

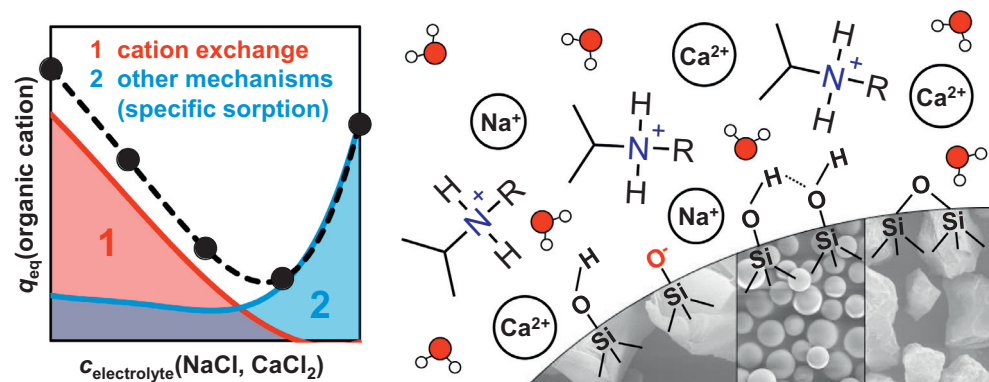


## Regular Article

## Sorption of organic cations onto silica surfaces over a wide concentration range of competing electrolytes

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## GRAPHICAL ABSTRACT



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## ABSTRACT

The fundamental understanding of organic cation–solid phase interactions is essential for improved predictions of the transport and ultimate environmental fates of widely used substances (e.g., pharmaceutical compounds) in the aquatic environment. We report sorption experiments of two cationic model compounds using two silica gels and a natural aquifer sediment. The sorbents were extensively characterized and the results of surface titrations under various background electrolyte concentrations were discussed. The salt dependency of sorption was systematically studied in batch experiments over a wide concentration range (five orders of magnitude) of inorganic ions in order to examine the influence of increasing competition on the sorption of organic cations. The organic cation uptake followed the Freundlich isotherm model and the sorption capacity decreases with an increase in the electrolyte concentration due to the underlying cation exchange processes. However, the sorption recovers considerably at high ionic strength ( $I > 1 \text{ M}$ ). To our knowledge, this effect has not been observed before and appears to be independent from the sorbent characteristics and sorbate structure. Furthermore, the recovery of sorption was attributed to specific, non-ionic interactions and a connection between the sorption coefficient and activity coefficient of the medium is presumed. Eventually, the reasons for the differing sorption affinities of both sorbates are discussed.

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## 1. Introduction

### 1.1. Motivation and objectives

A large number of polar organic contaminants detected in the aquatic environment are bases containing nitrogen moieties which are positively charged at environmentally relevant pH values ( $pK_a > 7$ ). These compounds are released into different parts of the water cycle due to their extensive use in industry, agriculture and pharmacy [1–6]. Therefore, comprehensive knowledge about their sorption on different sorbents is crucial in order to assess their ultimate environmental fate and bioavailability.

Numerous studies have shown that organic cations, in spite of their high polarity, sorb considerably onto negatively charged surfaces of many natural (e.g., sediments, clays, organic matter) [3,7–16] and technical sorbents (e.g., activated carbon, silica, ion exchange resins) [17–19]. Here, cation exchange processes are of major importance [8–12]. Depending on the sorbate structure (presence of functional groups with electronegative atoms), additional polar electron donor-acceptor mechanisms (e.g., hydrogen bonding) may also significantly contribute to the overall cation sorption [16,20–22]. The identification and separation of these potential sorptive interactions is very challenging due to the complex interrelation of many influencing factors such as compound structure (e.g., molecular size, functional groups), sorbent characteristics (e.g., surface area, ion exchange capacity, mineral composition) and the properties of the water phase (e.g., pH, ionic strength, dissolved organic matter). For example, decreasing sorption coefficients with increasing concentrations of competing inorganic ions, and thus a simultaneous shift of the exchange equilibrium in favor of the added cations, was observed in previous studies for natural as well as technical sorbents [8–12,18,19]. A considerable sorption of organic cations, even at very high background electrolyte concentrations ( $>1$  g/L), was still determined [19]. This observation suggests that additional sorptive interactions (e.g., hydrogen bonding, surface complexation) besides cation exchange play a crucial role. The identification and separation of these potential sorption processes has stimulated this research.

