Original Article

Effect of *Magnesium phosphoricum* 12c on sodium dodecylsulphate by ^{13}C nuclear magnetic resonance

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ABSTRACT

Sodium dodecylsulphate (SDS) dissolved in water forms aggregates whose thermodynamic properties are well defined. The interest in polymer-surfactant systems derives from increasing possibilities to apply them in pharmaceutics, cosmetics and environmental protection. Nutrient content of soils after many years of use is a concern in many areas; on the other hand, the metabolism of plants approaches equilibrium when the conditions necessary for their growth are present. Magnesium and phosphorus are important nutrients for plants and high dilutions of *Magnesium phosphoricum (Mag-p)* may carry information related to them. **Aims**: To study the influence of *Mag-p* on SDS aggregates. **Methods**: the effect of *Mag-p* dilution 12c on the structure of SDS aggregates was assayed through ^{13}C nuclear magnetic resonance. **Results**: The spectrum of SDS and *Mag-p* 12c in D_2O presented an extra signal in 221.41 ppm when compared to the SDS / D_2O spectrum. The C=O group of ketones and aldehydes absorb around 200 ppm. The carbon carbonyl shows large spin-lattice relaxation times (T1) and weak NOE (Nuclear Overhauser Effect) enhancement, thus signal from this type of atom are very weak when compared to signals from carbon atoms with hydrogen. The signal present in 221.41 ppm was comparable in size to the other signals in the spectrum indicating that it was not a machine-generated artifact. The experiments carried out in this work suggest that this signal was induced by a combination of SDS and the high diluted solution.

Keywords High Dilution, Sodium Dodecylsulphate, Magnesium phosphate; NMR

Introduction

Biological activity of substances used for therapeutic purposes are due to local interactions of their active principles with specific biomolecules (enzymes, receptors, etc). Consequently, such activity seems improbable when solutions do not contain one single biologically active molecule, viz. high dilutions (HDs). This allows suggesting that the effects of HDs on biological systems are similar to resonance between electromagnetic waves [1]. Most published results of physical-chemical measurements involving HDs could be neither predicted not reproduced [2,3]. The same applies to nuclear magnetic resonance (NMR) spectroscopy [4-7] which therefore could not be shown to be effective for demonstrating differences between remedies and controls.

On the other hand, HDs have been proposed as an alternative in the optimization of intake of nutrients in plants. Lack or excess of some nutrients is a problem in many areas after soils have been used for years. Magnesium and phosphorus are important nutrients for the plants and it has been suggested that HDs of magnesium phosphate - *Magnesium phosphoricum (Mag-p)* – carries the information of these nutrients [8].

Sodium dodecylsulphate (SDS) - $C_{12}H_{25}OSO_3Na$ -, probably the most researched anionic surfactant, is used in household products due to its thickening properties and its ability to make foam. The molecule has a tail of 12 carbon atoms, attached to a sulphate group, giving the molecule the amphiphilic properties required of a detergent [9,10]. (Figure 1)

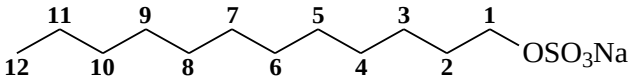

Figure 1. Structure of SDS ($C_{12}H_{25}OSO_3Na$)

SDS dissolved in water forms aggregates whose thermodynamic properties are well known as well as the association of SDS with inorganic salts and polymers. The interest in polymer-surfactant systems comes from the increasing possibilities of applying them in pharmaceutics, cosmetics and environmental protection as the properties of mixed surfactants are often better than in their individual states, thus justifying the interest in new systems [11-16]. This study aimed to observe the effects of *Mag-p* 12c on a solution of SDS in deuterium oxide by by ^{13}C NMR.

Materials and methods

Glassware and spatula were washed with detergent and running tap water followed by rinsing with distilled water and ethanol. They were kept for two days in aqueous 70% ethanol and dried at 70 ^{o}C for 1 hour.

The first solution was prepared from Magnesium monohydrogenphosphate dihydrated (1g, Vetec) dissolved in ethyl alcohol 90% (99 ml) and transferred to a 30 ml amber vial. In order to prepare *Mag-p* 1c, 0.12 g of the first solution was diluted in ethyl alcohol 70% (20 ml) in a 30 ml amber vial. The vial was capped and steadily shaken 100 times by mechanical shaker. The same procedure was successively repeated to obtain *Mag-p* 10c which was kept in a capped amber vial was wrapped in aluminum foil and stored at room temperature.

