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Sorption of the organic cation metoprolol on silica gel from its aqueous solution considering the competition of inorganic cations

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ABSTRACT

Systematic batch experiments with the organic monovalent cation metoprolol as sorbate and the synthetic material silica gel as sorbent were conducted with the aim of characterizing the sorption of organic cations onto charged surfaces. Sorption isotherms for metoprolol (>99% protonated in the tested pH of around 6) in competition with mono- and divalent inorganic cations (Na^+ , NH_4^+ , Ca^{2+} , and Mg^{2+}) were determined in order to assess their influence on cation exchange processes and to identify the role of further sorptive interactions. The obtained sorption isotherms could be described well by an exponential function (Freundlich isotherm model) with consistent exponents (about 0.8). In general, a decreasing sorption of metoprolol with increasing concentrations in inorganic cations was observed. Competing ions of the same valence showed similar effects. A significant sorption affinity of metoprolol with ion type dependent Freundlich coefficients $K_{F,0.77}$ between 234.42 and 426.58 (L/kg)^{0.77} could still be observed even at very high concentrations of competing inorganic cations. Additional column experiments confirm this behavior, which suggests the existence of further relevant interactions beside cation exchange. In subsequent batch experiments, the influence of mixtures with more than one competing ion and the effect of a reduced negative surface charge at a pH below the point of zero charge ($\text{pH}_{\text{PZC}} \approx 2.5$) were also investigated. Finally, the study demonstrates that cation exchange is the most relevant but not the sole mechanism for the sorption of metoprolol on silica gel.

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1. Introduction

A large number of polar micropollutants, such as pharmaceuticals, biocides, surfactants, and dyes, contain ionizable

nitrogen functionalities. Such basic compounds with logarithmic acid constants pK_a above the pH of the systems under investigation are predominately positively charged. The charge state of a molecule highly influences its sorption behavior onto surfaces of natural (e.g., sediments, minerals,

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organic matter, metal oxides) and synthetic materials (e.g., activated carbon, silica, ion exchange resins) (Parida and Mishra, 1996; Delle Site, 2001; Tolls, 2001; Kibbey et al., 2007; Schaffer et al., 2012a). The relevance of unspecific hydrophobic interactions to non-polar sorbent domains diminishes with an increasing fraction of charged species due to an increasing molecular polarity. However, a relatively strong and even increased sorption is often observed for the cationic species of organic bases (e.g., Sassman and Lee, 2005; Kah and Brown, 2007; Sibley and Pedersen, 2008; Hyland et al., 2012; Schaffer et al., 2012a). Consequently, the sorption of organic cations is dominated by electrostatic forces between the protonated nitrogen moieties of the sorbate and the negatively charged sorbent surfaces. Electrostatic forces includes both, electrostatic interactions and electrostatic attractions. According to Schwarzenbach et al. (1993), a distinction is made only between ion exchange and non-ion exchange processes in this study. Previous studies identified cation exchange as the major sorption process for several organic cations onto natural and synthetic sorbents (Sassman and Lee, 2005; Bäuerlein et al., 2012; Droge and Goss, 2012; Schaffer et al., 2012b; Niedbala et al., 2013). Depending on the sorbate structure, additional polar electron donor-acceptor mechanisms, such as hydrogen bonding, may also significantly contribute to cation sorption (Senesi, 1992; MacKay and Vasudevan, 2012).

The prediction of the sorption process of organic cations is highly complex, since especially cation exchange depends on numerous influencing factors, such as the properties of the aqueous phase as well as sorbent and sorbate properties. Therefore, reliable descriptive and predictive sorption models combining all influencing variables are not yet available (MacKay and Vasudevan, 2012).

