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Thermodynamic studies for adsorption of ionizable pharmaceuticals onto soil

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HIGHLIGHTS

- Adsorption thermodynamics of three ionizable, polar compounds were analyzed.
- Clear differences were observed in sorption thermodynamics depending on ionic form.
- Sorption mechanisms of PRO, SGD and SSX were demonstrated.

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ABSTRACT

Although pharmaceutical compounds (PCs) are being used more and more widely, and studies have been carried out to assess their presence in the environment, knowledge of their fate and behavior, especially under different environmental conditions, is still limited. The principle objective of the present work, therefore, is to evaluate the adsorption behavior of three ionizable, polar compounds occurring in different forms: cationic (propranolol – PRO), anionic (sulfisoxazole – SSX) and neutral (sulfaguanidine – SGD) onto soil under various temperature conditions. The adsorption thermodynamics of these researched compounds were extensively investigated using parameters such as enthalpy change ($\Delta H°$), Gibbs free energy change ($\Delta G°$) as well as entropy change ($\Delta S°$). These calculations reveal that sorption of PRO is exothermic, spontaneous and enthalpy driven, sorption of SGD is endothermic, spontaneous and entropy driven whereas sorption of SSX is endothermic, spontaneous only above the temperature of 303.15 K and entropy driven. Furthermore, we submit that the calculated values yield valuable information regarding the sorption mechanism of PRO, SGD and SSX onto soils.

1. Introduction

A diverse array of synthetic organic compounds are used in vast quantities by society for a range of purposes, including in the production and preservation of food, in industrial manufacturing processes, as well as in human and animal healthcare. More than 100,000 chemicals were introduced in the 20th century, with little realization of what their affects on the environment would be, and what the consequences either directly or indirectly would be for human health (Primel et al., 2012). Reliable data is required in order to be able to successfully evaluate the impact of these compounds on the environment. The predominant fate processes for pharmaceuticals in the different environmental compartments are sorption (e.g. tetracyclines and quinolones) and (bio)degradation. Photodegradation and hydrolysis can also be significant (Kümmerer, 2009). However, making an assessment of the distribution of a chemical between its soil and aqueous phases is not a straightforward process. It depends on: (i) the basic chemistry of the compounds (ii) the amount of the substances involved; (iii) climatic factors such as intensity of "rainfall" events and temperature; and (iiii) soil type (e.g. pH, organic matter (OM) content, clay fraction content) (OECD, 2000). These features greatly affect the transport, reactivity, and bioavailability of organic compounds in the environment. The temperature is a useful tool from which valuable information about sorption mechanisms can be ascertained (DiVincenzo and Sparks, 2001; Kah and Brown, 2006). However up to date studies on adsorption thermodynamic among organic polar compounds have been mainly carried out for reactive dyes (Allen et al., 2004; Önal et al., 2007; Al-Degs et al., 2008; Zawani et al., 2009; He et al., 2010; Pansuk, 2011; Bajpai and Jain, 2012). Very limited data is available for pharmaceuticals, especially sulfonamides (Guo et al.,

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2013) and beta-blockers representing different ionic forms in this study. The objective of this research therefore was to evaluate the adsorption thermodynamics of three pharmaceuticals representing different ionic species in variable environmental conditions represented by temperature fluctuations.

2. Materials and methods

2.1. Chemicals

Standards of propranolol hydrochloride (PRO), sulfisoxazole (SSX) and sulfaguanidine (SGD) (Table 1) as well as trifluoroacetic acid 99% (TFA) were purchased from Sigma–Aldrich (Steinheim, Germany). Deionized water was produced by HYDROLAB System (Gdańsk, Poland). Acetonitrile (ACN), methanol (MeOH), hydrochloric acid (HCl), potassium chloride (KCl), calcium chloride ($CaCl_2$) and potassium hydroxide (KOH) were purchased from POCH (Gliwice, Poland).

Standard stock solutions of two of the researched compounds (PRO and SGD) at concentrations of 800 mg L^{-1} were prepared by dissolving the pure compound in 0.01 M $CaCl_2$. The spike solutions (8 points) were prepared from stock solutions in accordance with the serial dilution method in a proper $CaCl_2$ solution, so that the other concentrations of PRO and SGD ranged between 6.25 mg L^{-1} and 400 mg L^{-1}. The solutions were sonicated for 15 min for complete dissolution.

