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# How does $\beta$-cyclodextrin affect oxygen solubility in aqueous solutions of sodium perfluoroheptanoate?

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**Abstract**

The solubility of oxygen in aqueous solutions of sodium perfluoroheptanoate (NaPFHept) at different concentrations was measured at 310.15 K with an apparatus based on the saturation method. The effect of adding $\beta$-cyclodextrin ($\beta$CD) on the solubility of oxygen was also studied. Conductimetry measurements showed that the presence of $\beta$CD in aqueous solutions of NaPFHept increases its critical micellar concentration (CMC). In the presence of $\beta$CD (15 mM), the characteristic minimum of oxygen solubility observed at the CMC is shifted from 83 to 114 mM, and the curvature at the minimum is reduced to 64% of the value in the absence of $\beta$CD. Chemical shift changes for the H5 protons of $\beta$CD, recorded as functions of the initial concentration of NaPFHept, point to the formation of a relatively strong 1:1 inclusion in $\beta$CD of the perfluoroheptanoate anion. Hence, it is suggest that the effect of adding $\beta$CD on the solubility of oxygen cannot be accounted for only by the perfluoroheptanoate anion inclusion in $\beta$CD, but has to be ascribed to the direct influence of this inclusion complex on disrupting the aggregation process reducing the increase of oxygen solubility after the CMC value.


*Keywords:* Sodium perfluoroheptanoate; $\beta$-Cyclodextrin; Oxygen solubility; Aqueous solution; Self-aggregation; Inclusion; NMR chemical shifts

## 1. Introduction

Perfluorosurfactants are a special and interesting class of surfactants when compared with their hydrogenated counterparts. Their CMC values are lower than for the corresponding hydrogenated surfactants and close to those of ordinary surfactants whose hydrocarbon chain lengths are about 1.5 times longer than in their fluorocarbon counterparts [1,2]. Strong hydrophobic and weak van der Waals interactions exhibited by fluorinated chains dramatically increase the tendency of fluorinated amphiphiles to self-assemble in water and to collect at interfaces, displaying strong surface activity [3]. They are powerful wetting agents and indispensable as emulsifiers in many industrial applications, including emulsion polymerization of chlorocarbons and fluorocarbons, and in a variety of biomedical applications, including the development of oxygen-carrying fluorocarbon emulsions, pulmonary drug and gene delivery [3,4]. The broad applications of fluorinated compounds together with their extreme inertness are responsible for an environmental concern that is starting to appear in the literature. In fact, it has been reported that quantifiable levels of perfluorinated carboxylic acids are found in polar bears both in Western and Eastern Arctic, Canada, revealing that these compounds persist in the environment and may represent a problem in the near future [5]. Therefore, knowledge of the fundamental physical properties of fluorinated compounds is necessary to understand how these materials move through the environment and to advance possible treatments for their removal from contaminated areas.

Highly fluorinated compounds are strongly hydrophobic. Hence, their study in aqueous solutions is only possible if they are modified to increase their solubility in water. In the case of fluorinated acids, the corresponding salts are used since they are soluble in aqueous media. Other attempts to solubilize highly fluorinated compounds in aqueous media may consist of their inclusion into cyclodextrins [6–8]. The ability of cyclodextrins (CDs) to include guests of suitable size is a consequence of the shape of their cavity (a hollow truncated cone), as this provides

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a number of close contacts with the guest, thus increasing the dispersion energy of the host–guest interaction [9,10].