A relatively new approach is to adapt empirical poly-parameter linear free energy relationships (pp-LFERs) based on Abraham predictors (Abraham et al., 1990) for estimating sorption to condensed phases (Goss and Schwarzenbach, 2001). Here, a distribution coefficient is expressed as a linear combination of known sorbate descriptors with sorbent- and system-specific coefficients, respectively. The coefficients are estimated by multiple regression analysis of experimentally derived calibration data sets. These relationships were applied to hydrophobic (e.g., Nguyen et al., 2005), polar (Bronner and Goss, 2011), and even ionizable compounds (Abraham and Acree, 2010; Droge and Goss, 2013). Generally, the disadvantage of the pp-LFER approaches is, however, that solely sorbate parameters are explicitly considered herein and all remaining influencing factors are incorporated into the fitted coefficients without differentiation. Thus, the derived predictors are only meaningful for similar sorbents and aqueous media conditions. The results from Sathyamoorthy and Ramsburg (2013) confirm this issue, since the predictive power of their pp-LFER approach did not further improve despite the integration of further sorbate descriptors into their model. Hence, the additional consideration of sorbent-related key parameters in modeling remains essential (MacKay and Vasudevan, 2012; Sathyamoorthy and Ramsburg, 2013). Furthermore, the properties of the water phase, especially its ionic composition, must be further considered, since competitive effects strongly influence the cation exchange

equilibrium of organic cations (Brownawell et al., 1990; Bilgiç, 2005; Bäuerlein et al., 2012; Schaffer et al., 2012b; Droge and Goss, 2012; Niedbala et al., 2013; Chen et al., 2013). However, these interrelations between competing organic and inorganic cations in conjunction with the sorbent characteristics are not yet well understood.

The key for a better understanding of organic cation sorption is in the separate quantification of these relations and their interdependencies. This is highly complex due to the heterogeneous composition of natural sorbent surfaces and waters. Therefore, this study focuses on the systematic investigation of competitive effects that govern the cation exchange equilibrium of organic cations under defined boundary conditions and on a largely homogenous, synthetic material. For this purpose, the experiments were conducted with synthetic water and the oxidic, negatively charged material silica gel was selected as sorbent. Batch experiments were carried out with the basic beta-blocker metoprolol ($pK_a = 9.63$) under the influence of systematically varied electrolyte concentrations. Isotherms for metoprolol were determined for the competitive sorption under the influence of single inorganic cations (Na^+ , NH_4^+ , Ca^{2+} , Mg^{2+}) as well as for the combined effect of two cation types. Furthermore, the contribution of oxidic surfaces (amorphous SiO_2) for further potentially occurring sorption processes (e.g., hydrogen bonding, hydrophobic interactions) can be elucidated. As a result, sorption on silica surfaces can be studied separately and valuable implications for more complex natural or technical systems may be derived. This is because many silanol-bearing materials, such as quartz and further minerals (Nyfeler and Armbruster, 1998), are essential components of natural sorbents. Thus, the experiments provide a deeper understanding of relevant sorption mechanisms for organic cations. Eventually, these findings give further implications for future model developments and can be used to assess the sorption behavior of organic cations in more complex systems.

2. Material and methods

2.1. Chemicals

The beta-blocker metoprolol as tartrate salt with a minimum content of 98% was purchased from Sigma–Aldrich (Steinheim, Germany). Its structure and its physicochemical properties are given in Table 1. Due to its high pK_a value, metoprolol is positively charged at neutral pH. Since the pH of the used aqueous solutions was always lower than 7, the secondary amine moiety is readily protonated (Schaffer and Licha, 2014) and, thus, metoprolol was cationic in all experiments. Stock solutions of metoprolol with a concentration of 10 g/L were prepared in methanol (HPLC grade, VWR, Leuven, Belgium). All other used chemicals were of high purity (analytical grade). NH_4Cl was purchased from Laborchemie Apolda (Apolda, Germany), $NaCl$ from Th. Geyer (Renningen, Germany), $CaCl_2 \cdot 2 H_2O$ and $MgCl_2 \cdot 6 H_2O$ from Merck (Darmstadt, Germany), and 1 M HCl from KMF (Lohmar, Germany). Ultrapure water for the preparation of all solutions was obtained from the water purification system GenPure from TKA

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