Due to lower water solubility of SSX, the standard stock solution was prepared at a concentration of 80 mg L^{-1}. For this reason experiments involving this compound were carried out without previous equilibration. The other spiked solutions in the range from 0.625 to 40 mg L^{-1} were prepared from a stock solution in accordance with the serial dilution method using aq. $CaCl_2$.

2.2. Soils

The experiments were conducted using natural peat soil possessing different physicochemical properties (see below). Sampled from the region of Pomerania in northern Poland, the soil was air-dried, ground in a mortar and passed through a 2 mm sieve, then re-ground in a mortar with a small rubber pestle. Soil pH was determined with a glass electrode in a 1:2.5 soil/water suspension using 1 M aq. KCl (exchangeable acidity) (6.22). Soil organic carbon (OC) was determined by loss-on-ignition (14.9%), and the cation exchange capacity (CEC) was determined using the $BaCl_2$ Compulsive Exchange Method (53.1 cmol(+) kg^{-1}). The clay fraction of the soil was 7.2%.

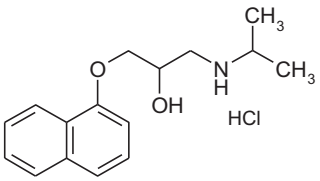
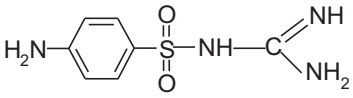
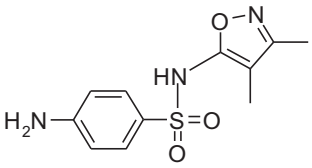
2.3. Description of the thermodynamic adsorption test

The sorption studies were carried out according to OECD Technical Guideline 106 (batch sorption experiments) (OECD, 2000). All of the samples were prepared in triplicate. Tests were carried out using a shaking water bath (Julabo SW22, Rose Scientific Ltd., USA), ensuring adjustment of temperature (293.15, 303.15 and 313.15 K) and constant contact with the soil sample solution containing analytes. To avoid photodegradation of the compounds being researched, the experiments took place in the dark. In our experiments we assumed constant structure/composition of the soil at the various temperatures.

The selection of the optimum soil/solution ratios was based on the calculated percentage of chemical adsorbed to soil, which should be >20%, and preferably >50%. Selected ratios were 1:2, 1:5 and 1:50 for SSX, SGD and PRO respectively. Equilibrium time was achieved for all the pharmaceuticals in all three media after 24 h.

The sorption experiment included the following steps: (1) 1 g (for SGD) or 0.5 g (for PRO) of air-dried soil samples were equilibrated by shaking with an appropriate volume (4.5 or 22.5 mL for SGD and PRO respectively) of $CaCl_2$ at a concentration of 0.01 M overnight (12 h) before the day of the experiment; (2) a certain volume (0.5 or 2.5 mL to the soils derived from sorbent/solution ratio) of the spike solutions of the test substance was added to adjust the final volume and achieve a 10-fold dilution. In this step, soil samples without any previous equilibration were spiked using 2 mL of solutions containing SSX at a concentration in a

Table 1
Structures and selected properties of the investigated pharmaceuticals.

Substance abbreviation [CAS]	Chemical structure	Selected physico-chemical properties
Propranolol hydrochloride PRO [318-98-9]		M = 295.8 g mol^{-1} pK_a = 9.53 log$P$ = 2.65 water solubility (25 °C) = 50 g L^{-1}
Sulfaguanidine SGD [57-67-0]		M = 214.2 g mol^{-1} pK_{a2} = 2.8 pK_{a3} = 12.0 log$P$ = −1.22 water solubility (25 °C) = 1 g L^{-1}
Sulfisoxazole SSX [127-69-5]		M = 267.3 g mol^{-1} pK_{a2} = 2.15 pK_{a3} = 5.00 log$P$ = 1.01 water solubility (25 °C) = 0.13 g L^{-1}