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INIS Categories and Descriptors

A12

CROSS SECTIONS
DBP
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SLOW NEUTRONS
TBP

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ABSTRACT

Differences between the properties of TBP and DBP, concerning the uranium extraction processes, may be related to certain characteristics of the molecular dynamics of each compound. In order to investigate the dynamical behaviour of hydrogen in these molecules, neutron transmission of TBP and DBP has been measured as a function of neutron wavelength in the range 4.0–6.0$\overset{\circ}{A}$, at room temperature. Scattering cross sections per hydrogen atom have been obtained. From the comparison with results previously obtained for n–butanol, similar dynamical behaviour of butyl radicals in these compounds could be observed. This similarity indicates that the presence of two or three butyl radicals in butylphosphate molecules does not exert influence in the hydrogen motic of methyl and methylene groups. This suggests that the different chemical behaviour between TBP and DBP is related to the dynamics of the hydrogen directly bound to the DBP phosphate group.

I – INTRODUCTION

Tributylphosphate (TBP) is the most important extracting for reprocessing spent nuclear fuels, where it is the active ingredient of certain solvent extraction processes that take place in the presence of strong radiation fields[2].

Radiolysis of TBP is of technical interest, since TBP is sensitive to radiation exposure by forming degradation products that interfere with the extraction and stripping of uranium or plutonium. These liquid products from gamma radiolysis of TBP, of which dibutylphosphate (DBP) is poduced in the largest yield, exhibit the undesirable property of forming stable complexes with uranium or plutonium, which are difficult to separate from the organic phase by stripping. They also form stable complexes with some fission products like zirconium, niobium and ruthenium, thereby lowering the solvent decontamination[7,3].

The differences between the properties of TBP and DBP concerning the extraction processes may be related to certain characteristics of the molecular dynamics of each molecular compound. In this regard, in the present work neutron transmission measurements were carried out on TBP and DBP samples aiming to observe the dynamical behaviour of the butyl radical in both compounds and to compare with results for the n–butanol previously measured[8].

Slow neutron transmission measurements in hydrogenous compounds can give information on the rotational dynamics of molecules and molecular groups containing hydrogen atoms. For sufficiently slow neutrons (energy $\ll 0.025$ e V), neutron scattering is essentially incoherent and due to hydrogen atoms. From the total cross section, measured by neutron transmission, it is possible to obtain the incoherent scattering cross section per proton $\sigma_{S/H}$, that varies linearly with the neutron wavelength λ. The slope of this cross section straight line depends on the incoherent inelastic scattering that comes from processes in which the neutron gains energy from 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. The slope $\sigma_{S/H} \times \lambda$ increases with the freedom of motion of the H atoms. This slope has been empirically

correlated with the barrier hindering the internal rotation of defined molecular groups (NH_4 and CH_3) and it was possible to obtain some calibration curves[8,5].

Since TBP and DBP are large molecules, the contribution of rotational motions of the whole molecule can be neglected, the inelastic scattering being essentially due to internal rotations of methyl and methylene groups of butyl radicals. The present work was undertaken in order to investigate possible differences in the dynamics of molecules where the butyl radicals are present.

II – EXPERIMENTAL

The neutron source for this work was the IPEN swimming pool research reactor operated at 2Mw. The total neutron cross section of n–butanol has been previously measured[8] using a curved slit slow-neutron chopper and time-of-flight spectrometer that has been described elsewhere[1]. The cross section for n–butanol was measured in the neutron wavelength range from $4.0 - 10.0$Å, by performing transmission measurements in the usual way, with the sample in and out the pulsed beam.

Neutron transmission of TBP and DBP as a function of neutron wavelength λ in the range of $4.0 - 6.0$Å have been measured using the IPEN crystal spectrometer that has been described thoroughly in a previous paper[4]. A mica crystal monochromator and a beryllium polycrystalline filter were used to select only neutrons from first order Bragg reflections; the elimination of higher order contamination was checked by measuring the total cross section of water, used as standard.

