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Calorimetric evaluation of interaction and absorption of polychlorinated biphenyls by biomembrane models

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HIGHLIGHTS

- Interaction and absorption of three PCB with biomembrane models was studied by DSC.
- The tested compounds affected the behaviour of biomembrane model.
- The medium effect on absorption of PCB by the biomembrane models was investigated.
- The absorption was hindered by the aqueous medium but favoured by the lipophilic one.

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ABSTRACT

Polychlorinated biphenyls (PCBs) are organic pollutants with lipophilic properties, due to their persistence, they are present in environment at potentially dangerous concentrations for humans health. In this work we investigated the interaction and absorption of 2,4,4′-trichlorobiphenyl (PCB 28), 2,3,3′,4,4′-pentachlorobiphenyl (PCB 105) and 2,3,3′,4,4′,5,5′-eptachlorobiphenyl (PCB 189) with dimyristoylphosphatidylcholine (DMPC) multilamellar vesicles (MLV), chosen as biomembrane models, by differential scanning calorimetry technique (DSC). The obtained results indicate that the tested compounds affected the thermotropic behaviour of MLV to different degree, modifying the phase transition peak and shifting it towards lower temperature. The effect of an aqueous or lipophilic medium on the absorption process of these compounds by the biomembrane models was also investigated revealing that the process is hindered by the aqueous medium but favoured by the lipophilic medium.

1. Introduction

A polychlorinated biphenyl (PCB) is any of the 209 configurations of a class of aromatic organic compounds with 1–10 chlorine atoms attached to a biphenyl ring system (Fig. 1) (Borja et al., 2006). Chemical properties of PCBs include a high dielectric constant and thermal conductivity, non-flammability (Hutzinger, 1974), high solubility in hydrocarbons and a low solubility in water, that further decreases with increase of chlorination degree (Anyasi and Atagana, 2011). They are non-volatile, chemically inert and do not undergo oxidation, reduction, addition, elimination or electrophilic substitution reactions except under extreme conditions. For these behaviours PCBs were widely used as dielectric and coolant fluids and also as plasticizers in paints and cements, lubricating oils, hydraulic fluids, pesticide extenders (Giesy and Kurunthachalam, 2002). However, the chemical properties that make PCBs ideal for industrial use are also the reason for their toxic effects. In fact, due to their persistence and the fact that they are poorly metabolized, PCBs accumulate in the environment by adsorbing into organic compounds, in soil, sediments and bioaccumulate in the food chain (Clayton et al., 1977; Opperhuizen and Stokkel, 1988; Thomann, 1989; Harrad and Smith, 1997). Due to their hydrophobicity PCBs also accumulate in many organism, including humans, with a risk of causing adverse effects on health (Binelli and Provini, 2003; Altshul et al., 2004; Anyasi and Atagana, 2011).

Individuals can be exposed to PCBs through breathing in contaminated air, consuming contaminated food, and by skin contact, PCBs may also collect in milk fat and be transmitted to infants through breast-feeding (Fromme et al., 2011). Once inside the body they are transported through the blood stream to liver, and to

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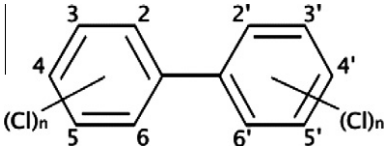

Fig. 1. Chemical structure of polychlorinated biphenyls (PCBs).

various muscles and adipose tissue, where they accumulate (Anyasi and Atagana, 2011). It was been demonstrated that the effects of PCBs on health depend on age, sex and areas of the body where they are concentrated. PCBs have shown toxic and mutagenic effects and were associated with specific kinds of cancer in humans, such as cancer of the liver and biliary tract, furthermore have been shown to both inhibit and imitate estradiol, inducing estrogen-dependent breast cancer (Ho et al., 2008), and possibly cause other cancers, such as uterine or cervical. The mechanism of action that causes this wide range of toxic effects depends on specific PCB. The toxicity of twelve PCBs, coplanar PCBs and mono-ortho-substituted-PCBs, is similar to that of dioxin and is mediated by binding to aryl hydrocarbon receptor (AhR) (Mukerjee, 1998). Because AhR is a transcription factor, abnormal activation may disrupt cell functions by altering the transcription of genes. Instead, di-ortho-substituted non-coplanar PCBs, interfering with intracellular signal transduction dependent on calcium, may lead to neurotoxicity (Simon et al., 2007). Ortho-PCBs may disrupt thyroid hormone transport by binding to transthyretin (Chauhan et al., 2000).

In this paper, the interaction and absorption of one not dioxin-like PCB 2,4,4′-trichlorobiphenyl (PCB 28) and two dioxin-like PCBs, 2,3,3′,4,4′-pentachlorobiphenyl (PCB 105) and 2,3,3′,4,4′,5,5′-eptachlorobiphenyl (PCB 189) with dimyristoylphosphatidylcholine (DMPC) multilamellar vesicles (MLV), chosen as biomembrane models, are investigated by differential scanning calorimetry technique (DSC).