Preparation of *Mag-p* 11c in D_2O started from sample 10c, of which 0.012 g was diluted in deuterium oxide (2.0 ml) in a 30 ml amber vial. The vial was capped and steadily shaken 100 times in a mechanical shaker to produce *Mag-p* 11c in D_2O which was immediately used to prepare sample 12c, by following the same procedure. Sample 12c in D_2O was prepared just before use.

Control samples *Mag-p* in H_2O were also prepared from sample 10c, according to the same procedure used for D_2O samples. All samples were prepared (in triplicate) according to the standards of the Brazilian homeopathic pharmacopoeia [17].

SDS (20 mg, 99+%, Sigma-Aldrich) was weighed in 10 ml vials, dissolved in deuterium oxide (0.7 g, 99.9%, Cambridge Isotope Laboratories, Inc.) and transferred to a 5 mm NMR tube for obtaining the spectra.

^{13}C NMR spectra were obtained in Varian Mercury 300 MHz equipment and to the SDS signal was assigned the shift of 22.69 ppm (Figure 2). Spectra were obtained with temperature control (25^{o}C), 1.132 seconds delay, 0.868 seconds acquisition time, 1024 transients and pulse of 45^{o}.

Results and discussion

^{13}C NMR of SDS in D_2O was obtained to verify its purity and eliminate any suspicion of contamination of SDS and D_2O. Therefore, any alteration in the SDS spectrum after the addition of the HD sample addition could be realized by the presence of new signals, coalescence of signals, SDS chemical shift modification (Figure 2).

Mag-p 12c in distilled water (0.003 g) freshly prepared was added to a vial containing SDS (0.020 g) and D_2O (0.70 g). The solution was gently stirred to avoid foaming and transferred to the NMR tube. ^{13}C NMR of this solution was obtained by employing the same conditions as to obtain the SDS/D_2O spectra. This spectrum presented an extra signal in 221.51 ppm compared to the neat SDS / D_2O spectrum. The tiny amount of *Mag-p* 12c (0.003 g) did not modify the chemical environment of the solution in a way to alter in great extension the relative positions of the SDS signals. (Figure 3).

Mag-p 12c in deuterium oxide (0.70 g) freshly prepared was added to a vial containing SDS (0.020 g). The solution was gently stirred to avoid foaming, and transferred to the NMR tube. ^{13}C NMR of this solution was obtained by employing the same conditions as to obtain the SDS/D_2O spectra. (Figure 4)

This spectrum presented a strong extra signal in 221.41 ppm compared to the neat SDS / D_2O spectrum. This signal was much larger than the same signal displayed in the spectrum of SDS plus 0.0030 g of *Mag-p* 12c in distilled water. It can be understood as corresponding to the SDS dissolved in the HD. In the first case (SDS+12c in D_2O) the concentration of high diluted magnesium phosphate was higher than in the second (SDS+D_2O+12c in water), producing a stronger NMR signal, unrelated to the D_2O concentration.

