



Experimental and molecular dynamics study on anion diffusion in organically modified bentonite



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ABSTRACT

The work presents experimental and molecular modeling study of the anion diffusion with nitrate as a model probe in the organically modified bentonite. Organoclay samples with different loadings of the two cations Hexadecyltrimethylammonium (HDTMA⁺) and Hexadecylpyridinium (HDPy⁺) were prepared. The diffusivity of NO₃⁻ in the interfacial area of the organo-bentonite is strongly affected by the packing density of the organic coating. Through-diffusion experiments verified that the retardation capacity of the organoclays increases with the increasing amount of both organic cations on the clay surface. Observed NO₃⁻ diffusion in HDTMA⁺- and HDPy⁺-bentonite is in a similar range. Further, classical molecular dynamics studies, performed on sets of HDTMA⁺- and HDPy⁺-montmorillonite models, explained a molecular mechanism of the diffusion process of the nitrate anion at the organoclay–water interface. The molecular simulations showed comparable trends of the dependence of the NO₃⁻ diffusion coefficient on the content of organic cations on the surface as observed in experiment. Calculations explained how the organic cations are arranged on the surface and revealed that the positively charged head groups of the organic cations play a key role in the decreasing of the diffusivity of nitrate ions.

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1. Introduction

Clays and clay minerals can form natural barriers preventing migration of toxic species to environment. Especially bentonites are frequently used in barrier systems to reduce pollutant discharge because of their high permeability, ductility and cation exchange capacity (CEC). The montmorillonite from the smectite group represents the main constituent of bentonites. High cation adsorption and swelling capacity are main advantages of the efficient application of this mineral in engineered barriers. Its aluminosilicate layers are negatively charged due to isomorphic substitutions, typically in octahedral but also, to some extent, in tetrahedral sheets. The negative charge of layers is balanced by hydrated inorganic cations (commonly Na⁺ and Ca²⁺) in the interlayer space and on the external surfaces. Moreover, cations adsorbed in the interlayers of montmorillonite can easily adsorb an additional amount of water resulting in swelling. Negatively charged layers and hydrophilic surfaces are responsible for a low adsorption capacity of anionic and non-ionic compounds (Boyd et al., 1988; Smith and Galan, 1995). An improvement of adsorption properties for these compounds is possible by modifying montmorillonites with specific organic cations that replace the original inorganic cations in the interlayer

space and on the surface. Such modified clays and clay minerals are known as organoclays. Depending on type and amount of the organic cation, adsorption capacities and surface properties of montmorillonites can change (Yariv, 2002). The exchange of the interlayer cations leads to a variation of interlayer space dimension (e.g. Meleshyn and Bunnenberg, 2006), surface charge and wettability (Schampera and Dultz, 2011), and swelling pressure (Rao and Sivachidambaram, 2013). The modification not only changes the surface properties but also affects the arrangement of clay mineral layers, the microstructure of particles and, consequently, the pore space characteristics. Improvement of the material properties of organoclays leads to (i) the capability to adsorb anions in relatively high amounts (An and Dultz, 2008; Behnsen and Riebe, 2008; Krishna et al., 2001; Li and Bowman, 1998) (ii) the ability to adsorb anions and cations simultaneously (Bors et al., 1997; Dultz et al., 2012), and (iii) the capacity for adsorption of nonpolar compounds (Lee and Tiwari, 2012; Oyanedel-Craver et al., 2007; Rytwo et al., 2007; Rytwo et al., 2012; Zhu et al., 2010). The type and amount of applied organic cations have a particular importance for the modification of organoclay properties and significantly influence magnitude and mechanism of adsorption (Bartelt-Hunt et al., 2003; Krishna et al., 2001).

Basic transport process in porous media controlling pollutant displacement in barriers of saturated compacted bentonites is diffusion as high swelling capacity induces low hydraulic conductivity of water (Glaus et al., 2007; Molera et al., 2003; Shackelford and Moore, 2013).

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Transport mechanisms are generally affected by material surface properties. Therefore, modification of surface characteristics towards increased adsorption capability leads to changes in diffusion coefficients and the retention behavior of the barrier material (Schampera and Dultz, 2011; Shackelford and Moore, 2013). Besides diffusive transport, the retardation of harmful chemicals through barrier systems is controlled by adsorption properties and accessible pore volume as well as its geometrical network. Those are, in addition, affected by several factors such as density, porosity, and tortuosity of the pore system, size and properties of the diffusing moiety, interface properties, and interactions in the clay-water-diffusing solute system (Molera and Eriksen, 2002; Shackelford and Moore, 2013). The diffusive solute flux of anions and cations is restricted additionally by electrostatic interactions in the diffuse double layer at clay mineral surface, whereas only a steric hindrance, e.g. by a pore size restriction, may reduce a movement of non-polar molecules (Grathwohl, 1998; Malusis et al., 2003). The diffusion of ions in bentonites are well examined (e.g. Bourg et al., 2006; Sato and Miyamoto, 2004), whereas much less is known about transport properties of ions or non-polar compounds in organoclays. In former studies we examined through-diffusion of conservative solutes in clays and organoclays by using a diffusion cell attached to the ATR-unit of the FTIR-spectrometer (Schampera and Dultz, 2009, 2011). First studies on diffusion of benzene in hexadecyltrimethylammonium (HDTMA⁺)-montmorillonite were presented by Zhao and Burns (2012, 2013). They also compared diffusion coefficients of benzene obtained from classical force-field molecular dynamics (FF-MD) simulations with experimental results. It was shown that the diffusive transport in organoclays depends on the diffusive moiety, accessible pore volume, and amount of organic cations on the clay mineral surface.