The samples of all the mentioned compounds were investigated in the liquid phase at room temperature ($293°$K) and were placed in aluminium cells with 2.5 mm thickness.

The total neutron cross section is given by: $\sigma = \ln T^{-1}/n$, where T is the measured neutron transmission and n is the number of molecules/cm^2, obtained from the sample thickness and bulk density. The average scattering cross section per proton, $\sigma_{S/H}$, is obtained from the total cross section by subtracting the total absorption cross section, proportional to the neutron wavelength, and a constant scattering from the remaining atoms, known from tabulated values[6], and dividing by the number of H atoms in the molecule.

III – RESULTS AND DISCUSSION

The values of total neutron cross sections for TBP and DBP at room temperature, obtained from transmission measurements in function of the neutron wavelength λ are shown in Figure 1. These data, with only the statistical errors indicated, represent the result of an average of at least five independently measured values. For almost all the experimental values the errors are smaller than 2% and for long wavelengths, near 6.0Å where fifty series of transmission measurements were performed, error bars are smaller than the dimensions of the points.

From Figure 1 one can observe that the experimental values of total cross sections for the TBP molecule, $C_{12}H_{27}O_4P$, are higher than for the DBP molecule, $C_8H_{19}O_4P$. This increase in σ is mainly due to the greater number of hydrogen atoms present in TBP. The contribution to the scattering of one hidrogen atom when bound in molecules is dependent on neutron energy and generally for hydrogenous compounds it is approximately eighty barns near 4.0Å[8]. So, since TBP has eight hydrogen atoms more than DBP a large increase in the total cross section is expected. With respect to the excess of four carbon atoms of BP in comparison with DBP, one can expect small contribution since the scattering cross section of each carbon atom is only 4.8 barns. Although considered in the $\sigma_{S/H}$ calculation for both compounds, the contribution to σ of absorption cross sections of hydrogen and carbon can be neglected since their values are very small in the thermal energy region.

Scattering cross sections per hydrogen atom, $\sigma_{S/H}$, for the atom bound in the molecules, as a function of neutron wavelength, for TBP and DBP are plotted in Figure 2. The slopes of the cross section curves were calculated by a least-squares fit to the data in the wavelength range from $4.0 - 6.0$Å.
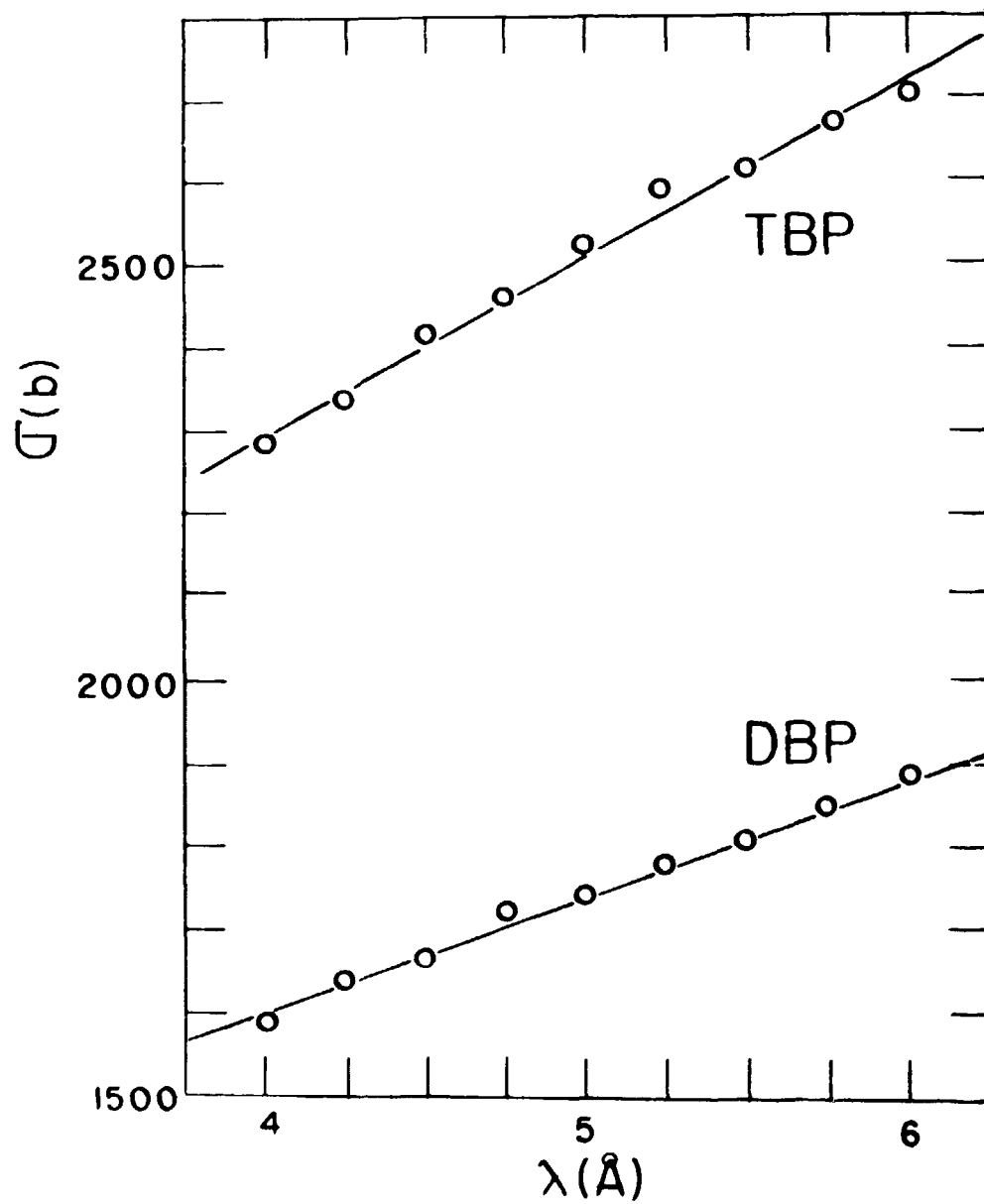