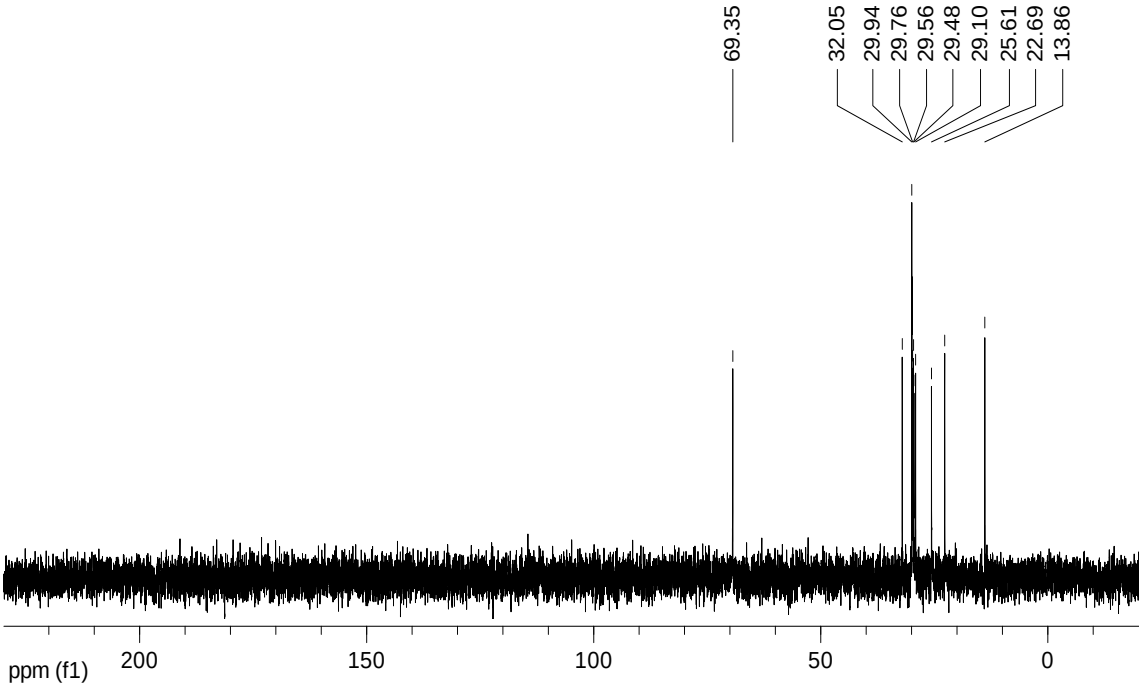

Figure 2. ^{13}C NMR of SDS (0.020 g) in D_2O (0.70 g)

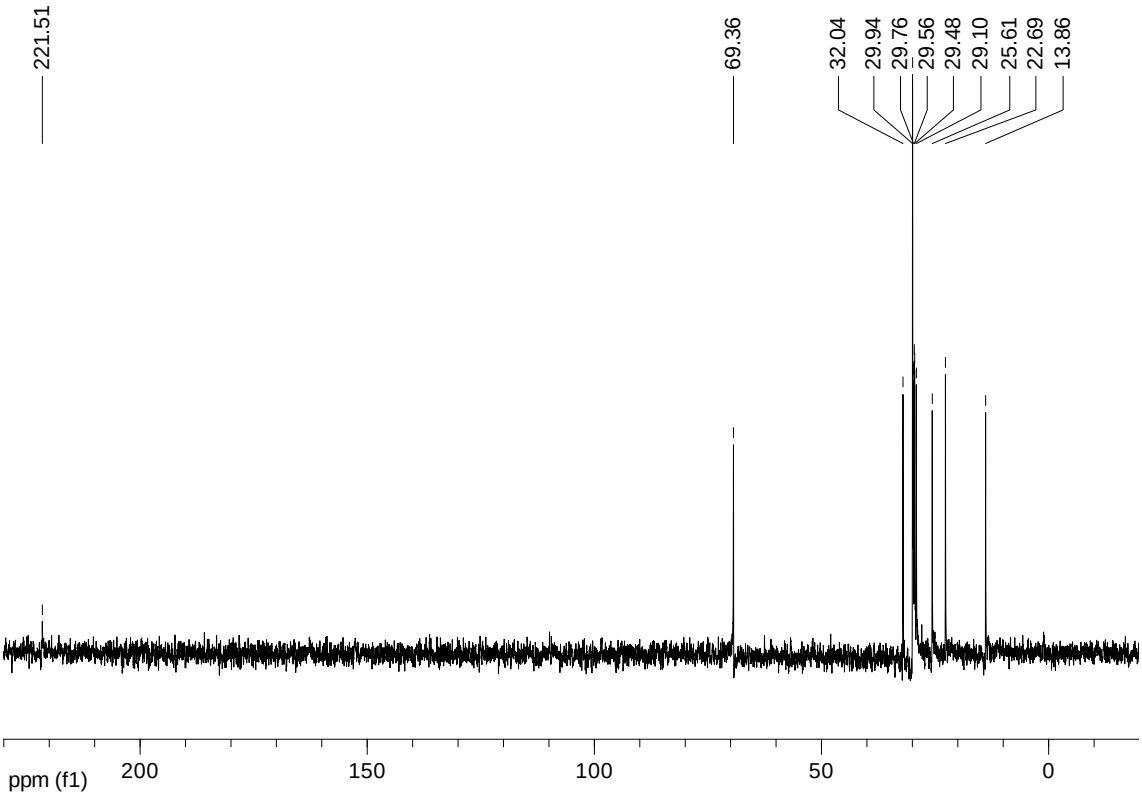

Figure 3. ^{13}C NMR of SDS (0.020 g) in D_2O (0.70 g) plus 0.0030 g of *Mag-p* 12c in H_2O.

