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^{13}C-NMR Analysis of Polyoxyethylenated Surfactants

C. Corno, E. Platone and S. Ghelli

Assoreni, Physical Chemistry Dept., 20097 San Donato Milanese, Milano, Italy

SUMMARY

^{13}C NMR spectroscopy at 75.46 MHz gives interesting information about the micellar aggregates in aqueous solutions of nonionic oxyethylenated surfactants.

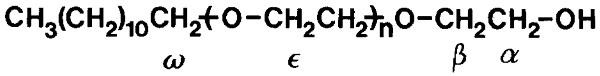
The carbon atoms of the ethoxy chain exhibit different chemical shifts depending on the length of the ethoxy chain. This behaviour seems to be related to conformational effects, in particular to the so called gauche-γ effect.

It is well known that nonionic oxyethylenated surfactants form micellar aggregates of differing size and shapes in aqueous medium. These systems have been extensively studied with the help of several techniques, ^{1}H and ^{13}C NMR included (DENNIS and RIBEIRO 1979, RIBEIRO and DENNIS 1976, RIBEIRO and DENNIS 1977, CHRISTENSON et al. 1981, PODO et al. 1973).

Recently we synthesized both polydisperse polyethyleneglycol-dodecanol ethers ($DDE_{\bar{n}}$ where $\bar{n}$ is the average number of ethoxy units) and a homologous series of monodisperse substances (DDE_n) having n=2,3 ...10.

We investigated by ^{13}C NMR spectroscopy aqueous solutions of single surfactants and some suitable mixtures of the same. These solutions, if the oxyethylene content is below about 50% ($\sim$ n=5), are turbid at room temperature, being above their cloud point (LINDMAN and WENNERSTROM 1980), and the resulting ^{13}C spectra show broad lines. On the contrary, the analysis of clear solutions ($n > 5$) gives interesting results since the carbon atoms of the ethoxy chain exhibit chemically shifted resonances sensitive to the micellar structure.

Fig. 1A) shows the resonance region of the methylene carbons in α position to an oxygen atom of the DDE_8 compound. The chemical shifts and the assignments of the peaks to the carbon atoms α, β, ω and ϵ



$$\mathrm{CH_3(CH_2)_{10}}\underset{\omega}{\mathrm{CH_2}}\!\left(\mathrm{O-}\underset{\epsilon}{\mathrm{CH_2CH_2}}\right)_{n}\mathrm{O-}\underset{\beta}{\mathrm{CH_2}}\underset{\alpha}{\mathrm{CH_2}}\mathrm{-OH}$$

are reported in table I.

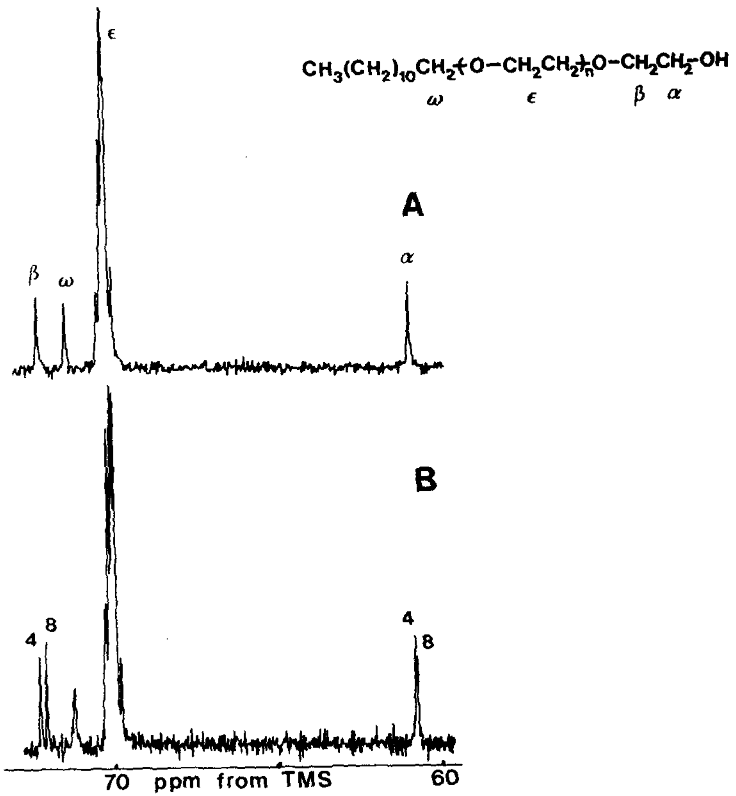


Fig.1-^{13}C NMR spectrum of: A) DDE_8, B) DDE_8+DDE_4. Region of the methylenes in α to an oxygen atom.

