) as the dispersion medium opens up the entire vibrational spectral range for the detection of bands due to adsorbed species. A problem of detection may arise if bands due to solute species in the adsorbed state and in solution coincide or overlap considerably. Computer facilities then become necessary to obtain difference spectra.[10]

In order to gain unambiguous information about adsorption *in situ* at the solid/aqueous solution interface it is important to have sufficient water present in the sols under investigation to provide a liquid phase rather than only a few layers of adsorbed water on the solid surface. The composition of the sols studied here was equivalent to a uniform 15 nm thick layer of water on the alumina surface. Sols with over three times this water content were also investigated and gave good quality spectra.

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