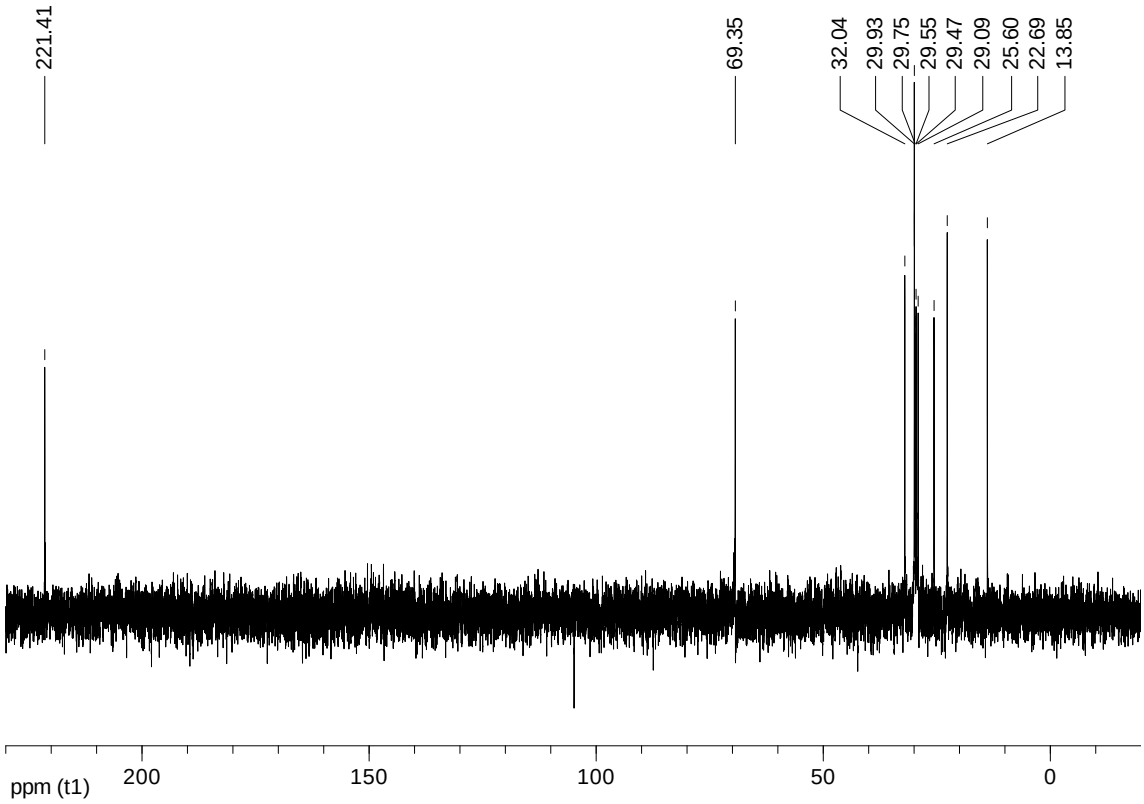

Figure 4. ^{13}C NMR of SDS (0.020 g) in 0.70 g of *Mag-p* 12c in D_2O.