The works by Zhao and Burns (2012, 2013) showed a great potential of MD simulations in exploring a detailed characterization on a distribution of host species in organoclays. FF-MD simulations were also successfully used in the simulations of the arrangement of various organic cations in the interlayer space and external surface of clay minerals, mostly montmorillonites. For example, a structure characterization of mica layers coated with octadecyltrimethylammonium showed that alkylammonium ions reside preferably above the cavities of the mica surface (Heinz et al., 2003; Heinz and Suter, 2004). The effect of the chain length and the head group structure in self-assembly of alkylammonium chains on montmorillonite was simulated by classical molecular dynamics on a set of structural models (Heinz et al., 2007) and the results were found to be very complementary to a wide array of experimental data (X-ray, IR-spectroscopy, nuclear magnetic resonance (NMR), and differential scanning calorimetry (DSC)). Monte Carlo (MC) simulation method was used in the study on models of montmorillonite modified by hexadecylpyridinium cation (HDPy⁺) to explain the structure and arrangement of cations in the interlayer space (Meleshyn, 2009a, b; Meleshyn and Bunnenberg, 2006). The study of the structure of alkyl chains on layered silicates and metal surfaces showed that packing density between 0.2 and 0.75 leads to an intermediate inclination of angles between the surface plane and alkyl chains (Heinz et al., 2008). A packing density above 0.75 results in nearly vertical alignment of the surfactants on the surface. A general review by Cygan et al. (2009) summarized the use and application of the methods of the computational chemistry in modeling of the layered minerals including clay minerals.

There are only several molecular simulations of diffusion processes in clay minerals. Diffusion of Na⁺ and Cs⁺ ions in montmorillonite was studied by using the MC method (Kosakowski et al., 2008). It was found that a low degree of hydration leads to a smaller diffusion coefficient of Cs⁺ than for Na⁺, whereas in higher hydration states, diffusion coefficient of Cs⁺ is larger than for Na⁺. Molecular-scale diffusion coefficients were determined by MD simulations for water tracers and cations such as Na⁺, Cs⁺, and Sr²⁺ in Na-montmorillonite interlayers (Bourg and Sposito, 2010). Using an upscaling approach the authors were able to predict the apparent diffusion coefficients at a continuum

scale comparable to experimental data. A two-step upscaling approach based on complex assumption of macroscopic material characteristics was used on a stack model of pyrophyllite nanoparticles in order to link molecular diffusion coefficients to a continuum scale (Churakov and Gimmi, 2011).

In this work we present a combined experimental and MD study of the diffusion of nitrate anion in organoclays with a varying amount of organic cations in the structure. Nitrate is used as model anion, because it is easily detectable by IR-spectroscopy and shows a diffusion coefficient comparable to coefficients of harmful ions such as radioactive Iodide. For illustration, self-diffusion coefficients in water were determined as $1.9 \times 10^{-9} \text{ m}^2/\text{s}$ for NO₃⁻ and $2.04 \times 10^{-9} \text{ m}^2/\text{s}$ for I⁻, respectively (Shackelford and Daniel, 1991). Moreover, NO₃⁻ is an environmentally important anion that can be found in a relatively high concentration in soils and ground waters (Camargo and Alonso, 2006). The aim of the study is a detailed characterization of the organoclay surface and transport properties of the NO₃⁻ anion at the solid/liquid interface by combining experiment and molecular modeling. Experiments are performed in order to determine diffusive transport and retardation capacity in the organoclay samples influenced by varying amount of the organic cations in the organoclay samples. Detailed material characterization included determination of organic cation uptake, interlayer structure, surface charge, specific surface area, and anion adsorption capacity. In addition, interface properties were examined by analysis of wettability and surface tension. Diffusion coefficients in free solution (D_0), effective diffusion coefficients (D_e), and apparent diffusion coefficients (D_a) were determined from the measurements to obtain material retardation characteristics. FF-MD simulations are specially aimed to obtain a better understanding of the molecular mechanism responsible for a retardation of NO₃⁻ anions at the organoclay surfaces and to support the interpretation of the experimental achievements.

2. Experimental and computational details

2.1. Materials

Wyoming bentonite (MX-80) obtained from AMCOL, Winsford, England was used in the experiments. The dominant component (>90%) of this bentonite is montmorillonite. The cation exchange capacity (CEC) of the bentonite determined by the Ag-thiourea method (van Reeuwijk, 2002) is 1.003 mol_c/kg (main exchangeable cations are Na⁺ (67%), Ca²⁺ (24%), Mg²⁺ (7%) and K⁺ (2%)). The Hexadecyltrimethylammonium chloride and Hexadecylpyridinium chloride salts (HDTMACl·H₂O, HDPyCl·H₂O), purchased from Fluka AG and Sigma Aldrich, were used for the preparation of the organoclay samples. Organoclays were prepared by dispersing each clay sample (350 mg) in 35 ml of deionized water before adding the HDTMA⁺ or HDPy⁺ solutions with two different concentrations corresponding to an amount of the CEC of original bentonite. The samples are referred as M-HDPy⁺/HDTMA⁺-40 and M-HDPy⁺/HDTMA⁺-200 indicating the amount of HDPy⁺/HDTMA⁺ cations expressed in % of the CEC

Table 1

Effective uptake of organic cations for two different loadings expressed in % of CEC of clay and corresponding models used in MD simulations.

Applied amount of organic cations			
40% of CEC		200% of CEC	
Uptake	Sample	Uptake	Sample
35	M-HDTMA ⁺ -40	112	M-HDTMA ⁺ -200
25	M-HDPy ⁺ -40	116	M-HDPy ⁺ -200
MD models			
% of CEC	Model	% of CEC	Model
67/133	M-HDTMA _{2/_4}	200/267	M-HDTMA _{6/_8}
67/133	M-HDPy _{2/_4}	200/267	M-HDPy _{6/_8}

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