DSC was already employed to evaluate the effects exerted by persistent environmental pollutants, such as Polycyclic Aromatic Hydrocarbons and their nitro-derivatives, with biomembrane models (Castelli et al., 2001, 2002, 2008a; Librando et al., 2003). In fact, it is a suitable technique to study the interaction of biologically active compounds and lipids and to monitor the uptake process of a compound by a biomembrane model, that is influenced by physical–chemical behaviours of compounds (Castelli et al., 2006; Castelli et al., 2008b).

Upon heating, DMPC MLV undergo a transition from an ordered, or gel state, to a disordered, or liquid–crystalline state, at a well defined temperature (transition temperature, T_m) and an enthalpy change (ΔH). Substances interacting with DMPC MLV act as an impurity destabilizing the lipid ordered structure and provoke a T_m and enthalpy decrease depending on the amount of compounds present in the lipid bilayer. In fact, to evidence the maximum interaction between PCBs and lipid bilayer, DMPC MLV containing increasing amount of PCBs have been prepared, and submitted to DSC analysis. We also carried out kinetic experiments in order to check the uptake process as a function of time, both on the absorption of PCBs by biomembrane model through an aqueous medium and on the transfer from PCBs loaded MLV to empty ones.

2. Materials and methods

2.1. Materials

DMPC (purity: 99%) was obtained from Genzyme (Switzerland). 2,4,4′-trichlorobiphenyl (PCB 28, purity: 96.5%), 2,3,3′,4,4′-pentachlorobiphenyl (PCB 105, purity: 97%) and 2,3,3′,4,4′,5,5′-eptachlorobiphenyl (PCB 189, purity: 99.4%) was purchase from Dr. Ehrenstorfer GmbH, Augsburg, Germany. A 50 mM Tris buffer solution, adjusted to pH 7.4 with HCl, was used for MLV production.

2.2. MLV preparation

Stock solutions of DMPC and PCBs were prepared in chloroform–methanol (1:1 v:v), then appropriate aliquots were mixed in glass flasks to obtain the same amount of DMPC (0.010325 mmol) and increasing molar fractions (X = 0.00, 0.015, 0.03, 0.045, 0.06, 0.09, 0.12) of PCBs with respect to the DMPC. The solvents were removed under a nitrogen flow and the resulting films were freeze-dried under vacuum to remove the residual solvents. Lipid films were suspended with 168 μL of Tris 50 mM, pH 7.4 and the MLV were prepared by heating to 37 °C (temperature above the gel-liquid

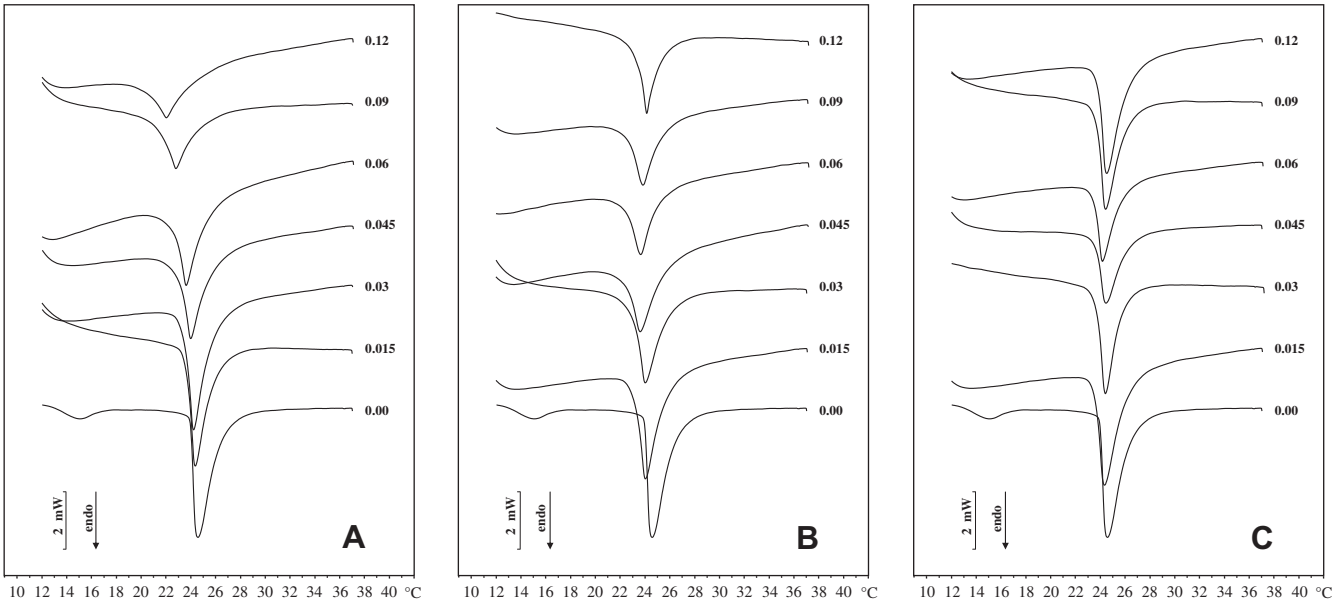

Fig. 2. Calorimetric curves, in heating mode, of DMPC MLV prepared in the presence of increasing molar fractions of 2,4,4′-trichlorobiphenyl (A), 2,3,3′,4,4′-pentachlorobiphenyl (B) and 2,3,3′,4,4′,5,5′-eptachlorobiphenyl (C).