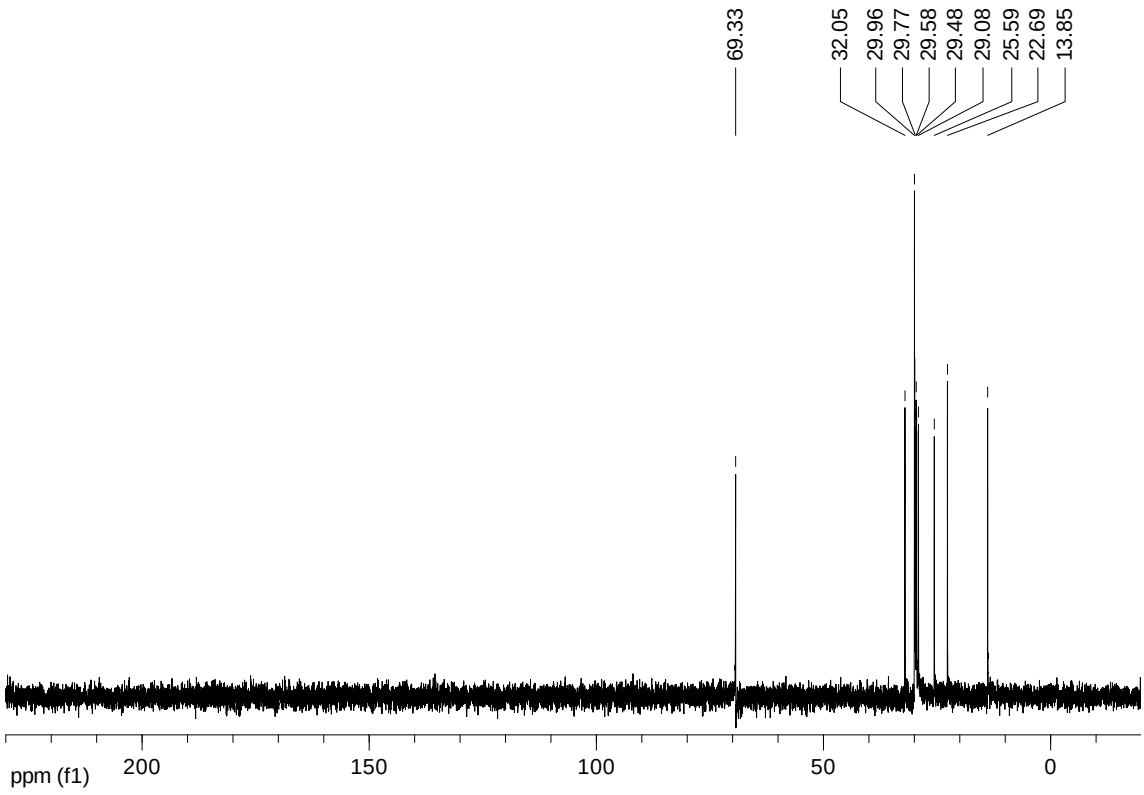

Figure. 5 ^{13}C NMR of SDS (0.020 g) in D_2O (0.70 g) plus 0.0030 g of *Mag-p* 12c in H_2O after 5 days.

