A MODIFIED METHOD FOR SLIT-LENGTH COLLIMATION CORRECTIONS

ured' intensities calculated by interpolation should not be employed with (4). However, if the interpolations are made over a small interval, the uncertainty in the interpolated intensities will be well approximated by the expression used with intensities which are directly measured. Since only approximate error estimates are necessary, more refined calculations normally are not worth while when some of the $F_i$ are obtained by interpolation. However, if the interpolations are employed with (4). However, if the interpolations are made over a small interval, the uncertainty in the interpolated scattering curve is likely to be spurious, since only variations in the scattering curve which are larger than the statistical uncertainty can be considered to be clearly representative of the structure of the scattering sample.

Estimates of the uncertainty in $I(\alpha)$ can be used to help decide whether maxima, minima, or other features of the corrected scattering curve are likely to be spurious, since only variations in the scattering curve which are larger than the statistical uncertainty can be considered to be clearly representative of the structure of the scattering sample. Figs. 1 and 2 illustrate the use of (4) in the analysis of some scattering studies which were an extension of an earlier investigation of argon near the liquid-vapor critical point (Bale, Dobbs, Lin & Schmidt, 1970).

In this investigation a theory was considered which predicted that the reciprocal of the scattered intensity was a linear function of the square of the scattering angle. This relation, which later study showed was not applicable, was tested by plots like Figs. 1 and 2, in which the uncertainty in the scattered intensity was relatively low and quite high.

The availability of the uncertainties in the corrected intensities permitted computation of a weighted least-squares fit in which the weights were proportional to $[\delta I(\alpha)]^{-2}$ (Bevington, 1969, pp. 106-108). The slope and intercept of the line, as well as the uncertainties in the slope and the intercept, were evaluated. As Figs. 1 and 2 and the associated least-squares calculations indicate, the availability of the uncertainties in the corrected data facilitates statistical analysis which makes use of the corrected data. In particular, comparison of the corrected data with theoretical curves can be made very conveniently.

In calculations of the radius of gyration from small-angle X-ray scattering data (Guinier, Fournet, Walker & Yudowitch, 1955), analyses like those in Figs. 1 and 2 can be conveniently used to find the radius of gyration, the extrapolated zero-angle intensity, and the statistical uncertainties in these two quantities.

Copies of the Fortran computer program for making collimation corrections by the new method and for computing the uncertainties in the corrected data are available from Paul W. Schmidt. The revised program also incorporates a subroutine for slit-width corrections (Taylor & Schmidt, 1967). The authors are grateful to the College of Arts and Science of the University of Missouri at Columbia for providing the funds necessary to carry out the numerical computations and to the College of Engineering Experiment Station for typing the manuscript.

References


A New Experimental Technique for the Study of Liquid Structure

By E. KÁLMÁN, S. LENGYEL, L. HAKLIK AND A. EKE

Central Research Institute for Chemistry of the Hungarian Academy of Sciences,

Pusztaszeri u. 59-67, Budapest II, Hungary

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The use of electron diffraction in studies of the structure of liquid water is discussed.

The main characteristics of liquid structure, i.e. the pair-correlation function, can be obtained by X-ray, electron and neutron diffraction methods. The three methods differ in the interaction between radiation and specimen. A complete structure analysis can only be given by the combinations of these three methods of adequate accuracy and involving sufficiently different values for the atomic scattering amplitudes. X-ray (see references in Narten, 1970; Narten & Levy, 1971; Narten, 1972) and neutron-diffraction methods (Page & Powles, 1971; Powles, Dore & Page, 1972; Narten, 1972) have been successfully used in the study of liquid
water; electron-diffraction studies alone have not been possible, because of technical difficulties. Considering the advantages of the electron-diffraction method (Kálmán, Lengyel, Pálinkás, Haklik & Eke, 1974; Lengyel & Kálmán, 1974) we tried to overcome the difficulties arising from the maintenance of a liquid-water layer in high vacuum.

