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SLOW-NEUTRON SCATTERING CROSS-SECTION FOR METHANOL, ETHANOL, PROPANOL, ISO-PROPANOL, BUTANOL, ETHANEDIOL AND PROPANETRIOL

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Abstract—Slow neutron scattering cross-sections per proton σ_s/H for methanol, ethanol, *n*-propanol, iso-propanol, *n*-butanol, ethanediol and propanetriol have been measured in the liquid phase, in order to study the freedom of rotational motion of hydrogenous groups. The measurements, at room temperature, were carried out using a curved slit slow-neutron chopper and time-of-flight spectrometer. The slopes of the cross-section curves as a function of neutron wavelength in the range 4·8 Å to 10·0 Å have been derived. The results show the importance of methyl groups rotational motion and give evidence of the contribution of methylene groups in the inelastic scattering of slow-neutrons. The curve σ_s/H for methanol is compared with the already calculated curve on basis of the Krieger–Nelkin model.

INTRODUCTION

RECENT interest in the behaviour of hydrogenous liquids as thermal neutron nuclear reactor moderators has led to investigations of the neutron-scattering characteristics of organic molecules including lower alcohols. The specific mechanisms contributing to the scattering are better studied by double differential scattering cross section measurements (LARSSON, 1965). However, measurements of the total scattering cross-section per proton, σ_s/H, for slow neutrons may still be considered as a useful complementary technique to other advanced methods in the study of the dynamics of hydrogenous groups in molecules. Moreover, $\sigma/_sH$ is by itself an important parameter in the evaluation of the quality of the hydrogenous compound as thermal and cold neutron sources (DINGEVEN, 1962 and PERSSON, 1967).

It is well known that for sufficiently slow neutrons (energy $\ll 0{\cdot}025$ eV) σ_s/H of hydrogenous compounds varies linearly with the neutron wavelength (RUSH, 1961). The slopes of these cross-section curves are determined by the inelastic scattering that comes from processes in which the neutron gains energy from the molecules in populated excited states. At room temperature the main contribution to the inelastic scattering is due to de-excitation of energy levels corresponding to torsional or free rotational motion of the molecule or molecular groups containing hydrogen atoms. This cross-section is a function of the displacement of protons involved in the excited mode and hence rotations and torsional oscillations with large amplitudes are very effective in scattering neutrons. The slope of the σ_s/H curve increases with the freedom of motion of the H atoms. This correspondence is well illustrated in a series of papers on the scattering cross-section per proton of hydrogenous compounds, (RUSH, 1961; JANIK, 1965; HERDADE, 1968 and ERICKSON, 1966).

In the present work the total cross-section of methanol, ethanol, *n*-propanol, iso-propanol, *n*-butanol, ethanediol (glycol) and propanetriol (glycerol) have been measured at room temperature. The data were analysed to determine σ_s/H. As the alcohol molecules in the liquid phase are associated in polymers by hydrogen bonding, the contribution of the rotational motions of the whole molecule to the scattering can

be neglected. The inelastic scattering is mainly due to rotations of methyl and methylene groups.

EXPERIMENTAL METHOD

The total neutron cross-section of the above mentioned compounds have been measured using a curved slit-slow-neutron chopper and time-of-flight spectrometer in operation at the IEA-R1 research reactor of the Institute of Atomic Energy, São Paulo, (AMARAL, 1968).

The total cross-section for methanol was measured within the neutron wavelength range 0·9–10·0 Å corresponding to neutron energy from 0·1 to 0·0008 eV. The cross-section for the other alcohols was measured in the range 4·0–10·0 Å (0·005–0·0008 eV).

The samples were investigated in the liquid phase at room temperature (296°K) and were contained in aluminium cells with nominal thickness of 2·5 mm.

The number of molecules per cm^2 of each compound has been determined from the measured thickness of the cell and the density of the liquid at room temperature. The internal dimensions of the cells were checked by measuring the total cross-section of water. Uncertainties in the number of molecules per cm^2 values amount to 3 per cent.

The scattering cross-sections per proton, σ_s/H, were determined by subtracting from the measured total cross-section the contribution brought by the carbon and oxygen scattering cross-sections and by the molecule absorption cross-section; the remaining cross-section value was divided by the number of hydrogen atoms in the molecule in order to obtain σ_s/H.