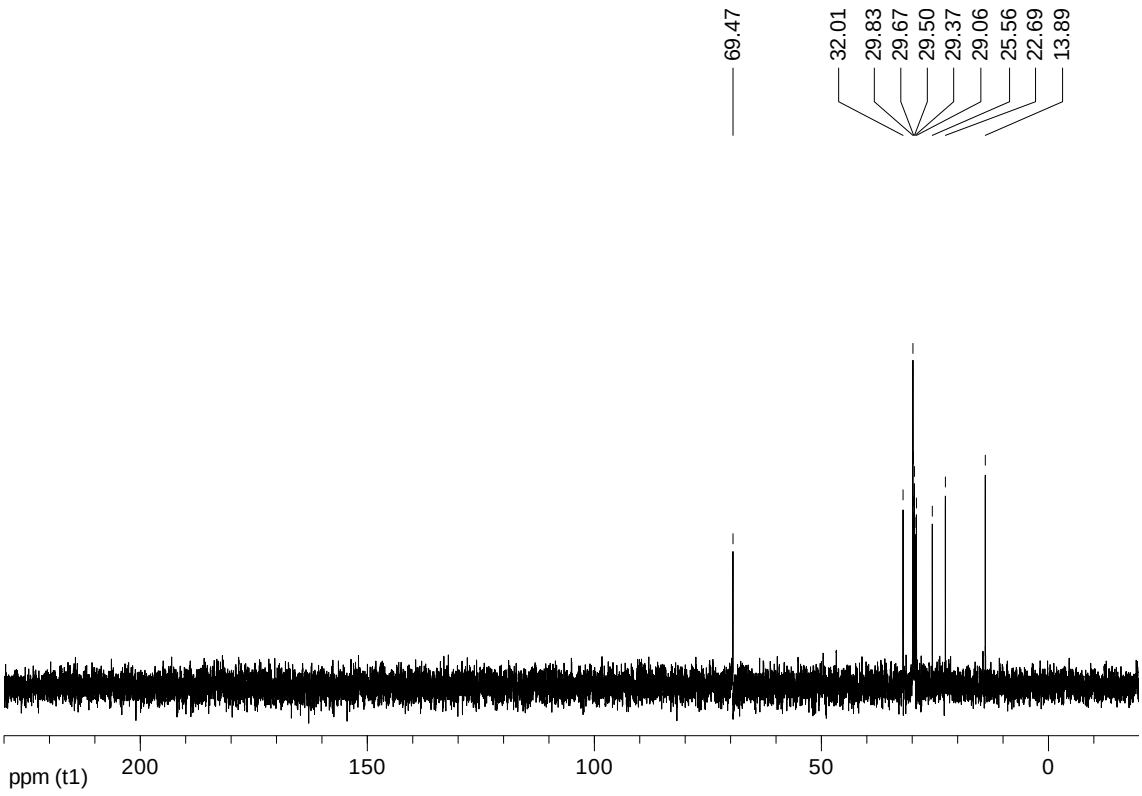

Figure. 6 ^{13}C NMR of SDS (0.020 g) in 0.70 g of *Mag-p* 12c in D_2O after 5 days.

The C=O group of ketones and aldehydes absorbed around 200 ppm. The carbon carbonyl displayed large spin-lattice relaxation times (T1) and weak NOE enhancement, thus signal from this type of atom are very weak compared to signals from carbon atoms with hydrogen. The signal present in 221.41 ppm was comparable in size to the other signals in the spectrum (from SDS) suggesting that it was not a machine-generated artifact. The experiments carried out in this work suggest that this signal was induced by a combination of SDS and the high diluted solution.

The samples of SDS/*Mag-p* were kept in their respective NMR tubes for 5 days. The NMR tubes were wrapped in aluminum foil and kept in an air conditioned room (22 ^{o}C) away from other chemicals, cellular and computer electromagnetic interferences. The spectra of SDS/*Mag-p* 12c (in either deuterium oxide or distilled water) did not display the extra signal. (Figures 5 and 6).

This suggests that the signal close to 221 ppm was not due to any kind of stable contamination or chemical species; otherwise the extra signal would have still been present in the spectra after 5 days. The coalescence of the extra signal after 5 days shows that the SDS-high dilution complex had changed through an unidentified channel, maybe due to the typical water dynamics [3,18,19]. Furthermore, the strong signal close to 221 ppm, a region where signals are generally weak, its reproduction (measured in triplicate) and its absence in the control samples weaken the possibility of experimental artifacts.

Conclusions

The peaks close to 221 ppm were observed only for samples containing high diluted *Mag-p*, both in H_2O as D_2O. These signals are comparable in size to the SDS ones, especially when D_2O HD was used. (Figure 4) The coalescence of such peaks after 5 days, returning the spectra to the control-pattern may indicate the existence of an metastable state, probably related to distilled water dynamics. If the peak were due to an instable contamination, degradation products would have been observed in the samples, which was not the case.

We conclude that the extra signal was induced by a combination of SDS and the HD, as this signal was not observed in the SDS/D_2O NMR (control samples). Furthers studies will be performed in order to unfold this hypothesis.

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Support: authors declare that this study received no funding
Conflict of interest: authors declare there is no conflict of interest
Received: 01 Dec 2008; Revised 03 Mar 2009; Published: 31 03 2009
Correspondence author: Elson Santiago de Alvarenga, elson@ufv.br
How to cite this article: Alvarenga ES, Oliveira APM, Silva RTB, Casali VWD. Effect of *Magnesium phosphoricum* 12c on Sodium Dodecylsulphate by ^{13}C Nuclear Magnetic Resonance [online]. 2009 [cited YYYY Month dd]; 8(26): 3-8. Available from: http://www.feg.unesp.br/~ojs/index.php/ijhdr/article/view/324/379.