Cyclodextrins originate a large variety of supramolecular host–guest inclusion compounds with a diversity of organic and inorganic guests including aromatic and aliphatic hydrocarbons [11–16], aromatic compounds containing varying degrees of fluorine substitution [17], and perfluorocarbon-substituted surfactants [18–21]. In the last case, studies have concluded that the inclusion strongly depends on the cavity diameter [22–24]. A detailed NMR investigation for the association of four anionic fluorocarbon surfactants with $\alpha$, $\beta$, and $\gamma$CD has concluded on the formation of 1:1 inclusion complexes [11–16,18–21]. Association constants for 1:1 complexes follow the order $\beta\text{CD} > \gamma\text{CD} \gg \alpha\text{CD}$, suggesting that the fluorocarbon chain cannot fit into the cavity of $\alpha$CD, fits snugly inside the cavity of $\beta$CD and loosely inside the cavity of $\gamma$CD [18–21]. Since the cavity interior is less polar than the aqueous phase, the inclusion of a fluorocarbon chain reduces the amount of the fluorocompound in interaction with the aqueous environment, thus being energetically favorable. The main driving force for the inclusion of perfluorosurfactants in CDs is the hydrophobic interaction, eventually leading to close contacts between the fluorine atoms of the fluorocarbon chain and the CH bonds in the interior of the CD cavity [7,25]. Other attempts to include fluorinated species into CDs used a semifluorinated *n*-alkane with $\beta$CD in water [21]. Because of the hydrophobic nature of both constituent blocks, guest and host cavity, the semifluorinated alkane readily penetrates the hydrophobic CD cavity to avoid contact with water producing a fine crystalline powder [19]. Atomic force microscopy confirms the presence of tubular structures obtained from dispersion of the semifluorinated *n*-alkane/$\beta$CD inclusion compound [21]. After most of the surfactant molecules are included in the CD cavities, a second $\beta$CD molecule is able to stack on top of the 1:1 complex to form a tunnel like structure including the fluorocarbon chain [18–21].

The topology of the $\beta$CD macrocycle (Fig. 1) and the mode and extent of host–guest interactions can be effectively probed by $^1$H NMR, in particular, by the chemical shifts variations of the H3 and H5 protons inside the $\beta$CD cavity [26,27]. Since the host–guest systems are in the NMR fast exchange chemical shift limit, the observed chemical shifts of the host and guest resonance's are averages of the chemical shifts for the free and complexed states weighted by the mole fractions of each state [28].

This work extends previous studies of the solubility of oxygen in aqueous solutions of highly fluorinated systems [29–32], by considering aqueous solutions of sodium perfluoroheptanoate (NaPFHept) in the presence of $\beta$CD. It addresses the following central question of its title: what is the effect of $\beta$CD in the solubility of oxygen in these aqueous solutions, before and after the CMC value of NaPFHept is reached? Since the size of the cyclodextrin cavity can only include perfluoroheptanoate monomers, it can be anticipated that inclusion in $\beta$CD starts to occur as $[\text{NaPFHept}]_0$ increases from zero. In order to confirm this expectation and determine the inclusion complex stoichiometry, $^1$H NMR chemical shift variations for the H5 $\beta$CD protons located inside the cyclodextrin cavity are recorded. Knowing the stoichiometry of the formed inclusion complex and the order by which inclusion in $\beta$CD and aggregation of NaPFHept occur is essential to answer the following questions: Is the cyclodextrin molecule simply retarding the approach to the CMC by including the perfluoroheptanoate ion in its cavity or is the aggregation process partly disrupted by the presence of inclusion complex entities? How is the characteristic minimum of oxygen solubility at the CMC point affected by the cyclodextrin presence? And the oxygen solubility curve?

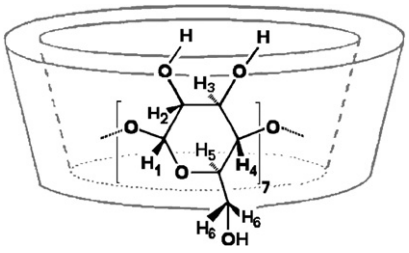


Fig. 1. The $\beta$CD macrocycle with a glucosidic unit highlighted.

## 2. Experimental

### 2.1. Materials and methods

Perfluoroheptanoic acid (Aldrich, >98%), $\beta$CD (kindly donated by Wacher), NaOH (Merck, >99%), and 1-butanol (Lab-Scan, 99%) were used as received without further purification. Oxygen was obtained from air liquid with 99.99% mol/mol minimum stated purity.