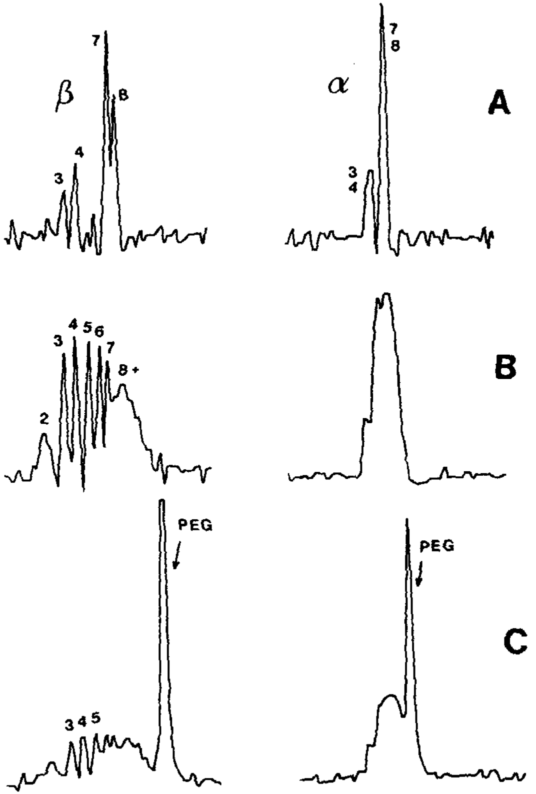


Fig.2-^{13}C resonances of the β and α carbons of: A) DDE_3+DDE_4+DDE_7+DDE_8, B) $\mathrm{DDE}_{\overline{6.5}}$ C) $\mathrm{DDE}_{\overline{6.5}}$+PEG

TAB. I - Chemical shifts of the methylenes in α to an oxygen atom in the ^{13}C NMR spectrum of DDE_8
(75.46 MHz, 0.2 mol/l solution in D_2O at 30°C)

	α	β	ω	ϵ
Chemical shift (in ppm from TMS)	60.77	72.21	71.36	70.15

The fine structure (not assigned by us) of the signal of the ϵ carbons is more complicated than the structure shown in the spectra reported in previous literature (RIBEIRO and DENNIS 1977), because of the high frequency (75 MHz) of the instrument used by us.

Fig. 1B shows the same region of the spectrum of a 50/50 mol mixture of DDE_8+DDE_4. The resonances of the α and β carbons split into doublets and a downfield shift is evident in the case of the two carbons belonging to the DDE_4 compound.

A similar behaviour was observed in the spectrum (fig. 2A) of a mixture of DDE_3, DDE_4, DDE_7 and DDE_8 whose composition is rich in DDE_7 and DDE_8 in order to maintain the solution well below the cloud point. Four peaks are evident for the β carbons while a doublet signal is observed for the α carbons. A downfield shift characterizes the shortest polyoxyethylene chains and this result is confirmed by the spectrum of a polydisperse $DDE_{\bar{n}}$ ($\bar{n}$=6.5) (fig. 2B).

The most interesting part of this spectrum is evidently the resonance of the β carbon. On the basis of the previous spectra the assignment of the peaks according to the sequence shown in the figure appears obvious. At high field the signals of the products having $n > 8$ overlap the peak of DDE_8 and resolution is lost.

Regarding the signal of the α carbon, it becomes broad and a fine structure is almost absent, because the shift changes are evidently too small.

The shieldings of the β and α carbons obtained by increasing the length of the ethoxy chain seem to be related to conformational effects, in particular to the γ effect (GRANT and CHENEY 1967).