On the basis of the attempts found in the literature [discussed in detail by Kálmán, Lengyel, Haklik & Eke (1974)] to study liquid structure by high-energy electron diffraction (Maxwell, 1933; Lufcy, Palubiskas & Maxwell, 1951; Roth, 1961, 1962, 1963 a, b) and utilizing the trials of electron microscopy on hydrated biological objects (Stoyanova & Mikhailovsky, 1959; Dupouy, Perrier & Durrieu, 1960; Heide, 1962; Parsons & Moretz, 1970; Ward & Mitchell, 1972; Parsons, Matricardi, Subjeck, Uydess & Wray, 1973; Allinson, Gosnold & Loweday, 1972), we developed after some preliminary experiments a new device (Kálmán, Lengyel, Haklik & Eke, 1973) - a chamber under pressure - in which the vapour pressure is near equilibrium, while the space for the electron beam is kept below $10^{-5}$ torr. Between the two apertures of the chamber a water layer can be reproduced, at any time, by a suitable mechanism, as can be seen in Fig. 1.

In the upper part (A) the entrance aperture can be seen (0.07 mm diameter), further away the connexion to the vacuum measuring device (H) and the temperature-controlling thermistor (I) (typ. K17, Siemens) in contact with the copper foil (C). This piece of foil (thickness: 0.02mm) with an opening (2mm diameter) in the middle holds the liquid sample.

The lower part (B) contains the exit aperture (0.2mm diameter). The liquid film is produced by introducing a certain amount of water through the tube (J-K) into the hole (R) and then smearing it over the copper foil (C) by the wiper mechanism (E). The copper spiral (L) serves as a thermostat. The large volume (S) contains the bulk water; its amount (~5cm³) does not change very much during the experiment. In this way a puffer system has been produced. In Fig. 2. the chamber can be seen (open).

The diffraction pattern is photographed on a photo-plate (Agfa-Gevaert Scientia 23D50) with a so-called $s^2$ - rotating sector (Kálmán et al., to be published), which is driven by an electric motor (800 r.p.m.) and which serves to counterbalance the very steep decrease of electron scattering function with increasing $s$.

In order to prevent deterioration of the vacuum by water vapour, two pump systems had to be built. In addition, two cooling traps (filled with liquid nitrogen) were fitted to the chamber at its upper and lower openings.

An electron-optical device (type Zeiss EF) has been reconstructed for liquid electron-diffraction experiments. The original distance between sample and photo-plate (camera distance), 20 cm, has been altered to 42 and 80 cm.

During the experiments the following observations were made on the fluorescent screen:

(1) If there is no liquid film, the sharp focus of the primary beam can be seen.

(2) At the beginning of the experiment the water film is too thick and the screen is almost dark, because all the electrons are absorbed. Within a few seconds
the primary beam becomes visible and the whole screen gradually becomes clearer.

(3) After a few more seconds diffuse concentric rings appear and the photoplate can be exposed. The necessary exposure time for photographing liquid electron-diffraction patterns is about two seconds. At this stage the thickness of the water layer amounts to 100 nm (the lifetime of such a liquid layer is a few seconds after which it bursts). Our electron-optical device is not suitable for studying thicker films, since the maximal accelerating voltage is 75 kV.

An electron diffraction pattern of water, at 4°C, taken with a camera distance of 42 cm (exactly determined by a cathetometer, type KM 6) is shown in Fig. 3. The electron beam current was about 10 nA, corresponding to the accelerating voltage (68 kV) and maximal accelerating voltage is 75 kV. The wavelength, corresponding to the accelerating voltage (68 kV) and kept constant during the experiment, was determined from the diffraction patterns of TICI. The s range of the scattering variable (0.4 < s < 3.0 A⁻¹) by extending the experimental pair-correlation function of water, at 4°C, (see Fig. 4) the characteristic inter- and intramolecular distances are as follows: the large maximum at 2.84 Å is due to the distance between oxygen atoms of neighbouring water molecules, the three maxima about 4.3, 4.9 and 6.85 Å correspond to second and more distant neighbour interactions, and the first maximum at 0.95 Å is ascribed to the intramolecular O-H bond distance, according to the interpretation of Narten (1970, 1972) and Narten & Levy (1972).

We plan to develop our experiments (with the two other camera lengths 20 and 80 cm) by extending the range of the scattering variable (0.4 ≤ s ≤ 30 Å⁻¹). By this method, further information about the water molecule in the liquid and the liquid water structure can be obtained.

Several other technical developments and refinements involving the methods of calculation and investigation, and measurement at different temperatures are in progress. Detailed interpretation of the pair-correlation function will follow.

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References


