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Colloids and Surfaces A: Physicochem. Eng. Aspects 321 (2008) 11–15
COLLOIDS AND SURFACES A
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Influence of perfluorinated compounds on model lipid membranes prepared using Langmuir and Langmuir–Schaefer techniques

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Received 29 June 2007; received in revised form 26 January 2008; accepted 5 February 2008
Available online 21 February 2008

Abstract

The influence of selected perfluorinated compounds, perfluorooctanoic acid (PFOA) and perfluorooctanesulphonic acid (PFOS), on the structure and organization of lipid membranes was studied using the Langmuir–Blodgett technique. Three phospholipids: 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC), 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine (DMPC) and 1,2-dimyristoyl-*sn*-glycero-3-phosphoethanoloamine (DMPE) characterized by different surface properties have been chosen as components of the model membranes. The presence of both PFOA and PFOS in the subphase leads to the formation of a more fluidic layer at the air–water interface. Moreover, perfluorinated compounds were found to interact with lipid layers transferred onto the electrode surface by means of Langmuir–Schaefer technique. Incubation in the solution of perfluorooctanesulphonic acid caused changes in the structure of the transferred monolayer monitored by voltammetric methods.

Keywords: Langmuir monolayer; Pefluorooctanoic acid; Perfluorooctanesulphonic acid; Phospholipids; Voltammetry; Kinetics; Rate constant

1. Introduction

Perfluorinated compounds (PFCs) are fully fluorinated fatty acid analogues which find application in the production of lubricants, paints, cosmetics and fire-fighting foams. This group of compounds has been recently intensively studied because of their presence in even remote locations [1–3]. Although the influence on human health after the exposure to PFCs has not been completely understood yet, it has been established so far that these chemicals can accumulate in blood and liver [4,5] and may affect such properties of cell membranes as their permeability [6,7]. Moreover, the results of animal studies suggest that they may also cause developmental and reproductive toxicity: postnatal mortality, birth defects and some growing defects in rodents [8,9] but no clear association has been established between animal studies and adverse health effects on humans. Therefore, additional studies on the perfluorinated compounds and their impact on the environment and humans are needed.

In the present study the influence of the two selected compounds, perfluorooctanoic acid (PFOA) and perfluorooctanesulphonic acid (PFOS) (Fig. 1), on the structure and organization of lipid membranes was studied using the Langmuir–Blodgett technique. In general, perfluorinated compounds may exhibit surface activity but the ones used in our experiments cannot form compressible and stable monolayers at the air–water interface due to the relatively short carbon chain. Therefore, the selected PFCs were added to the subphase on which phospholipid monolayer was formed. In order to avoid the possible formation of the micelles the final concentrations employed were lower than the reported CMC concentrations of approximately 6.5×10^{-3} M and 3×10^{-2} M for PFOS and PFOA, respectively [10–12]. The Langmuir–Blodgett experiments have been performed for the three phospholipids: 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC), 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine (DMPC) and 1,2-dimyristoyl-*sn*-glycero-3-phosphoethanoloamine (DMPE), whose structures vary either in hydrocarbon chain length or polar head group. Those structural differences lead to different surface properties of the phospholipids such as their fluidity [13,14]. In order to obtain other point of view into the nature of the interactions of PFCs with lipid membranes, DPPC monolayers were transferred onto the glassy carbon electrode surface by means of Langmuir–Schaefer technique and the changes in the properties of the modified electrode after the

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doi:10.1016/j.colsurfa.2008.02.013

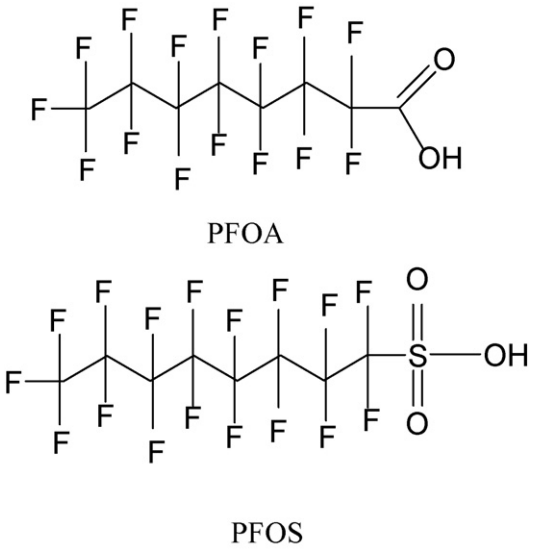

Fig. 1. The structures of perfluorooctanoic acid (PFOA) and perfluorooctanesulphonic acid (PFOS).

exposure to PFOS solutions were monitored by means of cyclic voltammetry.