RESULTS AND DISCUSSIONS

Scattering cross-section per hydrogen atom as a function of neutron wavelength for methanol is plotted in Fig. 1. The other cross section curves for ethanol, propanol, iso-propanol, butanol, ethanediol and propanetriol are shown in Fig. 2. Only

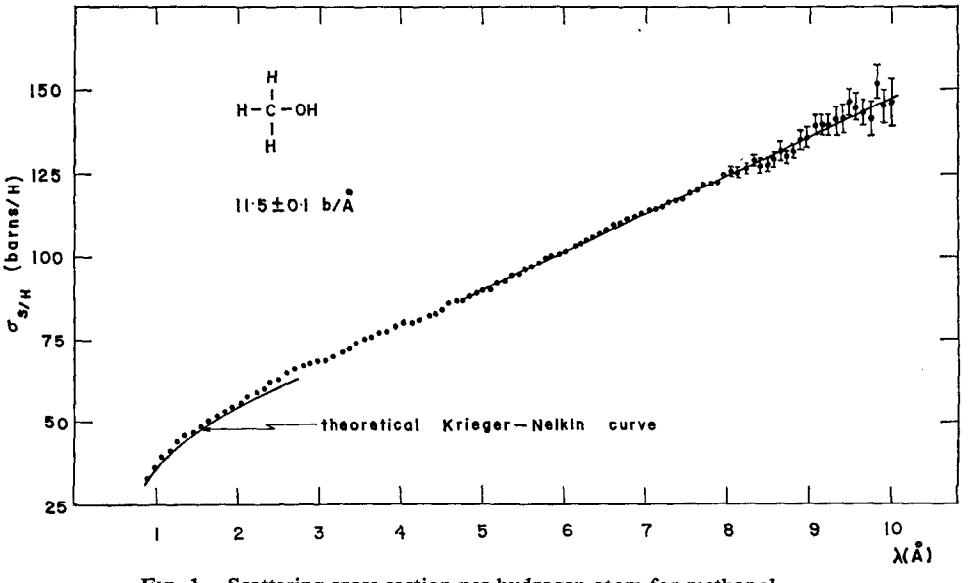

FIG. 1. Scattering cross-section per hydrogen atom for methanol.

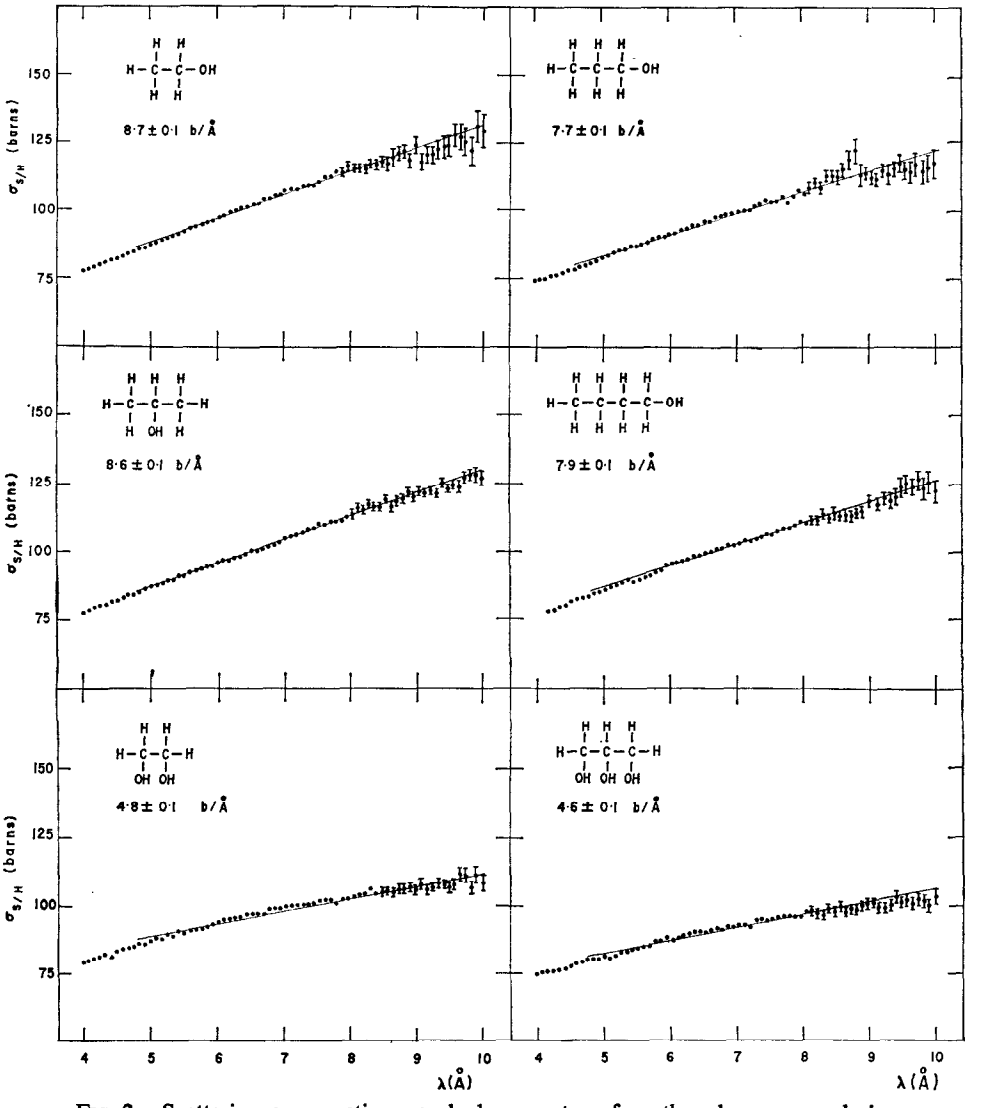

FIG. 2.—Scattering cross-section per hydrogen atom for ethanol, *n*-propanol, iso-propanol, *n*-butanol, ethanediol and propanetriol.

