

## 2.6. SMALL-ANGLE TECHNIQUES

surface scattering by scratches. The vanadium sample has to be hermetically sealed to prevent hydrogen incorporation (Wignall & Bates, 1987).

The coherent cross sections of the two protons and one oxygen in light water add up to a nearly vanishing *coherent*-scattering-length density, whereas the incoherent scattering length of the water molecule remains very high. The (quasi)isotropic incoherent scattering from a thin, *i.e.* about 1 mm or less, sample of  $^1\text{H}_2\text{O}$ , therefore, is an ideal means for determining the absolute intensity of the sample scattering (Jacrot, 1976; Stuhrmann *et al.*, 1976), on condition that the sample-to-detector distance  $L$  is not too large, *i.e.* up to about 10 m. A function  $f(\sigma_i[\text{H}_2\text{O}], \lambda)$  that accounts for deviations from the isotropic behaviour due to inelastic incoherent-scattering contributions of  $^1\text{H}_2\text{O}$  and for the influence of the wavelength dependence of the detector response has to be multiplied to the right-hand side of equation (2.6.2.6) (May, Ibel & Haas, 1982).  $f$  can be determined experimentally and takes values of around 1 for wavelengths around 1 nm.

Since the intensity scattered into a solid angle  $\Delta\Omega$  is

$$I(Q) = P(Q)NT_s I_0 g (\sum b_i - \rho_s V)^2, \quad (2.6.2.7)$$

where  $P(Q)$  is the form factor of the scattering of one particle, and the geometrical factor  $g$  can be chosen so that it is the same as that of equation (2.6.2.6) (same sample thickness and surface and identical collimation conditions), we obtain

$$I(Q) = 4\pi P(Q)NT_s f(\sigma_i[\text{H}_2\text{O}], \lambda) (\sum b_i - \rho_s V)^2 / (1 - T[\text{H}_2\text{O}]). \quad (2.6.2.8)$$

Note that the scattering intensities mentioned above are scattering intensities corrected for container scattering, electronic and neutron background noise, and, in the case of the sample, for the solvent scattering.

## 2.6.2.6.2. Detector-response correction

For geometrical reasons (*e.g.* sample absorption), and in the case of 2D detectors also for electronic reasons, the scattering curves cannot be measured with a sensitivity uniform over all the angular region. Therefore, the scattering curve has to be corrected by that of a sample with identical geometrical properties, but scattering the neutrons with the same probability into all angles (at least in the forward direction). As we have seen previously, such samples are vanadium and thin cells filled with light water. Again, water has the advantage of a much higher scattering cross section, and is less influenced by surface effects.

At large sample-to-detector distances (more than about 10 m), the scattering from water is not sufficiently strong to enable its use for correcting sample scattering curves obtained with the same settings. Experience shows that it is possible in this case to use a water scattering curve measured at a shorter sample-to-detector distance. This should be sufficiently large not to be influenced by the deviation of the (flat) detector surface from the spherical shape of the scattered waves and small enough so that the scattering intensity per detector element is still sufficient, for example about 3 m. It is necessary to know the intensity loss factor due to the different solid angles covered by the detector element and by the apparent source in both cases. This can be determined, for instance, by comparing the global scattering intensity of water on the whole detector for both conditions (after correction for the background scattering) or from the intensity shift of the same sample measured at both detector distances in a plot of the logarithm of the intensity *versus*  $Q$ .

## 2.6.2.6.3. Estimation of the incoherent scattering level

For an exact knowledge of the scattering curve, it is necessary to subtract the level of incoherent scattering from the scattering curve, which is initially a superposition of the (desired) coherent sample scattering, electronic and neutron background noise, and (sometimes dominant) incoherent scattering.

A frequently used technique is the subtraction of a reference sample that has the same level of incoherent scattering, but lacks the coherent scattering from the inhomogeneities under study. Although this seems simple in the case of solutions, in practice there are problems: Very often, the  $^1\text{H}/^2\text{H}$  mixture is made by dialysis, and the last dialysis solution is taken as the reference. The dialysis has to be excessive to obtain really identical levels of  $^1\text{H}$ , and in reality there is often a disagreement that is more important the lower the sample concentration is. If the concentration is high, then the incoherent scattering from the sample atoms (protons) themselves becomes important.

For dilute aqueous solutions, there is a procedure using the sample and reference transmissions for estimating the incoherent background level (May, Ibel & Haas, 1982): The incoherent scattering level from the sample,  $I_{i,s}$ , can be estimated as

$$I_{i,s} = I[\text{H}_2\text{O}]f_\lambda(1 - T_s)/(1 - T[\text{H}_2\text{O}]), \quad (2.6.2.9)$$

where  $I[\text{H}_2\text{O}]$  is the scattering from a water sample,  $T[\text{H}_2\text{O}]$  is transmission,  $T_s$  that of the sample.  $f_\lambda$  is a factor depending on the wavelength, the detector sensibility, the solvent composition, and the sample thickness; it can be determined experimentally by plotting  $I_{i,s}/I[\text{H}_2\text{O}]$  *versus*  $(1 - T_s)/(1 - T[\text{H}_2\text{O}])$  for a number of partially deuterated solvent mixtures.

This procedure is justified because of the overwhelming contribution of the incoherent scattering of  $^1\text{H}$  to the macroscopic scattering cross section of the solution, and therefore to its transmission. The procedure should also be valid for organic solvents. The precision of the estimation is limited by the precision of the transmission measurement, the relative error of which can hardly be much better than about 0.005 for reasonable measuring times and currently available equipment, and by the (usually small) contribution of the coherent cross section to the total cross section of the solution. A modified version of (2.6.2.9) can be used if a solvent with a transmission close to that of a sample has been measured, but the factor  $f_\lambda$  should not be omitted.

An equation similar to (2.6.2.9) holds for systems with a larger volume occupation  $c$  of particles in a (protonated) solvent with a scattering level  $I_{\text{inc}}$  in a cell with identical pathway (without the particles):

$$I_{i,s} = I_{\text{inc}}(1 - T_{\text{inc}}^{1-c})/(1 - T_{\text{inc}}). \quad (2.6.2.9a)$$

In this approximation, the particles' cross-section contribution is assumed to be zero, *i.e.* the particles are considered as bubbles.

In the case of dilute systems of monodisperse particles, the residual background (after initial corrections) can be quite well estimated from the zero-distance value of the distance-distribution function calculated by the indirect Fourier transformation of Glatter (1979).

## 2.6.2.6.4. Inner surface area

According to Porod (1951, 1982), small-angle scattering curves behave asymptotically like  $I(Q) = \text{constant} \times A_s Q^{-4}$  for large  $Q$ , where  $A_s$  is the inner surface of the sample. Theoretically, fitting a straight line to  $I(Q)Q^4$  *versus*  $Q^4$  ('Porod plot') at *sufficiently large*  $Q$  therefore yields a zero intercept, which is proportional to the internal surface; a slope