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Neutron diffraction studies of water and aqueous solutions under pressure

G. W. Neilson and S. Cummings

H. H. Wills Physics Laboratory, Tyndall Avenue, Bristol BS8 1TL, U.K.

Résumé. — Les résultats obtenus par des expériences de diffraction neutronique sur l'eau lourde à des pressions et températures élevées en utilisant trois types différents d'enclume à pression sont résumés dans ce papier. Les enceintes sont soit en acier dur (EN24T) (a), soit en alliage « nul » de titane-zirconium (b), soit en alliage d'aluminium 7075-T6 (c). Dans les cas (a) et (b), des pressions hydrauliques jusqu'à 6 kbar ont été appliquées directement à l'échantillon à travers l'interface huile/solution aqueuse. Dans le cas (c) le moyen de pressurisation — argon gazeux — a été appliqué de façon uniforme à travers le volume de l'échantillon, ce qui donne des pressions jusqu'à 2 kbar à des températures de 21° à 80 °C.

Abstract. — A summary is given of data obtained from neutron diffraction experiments on heavy water at elevated pressures and temperatures using three different types of pressure vessel. The pressure vessels were manufactured from (i) hard steel (EN24T), (ii) titanium-zirconium null alloy, and (iii) autofrettaged aluminium alloy (7075-T6). In cases (i) and (ii), hydraulic pressures up to 6 kbar were applied directly to the sample across the oil/aqueous solution interface. In case (iii) the pressurizing medium of argon gas was applied uniformly throughout the sample volume giving pressures up to 2 kbar at temperatures in the range 21 °C to 80 °C.

1. Introduction.

The object of this paper is to discuss the relative merits of pressure vessels presently used for neutron diffraction from aqueous solutions in terms of the quality of the experimental data and the extent to which such data can be used to obtain reliable quantitative information concerning the liquid structure.

Recall that in any diffraction experiment on a liquid the ultimate objective is to obtain information regarding the interatomic coordination as is calculated from the radial distribution functions, $g_{ij}(r)$, where i and j represent two types of atoms [1].

(For a detailed discussion of the mathematical link between the experimentally measured quantity $I(k)$ or $I(\theta)$, $k = 4\pi \sin \theta / \lambda$, λ = neutron wavelength, and the theoretically desired radial distribution functions $g_{ij}(r)$, the reader is referred to reference [2].)

In a diatomic system such as water there are three such functions — $g_{OO}(r)$, $g_{OH}(r)$ and $g_{HH}(r)$, and there are ten in an aqueous solution of the form $MX_n \cdot H_2O$. The difference methods of neutron diffraction based on the technique of isotopic substitution enables one to determine individual $g_{ij}(r)$'s [2]. Results for H/D substitution in water are beginning to appear in the literature [3, 4]. However, because of uncertainties in data analysis, especially concerning solutions of H_2O ,

there is still disputation regarding the quantitative aspects of the results, and as yet no isotope studies have been carried out on water at elevated pressures. In fact, the only neutron diffraction work we know of is that concerned with heavy water [5, 6]. (X-ray diffraction experiments have, however, been carried out on water and heavy water to pressures of 6 kbar at room temperature [7] and 1 kbar at temperatures of 1 000 °C) [8]. There have been several neutron diffraction experiments at 1 kbar in which isotopes of Ni and Cl in heavy water solutions of nickel chloride and lithium chloride were used [9].

2. Pressure vessels and experimental data.

The main requirement of a diffraction experiment on a liquid is that the data are sufficiently reliable that they can be used to derive quantitative structural information regarding interparticle conformations. Consequently primary attention must be paid to sample containment. For aqueous solutions the main requirements for a pressure vessel capable of providing useful neutron diffraction data are that it

- (1) is strong enough to withstand pressure up to 10 kbar at temperatures to 500 °C ;
- (2) is resistant to corrosion ;

Table I. — Pressure vessels for neutron diffraction.