statistical errors are indicated. The slopes of the cross-section curves were calculated by a least-squares fit to the data in the wavelength range 4·8–10·0 Å.

Table 1 presents the slopes of scattering cross-section curves determined in this work and the results obtained by NASOHOGLU and RINGO (1960) and by RAPEANU *et al.* (1967) for some of the compounds investigated in the present work. As the behaviour of σ_s/H proportional to the neutron wavelength is reached only asymptotically, the value of the slope depends on the considered wavelength range.

Figure 1 also shows, in the small wavelength region, the theoretical scattering cross-section curve calculated (BOROWISKI, 1965) for methanol based on the Krieger–Nelkin (K–N) formalism, which is expected not to be valid for long wavelength neutrons.

TABLE 1.

	Slope of cross-section curve (b/Å)		
	This work (4·8–10·0 Å)	NASUHOGLU and RINGO (1960) (5–20 Å)	RAPEANU *et al.* (1967) (3–8 Å)
Methanol	11·5 ± 0·1	10·8	10·4 ± 0·3
Ethanol	8·7 ± 0·1	7·9	—
n-Propanol	7·7 ± 0·1	7·1	—
Iso-propanol	8·6 ± 0·1	—	—
n-Butanol	7·9 ± 0·1	—	—
Ethanediol	4·8 ± 0·1	—	—
Propanetriol	4·6 ± 0·1	—	5·6 ± 0·2

This formalism is applicable to freely rotating hydrogenous molecules or molecular groups provided $A \ll En < E$ vib, where E vib is the vibrational threshold energy and A is the rotational level spacing.

Our experimental results for methanol agree with this theoretical K–N curve only at energies higher than about 0·02 eV, what is reasonable since the rotational constant for methanol is 0·1 meV (BOROWISKI, 1965).

The high value of the scattering cross section per hydrogen atom of methanol is an indication that it can be an excellent cold neutron moderator. PERSSON (1967) shows that methanol has an efficiency of 75 per cent of the efficiency of methane (the best cold neutron moderator) with the advantage of being in the liquid state at room temperature.

The slope of methanol, 11·5 ± 0·1 b/Å, compared with the value of 12·7 b/Å for methyl groups with free rotation in the liquid state (HERDADE, 1968) evidences a small barrier for internal rotation of this group in methanol. Indeed, the barrier height in methanol obtained by microwave methods is 1·07 kcal/mol (WILSON, 1959).

Results obtained by FISHER (1970) on methanol using isotopic substitution technique, revealed for the CH_3 group a slope of 12·1 b/Å and for the OH group a slope of 3·4 b/Å.

We observed decreasing slopes for methanol, ethanol and *n*-propanol, and then an increase for *n*-butanol. This fact can be assigned to the contribution of torsional oscillations of methylene groups (SAUNDERSON and RAINEY, 1963).

Rapeanu *et al.* (1967) obtained for pentanol a slope value of 9·6 ± 0·2 b/Å and attributed the increase regarding the lower alcohols to the contribution of CH_2 motions to the scattering cross section.

The contribution of an individual group to the scattering will be independent of the molecule in which it is located if the interaction with neighbour groups is small. Hydroxyl groups have considerable inter- and intra-molecular effects, hence short hydrocarbon chain compounds show features anomalous to the regular changes observed as the chain length increases. Assuming to a first approximation that the hydroxyl group affects both the adjacent carbon and the second neighbour, only for *n*-butanol and higher alcohols one could speak of "free" methylene groups; therefore the change in behaviour observed.

The difference in the slopes obtained for *n*-propanol and iso-propanol can be

explained by the weaker hydrogen bonding of the second and the existence of two methyl radicals.

The polyhydric alcohols have very strong intermolecular hydrogen bonding in the liquid phase; the boiling points are about 100°C higher per hydroxyl groups than the monohydric alcohols. No free internal rotation exist. Therefore the large difference in the slopes for ethanol and ethanediol and for *n*-propanol and propanetriol observed.

Because of the rather large number of mechanisms contributing to a total cross-section, specific classification could only be made by a systematic study of a larger number of similar compounds.

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