

LNF-90/114

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Estratto da: Conf. Proc. Vol. 25 XSR-89, A. Balerna, E. Bernieri, S. Mobilio (Eds.)
SIF Bologna, Pag. 941 (1990)

INTERACTION OF PROBES WITH MICELLES. AN X-RAY ABSORPTION STUDY

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Abstract: EXAFS measurements showed that the bromine K-edge spectra markedly differ in polar and nonpolar medium. These two types of spectra were systematically observed by using some brominated hydrocarbons in various samples. Thus, it is probable that many molecules with suitable probe atoms can be used both to monitor the polarity of the medium in which the probe atoms are buried and to provide information about the interactions between the probe atoms on the one hand and micelles, macromolecules, membranes, solvent molecules, host and guest molecules in inclusion compounds on the other.

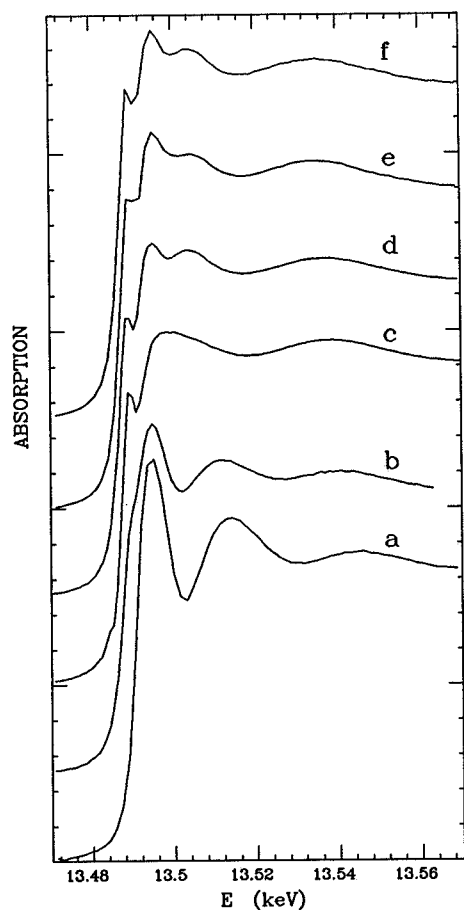
Structural features of the systems interacting with the probe atoms can be inferred. Among the others, micellar solutions of sodium and rubidium deoxycholate and sodium dodecyl sulfate containing the brominated hydrocarbons were investigated. Possible structural change of the micelle due to the probe molecule could be detected in some cases by studying two probe atoms on the same sample.

Probe molecules and ions are widely employed to obtain structural information by means of techniques as fluorescence, electron spin resonance, nuclear magnetic resonance and circular dichroism. Macromolecules, micelles, membranes, inclusion compounds and other molecular assemblies in the liquid and solid state are studied using very small amounts of the probe molecules in such a way as innocuously perturb their structures. The belief that the probe molecules are incorporated within the molecular assemblies is largely diffuse, so that it is often assumed that the probes sample the interior of the host assembly. The validity of this assumption is of paramount importance since, otherwise, an erroneous interpretation

can be inferred.

EXAFS and XANES measurements could monitor the medium surrounding the excited atom or ion. In fact, suppose that the excited atom is embedded in a polar medium formed by water molecules or in a nonpolar medium characterized by methylene and methyl groups. Neglecting the hydrogen atoms, the neighbors of the probe are oxygen or carbon atoms at distances generally different in the two cases and, reasonably, also the oscillations of the absorption coefficient above the K-edge of the probe will be different. Therefore, we decided to check if the EXAFS and XANES spectra are typical for each of these two situations by using bromine atoms and ions as probes.

Thus, the bromine K-edge of 2-bromopropane and 1- and 2-bromobutane (BP2, BB1 and BB2, respectively) solubilized in aqueous micellar solutions of sodium and rubidium deoxycholate and sodium dodecyl sulfate (NaDC, RbDC and SDS, respectively) was investigated. The preservation of the RbDC



micellar structure (1,2) was checked by monitoring the rubidium K-edge of a RbDC aqueous micellar solution containing bromobenzene, a molecule strongly interactive with the angular methyl groups of the steroid molecule. No difference was observed if the spectrum is compared with that of RbDC without bromobenzene.