Despite the fact that a number of studies on the sorption of organic cations were already carried out, there are still knowledge gaps regarding the fundamental understanding of the individual sorption mechanisms, their quantitative contribution to the total sorption, as well as the impact of boundary conditions. This is, however, a prerequisite for accurate quantitative predictions. For example, the interrelations between competing organic and inorganic cations in combination with sorbent-related key parameters are not yet well understood. Therefore, a series of systematic experiments was conducted focusing on the characterization of organic cation sorption on silica surfaces as a function of competing electrolyte concentrations. For doing so, a wide concentration range of competition was covered (five orders of magnitude). The initial aim of this study was to capture the effect of increasing competition on organic cation sorption until the point of maximum suppression for the cation exchange interactions is reached, thus enabling the separate study of the remaining non-ionic interactions. In order to decrease the complexity and to avoid ambiguities, defined model solutions with a known constitution, two different sorbate molecules, and largely homogenous and well determined sorbents were used in the experiments. Eventually, several comparative experiments were carried out with a natural sorbent to study the transferability of the findings to heterogeneous sorbents.

### 1.2. General aspects of the physical chemistry of dissolved ions in solution

Since very high electrolyte concentrations were applied, it is initially important to understand the physical chemistry of electrolyte solutions. Different theoretical approaches for the calculation of activity coefficients are described in the literature (e.g., Debye and Hückel [23], Güntelberg [24], Davies [25,26], Bromley [27] and Pitzer [28,29]). The majority of them are limited to low ionic strengths and fail for concentrated electrolyte solutions, as only long-range Coulomb attraction interactions of cations and anions are considered [30]. This interaction, however, is only relevant for highly diluted solutions where the interionic distances are large. Generally, every ion is preferably surrounded by a hydration shell and oppositely charged ions, which hinder its reactivity (activity coefficient is smaller than one). In concentrated solutions, short-range forces (ion/molecule, and molecule/molecule interactions) predominate, which are mostly of repulsive nature [30,31]. Moreover, Coulomb repulsion interactions of equally charged ions dominate at high electrolyte concentrations and an increasing proportion of water molecules are bound in ionic hydration shells. The concentration of free water molecules is thus considerably reduced. At very high concentrations, it is even possible that the number of available solvent molecules is insufficient to complete the formation of a hydration shell [31–33]. Consequently, the ions are more polarized and susceptible to chemical processes (e.g., surface reactions, ionic association of both ions and solvent molecules, formation of ion-pairs) resulting in a higher effective concentration (activity) than the real concentration of the ions [31–34]. Hence, in highly concentrated solutions the activity coefficients are considerably greater than one. This phenomenon is considered, for example, in the model approach of Pitzer [28,29].

## 2. Material and methods

### 2.1. Chemicals

The beta-blocker metoprolol (MET) as tartrate salt with a minimum content of 98% was purchased from Sigma-Aldrich (Steinheim, Germany). The internal reference standard metoprolol-D<sub>7</sub> as hydrochloride was purchased from EQ Laboratories (Augsburg, Germany). Isopropyl-(4-methylbenzyl)-amine (iP4MBA) and the used internal reference standard isopropyl-(2,4-dimethylbenzyl)-amine as hydrochloride with a minimum content of 95% were obtained from Evo Blocks (Budapest, Hungary). Stock solutions of MET and iP4MBA with a concentration of 37.4 mM (10 g/L and 6.04 g/L) were prepared in methanol. The pH was adjusted by adding 1 M HCl solution until a pH of 5.6 was reached. The internal standards were prepared in methanol with a concentration of 100 mg/L. All reference standard solutions were stored at  $-18$  °C. MET and iP4MBA are positively charged at the experimental pH of 5.6, as the secondary amine moiety is readily protonated due to its  $pK_a > 9$  [35]. MET and iP4MBA were selected as sorbates in this study because both compounds have a partially similar structure (secondary amine, *para*-substituted benzene ring) and therefore similar physicochemical properties (polarity, acidity constant, see Table 1). Since iP4MBA has no additional functional groups such as ether or hydroxyl groups, conclusions on the type and proportion of other relevant interactions, e.g., H-donor/acceptor mechanisms such as hydrogen bonds, can be drawn. All other used inorganic chemicals were of high purity ( $>99\%$ , analytical grade). Ultrapure water for the preparation of all solutions was obtained from the water purification system GenPure from TKA (Niederelbert, Germany).

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