Figure 1 — Total Neutron Cross Section of TBP and DBP (σ in barn) Versus Neutron Wavelength (λ in Angstron).

Figure 3 shows the scattering cross section curve for n—butanol, measured previously[8] in the neutron wavelength range from 4.10.0Å. Table I presents the slopes of the scattering cross sections curves for all the hydrogenous compounc. .nentioned in this work.
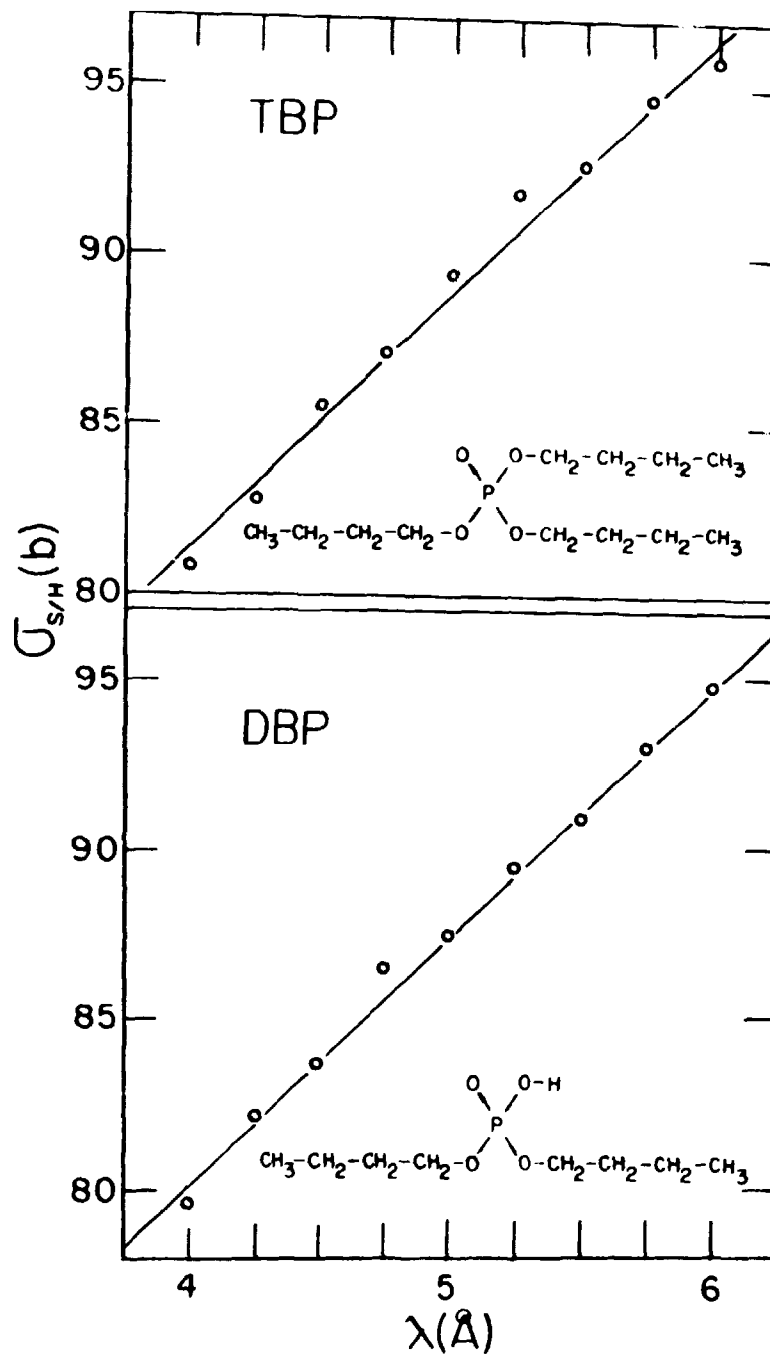

Figure 2 — Neutron Scattering Cross Section per Hydrogen Atom of TBP and DBP. The Straight Line Was Adjusted by Least-Square Fit.
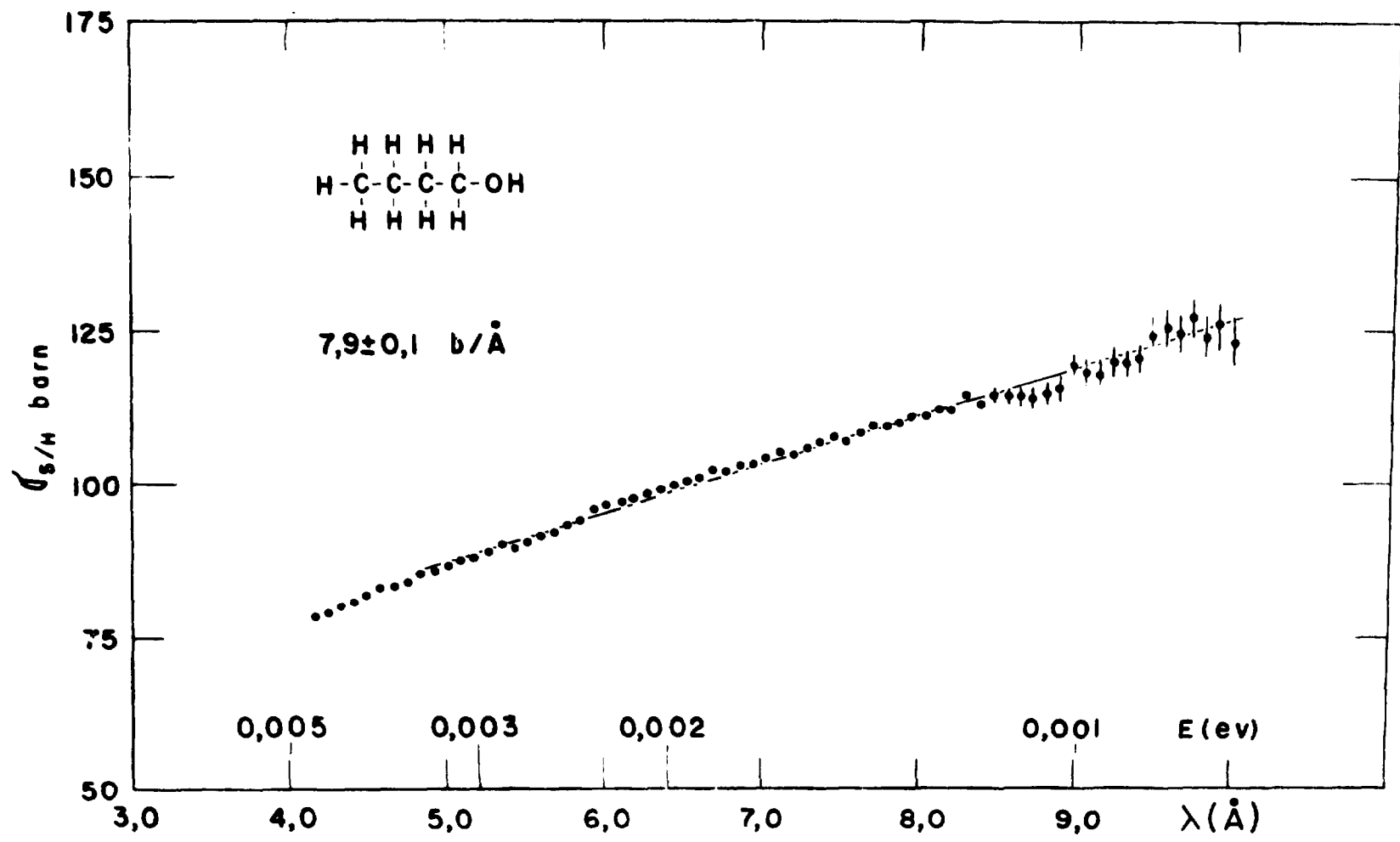
Figure 3 — Scattering Cross-Section per Hydrogen Atom for n—butanol.