Subsequently, the spectra of the brominated hydrocarbons in n-hexane, methanol and water showed two representative spectra. One, indicated as nonpolar, is recorded in n-hexane, and the other, indicated as polar, in water, for example. These two types of spectra differ from that of BP2 gas, due to intramolecular contributions only (Figure 1 collects some spectra as an example), and, reasonably, are influenced by the solvent molecules.

Figure 1: X-ray absorption (arbitrary units) around the K-edge of bromine versus energy : RbBr in water (0.15M) (a), BP2 in water (~40mM) (b), BP2 gas (c), BP2 in n-hexane (0.15M) (d), BB2 in methanol (0.15M) (e), BB2 in n-hexane (0.15M) (f).

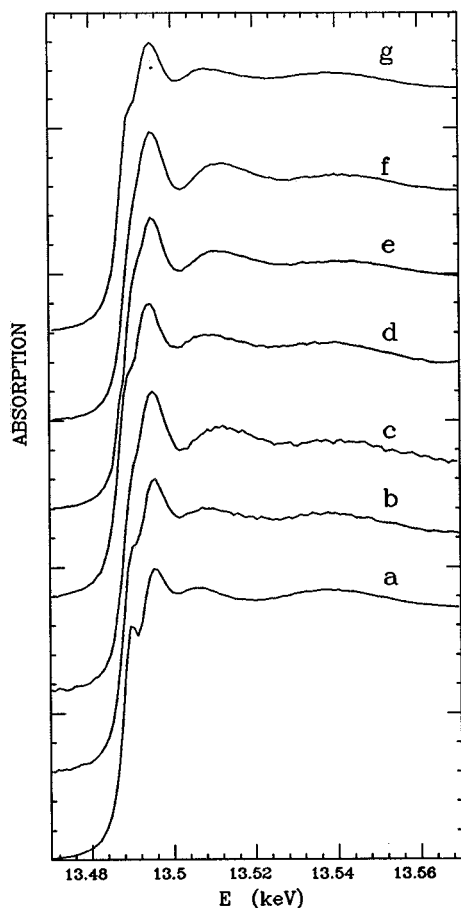


Figure 2: X-ray absorption (arbitrary units) around the K-edge of bromine versus energy: BP2 (60mM) in RbDC (0.20M) (a), BP2 (20mM) in RbDC (0.20M) (b), BP2 (~10mM) in RbDC (0.18M) (c), BP2 (23mM) in NaDC (0.20M) (d), BB1 (23mM) in NaDC (0.20M) (e), BP2 (20mM) in SDS (0.15M) (f), BB2 (46mM) in SDS (0.20M) (g).

It is interesting to note that the spectrum of BB2 in methanol is nonpolar in agreement with a Br atom surrounded by methyl groups and, perhaps, by one or more Br atoms if the BB2 molecules associate. The polar spectrum results very similar to that of Br⁻ in water (see Figure 1, RbBr in water), whereas the nonpolar one presents a pre-edge peak, generally attributed to 1s → 4p electronic transitions, which gradually disappears passing from nonpolar to polar spectra. Moreover, the first oscillation peak approaches the continuum threshold decreasing the polarity of the medium. Some representative spectra of the brominated hydrocarbon-micelle systems are reported in Figure 2 as an example. Mainly, the behaviour

of BP2 is shown. The polarity of the medium surrounding the bromine atom seems to decrease by increasing the BP2 concentration in aqueous micellar solutions of RbDC, which behaves similarly to NaDC. Probably, at BP2 concentrations less than 10 mM the hydrocarbon, slightly soluble in water, is surrounded by water molecules, and the Br spectrum is polar. At higher concentration of the hydrocarbon the Br atoms could interact with the hydrophobic region of the steroid molecule containing the angular methyl groups and two hydrogen atoms belonging to C₈ and C₁₁. Furthermore, the hydrocarbon promotes the aggregation and, hence, the precipitation of NaDC and RbDC. Thus, the aggregation of helices could form hydrophobic canals or pockets where the hydrocarbon molecules are accommodated.

A similar situation is observed for SDS, even though the hydrocarbon concentration must be greater than in the NaDC or RbDC case in order to obtain the same effect. However, the

classical structure of the SDS micelle, polar in the outer surface, requires a different mechanism. In fact, if the structural model is correct, the Br atoms at lower concentrations are surrounded by oxygen atoms of water molecules and/or of sulfate groups, whereas at higher concentrations are incorporated within the micelles.

Work is in progress to clarify some dubious points and to interpret the spectra by assuming some structural models.

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