Journal of

The Chemical Society,

Chemical Communications

NUMBER 18/1977 21 SEPTEMBER

Infrared Spectra of the Surface of Silica Immersed in a Three-component Liquid Mixture

By Colin H. Rochester* and Deborah-Anne Trebilco

(*Chemistry Department, The University, Nottingham* NG7 2RD)

Summary I.r. spectra have been measured of silica immersed in heptane–toluene–acetone liquid mixtures and three i.r. bands which could be distinguished were assigned to surface silanol groups perturbed by interactions with heptane, toluene, or acetone molecules; the proportion of silanol groups perturbed by the adsorption of each component of the liquid mixture could be deduced from absorbance data and the method provides a novel technique for the study of adsorption from three-component liquid mixtures.

The importance of further studies of adsorption at the solid–multicomponent liquid interface has been emphasized by Everett.[1] Preliminary measurements have shown that i.r. spectroscopy may be used to gain direct information about interactions involving surface silanol groups on silica and each of the constituents of suitably chosen three-component liquid mixtures. Experimental procedures were identical to those used in the measurement of i.r. spectra of silica immersed in heptane–benzene and heptane–toluene mixtures.[2] The results for these hydrocarbon mixtures suggested that the measurement of spectra of silica in three-component liquid mixtures would be worthwhile providing the strengths of adsorption of the three components on to silica were significantly different. Toluene was more strongly adsorbed than heptane on silica; surface silanol groups on silica interacted more strongly with adsorbed toluene than adsorbed heptane molecules.[2] Acetone interacts more strongly than either toluene or heptane with surface silanol groups.[3] Heptane–toluene–acetone mixtures were therefore chosen to test the extension of the i.r. method to studies of adsorption from three-component systems.

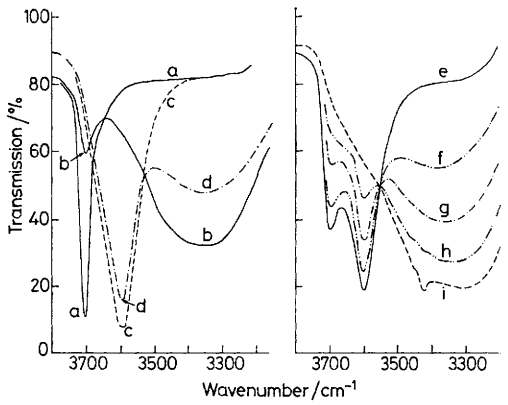

Figure. Spectra of silica immersed in (a) heptane, (b) heptane–acetone (27 mmol dm^{-3}), (c) toluene, (d) toluene–acetone (33 mmol dm^{-3}, (e)—(i) heptane–toluene mixtures (mole fraction ratio $x_t : x_h = 0{\cdot}2 : 1$) containing acetone at concentrations of 0, 5, 12, 61, and 680 mmol dm^{-3}, respectively.

Silica was evacuated at *ca.* 873 K before immersion in pure solvents or liquid mixtures. A band at 3680 cm^{-1} due to bulk OH-groups in the windows of the i.r. cell[2] was subtracted from the spectra presented here. Surface silanol groups gave i.r. bands at 3706 cm^{-1} when silica was immersed in heptane (Figure, a) and at 3595 cm^{-1} for silica in toluene (Figure, c). Addition of acetone to either solvent gave an i.r. band at 3360 cm^{-1} (Figure, b,d) due to silanol groups involved in hydrogen-bonding interactions with adsorbed acetone molecules. Concomitant decreases occurred in the intensity of the band at 3706 or 3595 cm^{-1}.

Absorbance values interpolated from the spectra enabled[2] the fractions of surface silanol groups perturbed by the adsorption of acetone to be evaluated as a function of acetone concentration. Comparison of the acetone concentrations for those spectra which are shown in the Figure (b,d) demonstrates the result, more clearly shown by the spectroscopic isotherms, that the extent of adsorption of acetone on silica was greater from heptane than from toluene solvent.

Spectra of acetone in heptane–toluene mixtures exhibited three distinct maxima at 3706, 3595, and 3360 cm^{-1} due to surface silanol groups interacting with heptane, toluene, and acetone molecules, respectively (Figure, f—h). Spectrum (e) in the Figure is for silica in a heptane–toluene mixture. Spectrum (i) corresponds to silica in the same heptane–toluene mixture but containing sufficient acetone for nearly all the surface silanol groups to be perturbed by the adsorption of acetone molecules. Measurement of absorbance values at 3706, 3595, and 3360 cm^{-1} allowed the fractions of silanol groups perturbed by contact with heptane, toluene, and acetone molecules to be calculated. The i.r. method therefore enabled simultaneous determination of spectroscopic isotherms for the adsorption of all three components of heptane–toluene–acetone mixtures on to specific surface sites (silanol groups) on silica. The experimental procedures were simple,[2] and could be improved to give better thermostatting of the i.r. cell if necessary.[4] A wide variety of three-component systems, and also possibly oxide adsorbents other than silica, should be amenable to study by similar i.r. spectroscopic examination of surface–adsorbate interactions at the solid–liquid interface.

(*Received*, 30*th May* 1977; *Com.* 533.)

[1] D. H. Everett, 'Colloid Science,' Chemical Society Specialist Periodical Report, 1973, vol. 1, p. 101; 1975, vol. 2, p. 75.
[2] C. H. Rochester and D.-A. Trebilco, *J.C.S. Faraday I*, 1977, **73**, 883.
[3] D. M. Griffiths, K. Marshall, and C. H. Rochester, *J.C.S. Faraday I*, 1974, **70**, 400.
[4] K. Marshall and C. H. Rochester, *J.C.S. Faraday I*, 1975, **71**, 2478.