Sodium perfluoroheptanoate (NaPFHept) was prepared by neutralizing 25.0 g of the corresponding acid with 2.8 g of NaOH in ca. 100 ml of 1-butanol. After recrystallizing the salt from 1-butanol, 14.4 g of NaPFHept were obtained and dried in high vacuum for several hours at ca. 200 °C. The purity of NaPFHept was confirmed by IR and $^1$H NMR.

Solutions for oxygen solubility were prepared from a 200 mM stock solution of NaPFHept in ultra pure $H_2O$, obtained by heating an appropriate weight of NaPFHept in 105 ml of $H_2O$ at approximately 50 °C for 1 h, followed by ultrasonification for 15 min. Aqueous solutions 15, 50, 80, 150 mM in NaPFHept were obtained by dilution from the 200 mM NaPFHept solution. The presence of $\beta$CD (15 mM) was considered by adding the appropriate weight of $\beta$CD to ultra pure $H_2O$ and to 200, 150, and 40 mM NaPFHept solutions.

An apparatus previously described in detail and based on the saturation method proposed by Ben-Naim and Baer was used to study the solubility of oxygen in pure perfluoroheptanoic acid and in NaPFHept aqueous solutions at 310.15 K [32–34]. The oxygen solubility was determined by measuring the quantity of gas dissolved in an accurately known volume of solvent, at constant pressure and temperature. It consists mainly of a mercury manometer, with a mercury reservoir, a calibrated dissolution cell and a gas line with a pre-saturator, where the gas phase is pre-saturated in the solvent. Conductimetry measurements were performed using a Russel RL 105 conductivimeter.

$^1$H NMR (reference TSP) spectra were recorded on a Bruker DRX 300 spectrometer. The NMR spectra were always record-

ed using freshly prepared and unbuffered $D_2O$ solutions [35]. This precaution was taken in order to avoid any effect resulting from inclusion of buffer anions in $\beta$CD [36].

### 2.2. Solubility data reduction

The Ostwald coefficient is frequently used for measuring the solubility of a gas in a liquid. It can be defined through experimentally accessible quantities as

$$L_{2,1}(T, P) = \frac{V^{\mathrm{V}}}{V^{\mathrm{L}}}, \tag{1}$$

where $V^{\mathrm{V}}$ is the volume of the solubilized gas, $V^{\mathrm{L}}$ is the volume of the liquid solution after the equilibrium is attained. While $L_{2,1}$ depends both on temperature and total pressure, well below the critical point of the solvent, the pressure dependence is usually very small.

Solubility data is also usually presented in terms of the solute mole fraction. The mole fraction of component 2 (the gaseous solute) in the liquid solution can be directly related to the Ostwald coefficient by

$$x_2 = \frac{L_{2,1}(T, P) P_2 V^{\mathrm{L}}(T, P)}{Z_{12} RT}, \tag{2}$$

where $P_2$ is the partial pressure of the solute, $V^{\mathrm{L}}(T, P)$ is the molar volume of the liquid solution, and $Z_{12}$ the compressibility factor of the gaseous mixture [37]. In this work, the gaseous phase was treated as ideal and the molar fractions were calculated at a total pressure of 101.325 kPa. Hence, Eq. (2) can be simply written as

$$x_2 = \frac{L_{2,1}(T, P) P}{\rho^{\mathrm{L}} RT}, \tag{3}$$

where $P$ is total pressure and $\rho^{\mathrm{L}}$ the density of the liquid solution.

Liquid densities were measured in our laboratory with a vibrating tube Antón Paar DSA-48 densimeter at atmospheric pressure. The measuring principle is based on the calculation of the frequency of resonance of a mechanic oscillator with a given mass and volume, excited to be in resonance. The precision of the measurements is $\pm 5 \times 10^{-5}$ g cm$^{-3}$. The experimental data is presented in Table 1.