Table I

SLOPE OF CROSS-SECTION CURVE (b/Å)	
Compound	Slope
TBP	7.6 ± 0.3
DBP	7.4 ± 0.3
n—butanol	7.9 ± 0.2

The experimental values of the slope for each compound are practically identical, therefore one is allowed to affirm that the dynamics of the butyl radical is similar in the three compounds. As the n—butanol molecules are associated in polymers by hydrogen bonding, the contr.bution of the rotational motions of the whole molecule to the scattering can be neglected. Then the scattering must be ascribed to the motions of methyl and methylene groups. The similarity of the dynamical behaviour for the butyl radicals in TBP and DBP are indicating that the presence of two or three butyl radicals in the butylphosphate molecules does not exert an influence in the hydrogen motion of methyl and methylene groups that are constituent of the radicals. So, our results may indicate that the different behaviour between TBP and DBP concerning the uranium extraction is not related with the butyl radical dynamics but rather probably to dynamical behaviour of the hydrogen directly bound to the DBP phosphate group.

RESUMO

As difereças entre as propriedades do TBP e DBP, com respeito aos processos de extração de urânio, podem estar relacionadas a certas características da dinâmica molecular de cada composto. Com o propósito de investigar o comportamento dinâmico do hidrogênio nessas moléculas, foram efetuadas medidas de transmissão de nêutrons através de amostras de TBP e DBP, à temperatura ambiente, em função do comprimento de onda do nêutron no intervalo de 4, 0—6, 0Å Foram determinadas as secções de choque por átomo de hidrogênio. A partir de comparações com resultados previamente obtidos para o n—butanol, foi possível observar que o comportamento dinâmico dos radicais butila é similar em todos os compostos. Esta similaridade indica que a presença de dois ou três radicais butila nas moléculas dos butilfosfatos não exerce influência no movimento dos hidrogênios dos grupos metil e metileno, sugerindo que o comportamento químico diferente entre o TBP e o DBP está relacionado à dinâmica do hidrogênio diretamente ligado ao grupo fosfato do DBP.

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