Label	Material	Maximum pressure kbar	Maximum temperature °C	Sample volume cm ³	Degree of corrosion	Percent of total scattering	References
A	Steel (EN24T)	2	70	5	small	50	[10]
B	Autofrettaged Al alloy (7075-T6)	4	75	7.5	negligible with Teflon insert	60	[11]
C	Titanium/Zirconium	2	80	5	negligible	40	[5]
D	Titanium/Zirconium	6	80	1	negligible	90	[12]
E	Al alloy	16	85	< 1	small	< 5	[6]

(3) scatters neutrons in a way which can be easily accounted for in the data analyses, thereby facilitating the determination of quantitative information.

Over the past few years several different types of containers have been used to gather information on heavy water and its solutions at elevated pressures (Table I).

All containers used were able to work at pressures of a few kbar, and indeed the pressure vessel fabricated by Wu *et al.* [7] was used at pressures of 16 kbar at 85 °C. Diffraction patterns from pressure vessels A, B, C and D containing samples of heavy water are shown in figure 1. The equivalent pattern for pressure vessel E is shown in figure 2 of reference [6], where because of the type of geometry adopted in what was basically a triple axis experiment, the background from the container is much less than in all other cases. For all vessels except B there is a negligible amount of container scattering in the region to 3 Å⁻¹. For containers A and B there are several Bragg peaks in the region > 3 Å⁻¹, and their presence prevents a complete quantitative analysis of the data. By way of contrast, Ti/Zr containers, C and D, show very little structure over the entire *k* range and because the sample volume is completely in the neutron beam a complete analysis of the data can be carried out directly. For the vessels B and E, which occupy a volume larger than the neutron beam profile, data analysis and interpretation of the results can only be carried out with reference to an external standard.

Pressure vessel B was originally built for inelastic neutron work on solids and is not therefore well suited for diffraction of aqueous liquids. To avoid the occurrence of corrosion of the Al, it is necessary to use a teflon insert and this introduces a large broad peak centred at ~ 1.3 Å⁻¹ into the diffraction data, figure 1b. The sample is uniformly compressed by Ar gas, and comparisons of pressure data for heavy water using cell E and using a Ti/Zr vessel, where the pressure is communicated directly through the oil-water interface, are markedly different. In particular,

Fig. 1. — Neutron diffraction intensity data *I(k)* for 4 pressure vessels containing heavy water. Curves A — empty container. Curves B — container filled with heavy water. 1a. Steel container (A in Table I), crosses : D₂O at 1 bar, open circles : D₂O at 1 kbar. 1b. Autofrettaged Al container (B in Table I). 1c. Titanium-zirconium container (C in Table I), crosses : D₂O at 1 bar, open circles : D₂O at 1 kbar. 1d. Titanium-zirconium container (D in Table I).

the pressure induced shift in the main water peak ~ 2 Å⁻¹ is measurably different in the two cases, a consequence we believe of the dissolution of argon in water. A further difficulty with the Al autofrettaged cell is that a shift in background level is often observed in going from one pressure run to another.

3. Conclusions and future prospects.

The results discussed above indicate that successful neutron diffraction experiments can be undertaken at pressures of a few kbar at temperatures of $\sim 100^\circ\text{C}$. Although several types of pressure vessels exist, it is clear, that in order to obtain reliable quantitative data, particular care must be taken to ensure against large coherent scattering effects and corrosion of the container.

In the short term, there is an obvious need for mea-

surements to include temperature variations and move to regimes of P and T where many interesting phenomena have already been observed [1]. For aqueous electrolyte solutions this regime might well be defined by $p \sim 1$ kbar and $T \sim 600^\circ\text{C}$, i.e. in the super critical region.

In the longer term, the high flux pulsed sources, such as the SNS at Rutherford Appleton Laboratory, will enable the use of fixed geometry instruments which are particularly well suited to experiments under non ambient conditions.

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