CHEMISTRY

Multi-reflexion Attenuated Total Reflectance Infra-red Spectroscopy

THE concept of attenuated total reflectance was developed by Fahrenfort¹ for the determination of optical constants and as a means of obtaining intense infra-red spectra from samples which were difficult or not amenable to examination by normal transmission techniques.

The radiation incident on the interface between the analysing crystal and the sample, at angles of incidence greater than the critical angle, will be totally reflected at those wave-lengths where the sample shows no absorption. However, at those wave-lengths where the sample absorbs, part of the incident radiation will be absorbed, causing a decrease, that is an attenuation, in the intensity of the reflected radiation. This will produce a spectrum which strongly resembles the transmission spectrum, although the shape of the bands will be different².

The use of multi-reflectance attenuated total reflectance, in which the beam is internally reflected many times, was suggested by Harriek³. Since attenuation occurs at each internal reflexion the resulting spectrum will show a considerable amplification of weak absorptions when compared with a single reflexion attenuated total reflectance spectrum. Various designs of analysing crystals for obtaining multi-reflectance attenuated total reflectance spectra have been suggested^{4,5}.

Attenuated total reflectance is ideal, since it is dependent on surface reflexion, for obtaining the infra-red spectrum of a film fixed to a non-transparent support and the identification of coatings on paper, by this technique, has been reported previously⁶.

The purpose of this communication is to show the vastly superior detail that can be obtained from a multi-reflectance attenuated total reflectance spectrum. The example shown in Fig. 1 is of a coating on a paper-backed aluminium foil. These spectra were determined on a Unicam SP 200 infra-red spectrometer. The multi-reflexion spectrum was obtained using a simple multi-reflexion unit manufactured by Research and Industrial Instruments Co. This attachment, the TR9, consists of a trapezoidal KRS-5 analysing crystal, giving 9 or 19 internal reflexions, with a fixed 45° angle of incidence and two plane mirrors. This spectrum is compared with that obtained from a single reflexion unit, equipped with a KRS-5 prism, and set at 45° angle of incidence. In both cases no contacting medium between the sample and the analysing crystal was used, the sample being merely held in contact with the crystal by pressure. It can be seen that apart from giving much more intense absorption

bands there is a very significant improvement in the detail of the weak absorptions, particularly at 750, 800, 950 and 1,040 cm^{-1} and in the region 1,400–1,660 cm^{-1} . Recording the single reflexion attenuated total reflectance spectrum at an angle less than 45° would have increased the intensity to some extent since effective penetration is a function of angle of incidence, as well as of wave-length and complex refractive index of the sample.

As has been pointed out previously⁷, it is not possible to make a quantitative comparison of the 'absorbance' values obtained from these two spectra since such values are non-reproducible for this type of sample; this is due to the fact that reproducible contact between the analysing crystal and the sample cannot be obtained.

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¹ Fahrenfort, J., *Spectrochim. Acta*, **17**, 698 (1961).

² Fahrenfort, J., and Visser, W. M., *Spectrochim. Acta*, **18**, 1103 (1962).

³ Harriek, N. J., *Phys. Rev. Letters*, **4**, 224 (1960).

⁴ Hansen, Wilford, N., and Horton, J. A., *Anal. Chem.*, **36**, 783 (1964).

⁵ Harriek, N. J., *Anal. Chem.*, **36**, 188 (1964).

⁶ Deley, J. P., Gigi, R. J., and Liotti, A. J., *Trans. Amer. Pulp and Paper Indust.*, **46**, 118A (1963).

⁷ Putnam, N. A., Eleventh C.S.I., Belgrade (1963).

Polyhedral Emulsion Particles

It would appear to be an implicit assumption that the disperse phase particles of an emulsion system are spherical droplets^{1,2}. This generalization has been a convenient starting point for investigations of emulsions such as, for example, those of Lawrence and Mills³.

However, microscopic inspection of an emulsion will occasionally reveal the presence of irregularly shaped particles. During a recent investigation of the particle-size distribution of a semi-solid emulsion we have repeatedly noted the presence of straight-sided particles. We wish to report this and to offer for this phenomenon an explanation alternative to those in the literature.

The system we are investigating consists of 10 per cent w/w liquid paraffin and 10 per cent w/w cetostearyl alcohol emulsified by 0.5 per cent w/w cetrimide in distilled water. The emulsion is prepared by heating a mixture of the paraffin and long-chain alcohol at 60° until a homogeneous melt is obtained. This is then added to an aqueous cetrimide solution also at 60°. A white emulsion forms immediately and on cooling the preparation sets to a semi-solid oil-in-water emulsion. Since the disperse phase alone softens and melts over the range 30°–35° the preparation at ambient temperature is more correctly considered as a solid-liquid dispersion⁴. Nevertheless, it is clear that a liquid-liquid emulsion exists above 35° and is formed at the moment of mixing the two phases.

Fig. 1 was taken during the microscope size analysis of a sample of the foregoing system which had been allowed to cool from 60° to 30° while being subjected to ultrasonic irradiation. Fig. 2 is an electron photomicrograph of a sample allowed to cool undisturbed after initial gentle mixing at 60°. This latter sample contained a higher proportion of polyhedra than the former when examined by optical and electron microscope.

Phipps⁵, investigating dispersions of large hydrocarbons, noted that particles were sometimes slightly irregular in shape, whereas glyceride particles were usually uniformly spherical. Axon, in the discussion to his paper⁶, suggested that particles in aged systems similar to our own, but emulsified with sodium lauryl sulphate, tended to have a crystalline appearance if the ratio of cetyl alcohol to liquid paraffin was greater than 8 : 5. We examined aged and freshly prepared cetrimide emulsions with ratios of 10 : 1 and 1 : 10 alcohol to oil respectively. There was apparently little difference between freshly prepared samples and those which had been stored at room temperature for

Fig. 1. Attenuated total reflectance spectra of coating on paper-backed aluminium foil. *a*, Single reflexion; *b*, multi-reflexions (9 reflexions)