It is known that in alkanes an upfield shift of the resonance of a carbon atom is associated with the introduction of a gauche γ-substituent, this shift being attributed to non bonded interactions between the hydrogens on the carbon in question and on the γ-substituent. In the trans conformation this contribution is assumed to be negligible. Therefore a change of the ratio of gauche and trans conformers is accompanied by resonance variations, in particular an increase of the trans conformation involves a downfield shift.

In our case we can infer that micelle formation increases the relative population of trans conformers. Regarding the oxyethylene terminal unit, the conformational change seems to be dependent on the distance from the hydrophobic core of the micelle.

If n is small (2,3,4 .....) the fraction of trans conformers is high while in the case of long ethoxy chains ($n > 8$) the terminal unit tends, in a continuous way, to the situation of the free molecule. In fact (fig. 2C) the chemical shifts of the α and β carbons of a low molecular weight (~ 400) polyoxyethylene (PEG) (which evidently does not form aggregates) appear at the upper limits of the resonance regions of the two carbon atoms.

Table II presents the chemical shifts of the β carbons of DDE_n and PEG

TAB.II - Chemical shift of the β carbons in DDE_n and PEG

n	2	3	4	5	6	7	8	PEG
δ	72.54	72.44	72.39	72.33	72.28	72.25	72.21	72.04

The upfield shift linked with micelle formation was observed for carbons of alkyl chains of many surfactants (PERSSON et al. 1976, ROSENHOLM et al. 1978, MAEDA et al. 1980). In general the change was maximal for the carbons in the middle of the chain and relatively small for those at the end. In our case the β carbon exhibits a much larger shift with respect to the α carbon while it is difficult at present to clarify the behaviour of the carbons in the middle of the chain because of the complexity of their signals.

Studies are in progress in this sense, in particular with monodisperse compounds having $n > 10$, in order to verify the transition between the zig-zag form and the "meander" form proposed for the ethoxy chain, depending on the degree of alkoxylation (AKSTINAT 1981, ROSCH 1971).

However, besides the information about the structure of the micellar aggregates, the results obtained are useful from the analytical point of view. In fact ^{13}C NMR analysis of aqueous solutions permits to study the dispersion of polyoxyethylenated surfactants and to identify possible free polyglycol in a way that is both simple and accurate, also if the alcohol is a mixture of different molecular weights and of linear and branched isomers.

EXPERIMENTAL PART

Polyethoxylated alcohols have been synthesized from n-dodecanol and ethylene oxide, at 150°C, with 0.2wt% of KOH as catalyst. The products have been extracted with ethyl acetate/saturated aqueous NaCl solution in order to remove polyglycols; unreacted alcohol has been distilled off under vacuum. The mean degree of ethoxylation has been confirmed by chemical methods and NMR analysis.

Monodisperse ethoxylates have been obtained by a modified Williamson reaction of n-dodecylbromide and polyglycols of suitable length. Higher ethoxylates ($n > 4$) have been prepared in several steps, reacting the same polyglycols ($n = 2,3,4$) with the chlorides obtained from lower ethoxylates and $SOCl_2$.

Final purity higher that 99% has been achieved by vacuum distillation and/or crystallization from diethyl ether, and tested by GLC on silylated samples.

^{13}C NMR spectra were obtained at 75.46 MHz on a BRUKER CXP-300 from solu-

tions 0.2 mol/l in D_2Oat 30°C. The critical micellar concentrations (CMC) of these products are in the range 10^{-5}-10^{-4} mol. (BRANDRUP and IMMERGUT 1975) well below our working concentration. Proton noise decoupling and deuterium lock were used. The FT conditions were: Spectral width 7500 Hz, acquisition time 1.098, recycling time 3 sec., 90° pulse (26 μ sec.), number of scans. 2000, Hz/point 0.911.
Chemical shifts are reported in ppm from TMS by assuming that the shift of the methyl carbon of dodecanol is 14.1 ppm downfield the TMS. In some cases, for resolution enhancement, a moderate Gaussian multiplication (GM) was used.

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