2. Experimental

DPPC, DMPC and DMPE were purchased from Avanti Polar Lipids Inc., PFOA was purchased from Aldrich and PFOS was purchased from Apollo Scientific Ltd. Chloroform and methanol used for preparing lipid solutions, sodium and potassium phosphates used for buffer preparation and potassium hexacyanoferrate were purchased from POCh Gliwice, Poland. Distilled water used throughout the experiments was passed through a Milli-Q® water purification system (resistivity 18.2 MΩ/cm).

Surface pressure and surface potential vs. area per molecule isotherms were recorded using KSV LB Trough 5000 and KSV Mini Trough (KSV Ltd., Finland) controlled by KSV-5000 software version and equipped with a Wilhelmy balance and 5000SP surface potential meter (vibrating capacitor method [15]). Water with or without perfluorinated compound was used as the subphase. The spreading solutions were prepared by dissolving DPPC or DMPC samples in chloroform and DMPE samples in methanol/chloroform mixture (10:90, v/v). After spreading, the solution was left for 10 min for solvent evaporation. Compression of the film was performed at a speed of 7.5 cm^2/min (10 mm/min) and temperature was kept constant at 22 ± 1 °C. Electrochemical experiments were performed using AutoLab AUT 71819 with the GPES 4.9 software in three electrode cell with Ag/AgCl as a reference electrode and platinum foil as a counter electrode. The supporting electrolyte was 50 mM phosphate buffer.

3. Results and discussion

Isotherms of DMPC monolayers formed on subphases containing 10^{-4} M concentrations of the two perfluorinated compounds were compared with the DMPC isotherm obtained on pure water subphase. During the compression of the monolayer molecules of both PFOS and PFOA were incorporated into the lipid layer causing the increase in the area per molecule in the organized monolayer (Fig. 2A and Table 1). The fluidic character of the phospholipid monolayer becomes more pronounced which is manifested by the decrease in the maximum value of compression modulus (Table 1). The compression modulus (reciprocal of compressibility) is defined as [16]:

$$Cs^{-1} = -A\left(\frac{d\pi}{dA}\right),$$

where A is area per molecule, and π is surface pressure. Moreover, the influence of PFOS is significantly greater than that of PFOA, which might be explained by the stronger interactions between polar head group region of DMPC and sulphonic group of PFOS. Additional information was obtained from surface potential measurements of DMPC monolayers formed on subphases containing PFCs (Fig. 2B). It is a common observation that surface potential measurement is a method of choice in order to detect subtle changes of the monolayer properties at early stages of monolayer formation when the surface pressure is still close to 0 and the π–A isotherm is featureless. For a semi-quantitative analysis of the surface potential isotherm the Helmholtz equation has been used [17]:

$$\mu = \varepsilon\varepsilon_0 \Delta V A,$$

where μ is the vertical component of the dipole moment, A is the area per molecule and ε and ε_0 are the permittivities of the monolayer and of vacuum, respectively. The maximum apparent dipole moment is calculated as $\mu_A = \mu/\varepsilon$. In the presence of perfluorinated compounds, the changes in the organization of the lipid monolayers manifested by the onset of surface potential may be observed at larger areas per molecule compared to DMPC monolayer formed on pure water. Interestingly, in case

Table 1
Characteristic parameters of phospholipid Langmuir monolayers formed on subphases containing 10^{-4} M PFOS concentrations.

Phospholipid monolayer	Subphase	A_0 [Å^2]	A_{coll} [Å^2]	Maximum Cs^{-1} value [mN/m]
DPPC	Water	53.0 ± 0.1	38.9 ± 0.8	191.2 ± 3.0
	10^{-4} M PFOS	63.0 ± 0.9	38.7 ± 0.3	145.9 ± 7.4
DMPC	Water	73.0 ± 0.3	43.9 ± 0.5	88.7 ± 1.6
	10^{-4} M PFOS	92.7 ± 0.8	44.8 ± 0.8	61.4 ± 4.7
DMPE	Water	44.3 ± 0.4	35.3 ± 0.6	212.5 ± 1.4
	10^{-4} M PFOS	46.0 ± 0.7	31.9 ± 0.9	151.0 ± 5.4