The performance of the solubility apparatus was tested by measuring the solubility of oxygen in pure water at 310.15 K. When the results were compared with literature values [38], deviations of about 0.5% were obtained. The experimental results are shown in Table 2. Mole fractions of the dissolved gas at 101.325 kPa were calculated assuming the validity of Henry and Raoult's laws and an ideal behavior for the vapor phase was assumed.

Table 1
Experimental liquid densities for perfluoroheptanoic acid and aqueous solutions of NaPFHept and NaPFHept/$\beta$CD

| Concentration (mM) | $T$ (K) | $\rho$ (g cm$^{-3}$) |
|---|---|---|
| Pure $CF_3(CF_2)_5COOH$ | | |
| – | 310.15 | 1.7523 |
| – | 313.15 | 1.7461 |
| – | 318.15 | 1.7357 |
| Sodium perfluoroheptanoate in aqueous solution | | |
| 15 | | 0.9958 |
| 50 | | 1.0029 |
| 80 | 310.15 | 1.0087 |
| 150 | | 1.0253 |
| 200 | | 1.0283 |
| Sodium perfluoroheptanoate and 15 mM of $\beta$CD in aqueous solution | | |
| 40 | | 1.0031 |
| 150 | 310.15 | 1.0264 |
| 200 | | 1.0350 |

Table 2
Experimental solubility of oxygen in the studied systems at 310.15 K expressed as Ostwald coefficients, $L_{2,1}(T, P)$, and mole fraction solubilities, $x_2(T, P)$ at a solute partial pressure of 101.325 kPa

| Concentration | $P$ (MPa) | $L_{2,1}(T, P)$ | $x_2(T, P)$ |
|---|---|---|---|
| Pure $CF_3(CF_2)_5COOH$ | | | |
| – | 0.101 | 0.354 | $3.86 \times 10^{-2}$ |
| Sodium perfluoroheptanoate in aqueous solution | | | |
| 0 | 0.102 | 0.0266 | $1.89 \times 10^{-5}$ |
| 15 | 0.101 | 0.0259 | $1.84 \times 10^{-5}$ |
| 50 | 0.102 | 0.0254 | $1.79 \times 10^{-5}$ |
| 80 | 0.102 | 0.0253 | $1.77 \times 10^{-5}$ |
| 150 | 0.101 | 0.0268 | $1.85 \times 10^{-5}$ |
| 200 | 0.102 | 0.0289 | $1.99 \times 10^{-5}$ |
| Sodium perfluoroheptanoate and 15 mM of $\beta$CD in aqueous solution | | | |
| 0 | 0.102 | 0.0263 | $1.89 \times 10^{-5}$ |
| 40 | 0.101 | 0.0257 | $1.81 \times 10^{-5}$ |
| 150 | 0.101 | 0.0257 | $1.77 \times 10^{-5}$ |
| 200 | 0.102 | 0.0268 | $1.83 \times 10^{-5}$ |

## 3. Results and discussion

It is generally recognized that cyclodextrins increase CMC values, as the inclusion in CD of surfactant monomers competes with the micellization process by decreasing the amount of surfactant monomers in solution [39–41]. Spectroscopic methods show that the interaction between CDs and surfactants is stronger than that between surfactant monomers [42–46]. In order to confirm that the CMC deviates to higher values by addition of $\beta$CD to the NaPFHept aqueous solution, the conductivity of the studied solutions was measured. Plots of specific conductance vs concentration of ionic surfactants are known to be approximately linear below and above the CMC, the interception of the two slopes giving the CMC of the system [47]. The results obtained are presented in Fig. 2. The conductivity results confirm that the surfactant CMC increases by about 20 mM relatively to the same system without $\beta$CD. Since $[\beta\mathrm{CD}]_0 = 15$ mM, the increase in the CMC concentration due to the presence of $\beta$CD can be partly accounted for by a 1:1 perfluoroheptanoate anion inclusion in $\beta$CD.

In order to determine the stoichiometry of the inclusion complex and the concentration range where inclusion dominates over aggregation, chemical shift variations of the $\beta$CD H5 protons located inside the cavity (Fig. 1), measured with respect to the chemical shift of the same protons in the absence of

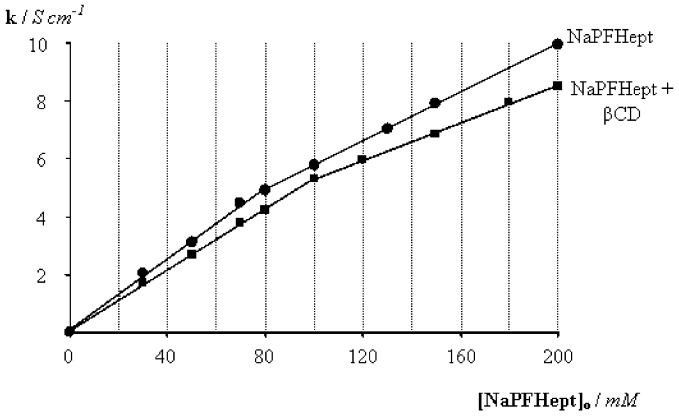


Fig. 2. Conductivity results measured for the different systems studied in this work: (■) aqueous solutions of NaPFHept; (◆) aqueous solutions of NaPFHept + 15 mM of $\beta$CD.

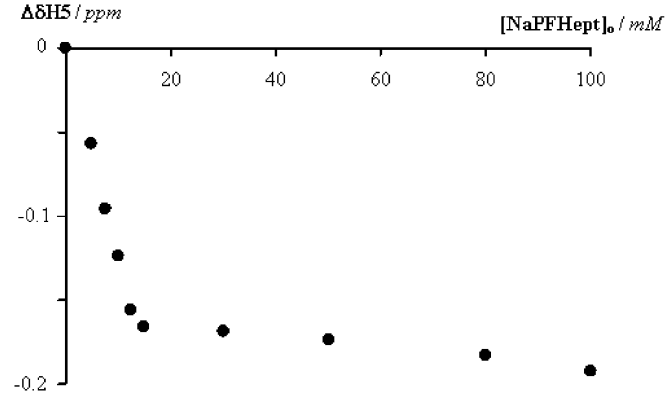


Fig. 3. $\Delta\delta[\beta\text{CD}]_0$ vs $[\text{NaPFHept}]_0$: chemical shifts changes for $\beta$CD H5 protons multiplied by the initial concentration of $\beta$CD (15 mM), at different concentrations of NaPFHept, in $D_2O$.

NapFHept, were recorded as functions of the initial concentration of the guest, $[\text{NapFHept}]_0$, for $[\beta\text{CD}]_0 = 15$ mM. Fig. 3 plots $\Delta\delta$ values as functions of $[\text{NapFHept}]_0$. As observed, $\Delta\delta$ values decrease linearly for $[\text{NapFHept}]_0$ below $[\beta\text{CD}]_0$ (slope $= -0.0126$ ppm, $R^2 = 0.998$), and stay approximately constant for $[\text{NaPFHept}]_0$ above $[\beta\text{CD}]_0$. These results point to the formation of a 1:1 inclusion complex, as the abrupt change of slope occurs about 15 mM, when the stoichiometric point ($[\text{NaPFHept}]_0 = [\beta\text{CD}]_0$) is reached.

Since the maximum $\Delta\delta$ value, $\Delta\delta_{\max}$, is obtained in the limit situation in which the inclusion complex concentration, $[\beta\text{CD.G}]$, is equal to $[\beta\text{CD}]_0$ (i.e., when all the CD cavities are occupied by the guest, G), one can conclude that $\Delta\delta/\Delta\delta_{\max} = [\beta\text{CD.G}]/[\beta\text{CD}]_0$. Hence, as $[\beta\text{CD}]_0$ is constant during this experiment, the measured chemical shift variation, $\Delta\delta$, is proportional to $[\beta\text{CD.G}]$ [35]. A reasonably high inclusion constant can be inferred from the observed linear $\Delta\delta$ vs $[\text{NaPFHept}]_0$ dependence ($R^2 = 0.998$). In addition, the negative $\Delta\delta$ and slope values express the shielding of the $\beta$CD H5 protons relative to the same protons in the absence of NapFHept, that is, guest inclusion leads to the shielding of the $\beta$CD H5 protons as expected [35].

Fig. 4 shows the results obtained for the solubility of oxygen expressed by its mole fraction, $x_2$, in the different studied systems, as a function of the surfactant concentration at 310.15 K. It can be seen that the solubility of oxygen in the more dilute solutions of NaPFHept decreases for concentrations of the surfactant lower than the CMC. Above the CMC, the solubility increases with surfactant concentration, an indication that the micelles promote the solubility of the gas molecules. The same conclusion had been previously suggested for the solubility of argon in micellar solutions of sodium dodecyl sulfate [48]. Oxygen is paramagnetic and will affect the NMR longitudinal relaxation time $T_1$. In fact, determination of the NMR longitudinal relaxation time $T_1$ in polyfluorinated micelles enables an estimation of the local oxygen concentration in micelles, leading to the conclusion that it should be low in the microenvironment surrounded by water, whereas the hydrophobic microenvironment provided by perfluoroalkane chains would have higher dissolved oxygen [49].

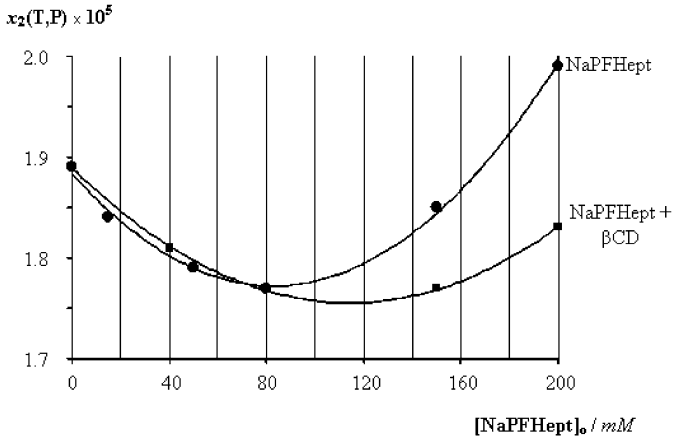


Fig. 4. Oxygen mole fraction in aqueous solutions of NaPFHept (0, 15, 50, 80, 150, 200 mM) (■) and in aqueous solutions of NaPFHept (0, 40, 150, 200 mM) + 15 mM of $\beta$CD (◆).

The effect of adding $\beta$CD on the oxygen solubility is shown in Fig. 4. The shapes of the observed curves are essentially the same, thus suggesting that the phenomena governing the solubility of oxygen in the absence or presence of cyclodextrin are the same, resulting from interactions of the gas molecules with free perfluoroheptanoate ions in solution. In the presence of $\beta$CD (15 mM), the characteristic minimum of oxygen solubility observed at the CMC is shifted from 83 mM (this value is consistent with previously reported values [2]) to 114 mM. Since this increase in the CMC value caused by the presence of $\beta$CD is larger than $[\beta\text{CD}]_0$, it cannot be accounted for simply by the inclusion of the perfluoroheptanoate anion in $\beta$CD. In addition, in the presence of $\beta$CD, the curvature (in the calculus sense, that is, the slope of the slope function) at the minimum decreases to 64% of the value in the absence of $\beta$CD by appreciably reducing the increase of oxygen solubility after CMC (Fig. 4), thus suggesting that the $\beta$CD inclusion complex systems disrupt the aggregation process to some extent.

## 4. Summary

The present study showed that sodium perfluoroheptanoate forms relatively strong complexes with $\beta$CD. It was also shown

that in the presence of these complexes, the characteristic minimum of gas solubility at CMC deviates to higher values. Moreover, the solubility curve widens indicating lower gas solubilities for concentrations higher than CMC. These observations indicate that both anion inclusion and disruption of the aggregation process play an important role on the oxygen solubility phenomena.

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