Journal of Contaminant Hydrology 149 (2013) 76–87

Contents lists available at SciVerse ScienceDirect

Journal of Contaminant Hydrology

journal homepage: www.elsevier.com/locate/jconhyd

Complex resistivity signatures of ethanol in sand–clay mixtures

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ARTICLE INFO

Article history:
Received 6 September 2012
Received in revised form 17 March 2013
Accepted 22 March 2013
Available online 29 March 2013

Keywords:
Complex resistivity
Ethanol
Biofuels
Clay

ABSTRACT

We performed complex resistivity (CR) measurements on laboratory columns to investigate changes in electrical properties as a result of varying ethanol (EtOH) concentration (0% to 30% v/v) in a sand–clay (bentonite) matrix. We applied Debye decomposition, a phenomenological model commonly used to fit CR data, to determine model parameters (time constant: τ, chargeability: m, and normalized chargeability: m_n). The CR data showed a significant ($P \leq 0.001$) time-dependent variation in the clay driven polarization response (~12 mrad) for 0% EtOH concentration. This temporal variation probably results from the clay–water reaction kinetics trending towards equilibrium in the sand–clay–water system. The clay polarization is significantly suppressed ($P \leq 0.001$) for both measured phase (ϕ) and imaginary conductivity (σ'') with increasing EtOH concentration. Normalized chargeability consistently decreases (by up to a factor of ~2) as EtOH concentration increases from 0% to 10% and 10 to 20%, respectively. We propose that such suppression effects are associated with alterations in the electrical double layer (EDL) at the clay–fluid interface due to (a) strong EtOH adsorption on clay, and (b) complex intermolecular EtOH–water interactions and subsequent changes in ionic mobility on the surface in the EDL. Changes in the CR data following a change of the saturating fluid from EtOH 20% to plain water indicate strong hysteresis effects in the electrical response, which we attribute to persistent EtOH adsorption on clay. Our results demonstrate high sensitivity of CR measurements to clay–EtOH interactions in porous media, indicating the potential application of this technique for characterization and monitoring of ethanol contamination in sediments containing clays.

1. Introduction

The development of non-invasive geophysical techniques for characterizing organic contaminants in the subsurface is desirable as most organic contaminants cause environmental and health problems. Low-frequency complex resistivity (CR) measurements could potentially be applied for monitoring the spatiotemporal distribution of subsurface contaminant plumes, thus for assessing the effectiveness of remediation design efforts aimed at reducing organic contaminant concentrations in clayey soils. Organic contaminants may affect the petrophysical properties as a result of induced changes in pore fluid chemistry and mineral surface properties via mineral–fluid interactions, leading to a distinctive geophysical response. The potential application of low-frequency (<1000 Hz) electrical geophysics for mapping clay–organic interactions was first investigated in the mid 1980s (Olhoeft, 1985, 1986; Sadowski, 1988). Olhoeft (1985) performed a series of CR measurements that showed a significant difference in phase (ϕ) response between uncontaminated and organic-contaminated clayey (either montmorillonite or smectite) soils. This work stimulated further research on clay–organic interactions and associated

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http://dx.doi.org/10.1016/j.jconhyd.2013.03.005

changes in the CR response. Significant ϕ responses as high as ~100 mrad were recorded from CR measurements on clay–toluene mixtures (Sadowski, 1988; Olhoeft and King, 1991). These authors concluded that toluene oxidizing polymerization reactions in the presence of clays led to distinctive electrochemical signatures detectable by CR measurements.

Such work stimulated experimentation regarding the sensitivity of CR for detecting chlorinated solvents, particularly dense non aqueous phase liquid (DNAPL) pollution (Olhoeft, 1985; Sadowski, 1988; Olhoeft and King, 1991). However, efforts by others to confirm that clay–organic interactions impact CR measurements and to test the capabilities of complex resistivity technique for mapping DNAPL have been inconsistent (Börner et al., 1993; Brown et al., 2004; Roberts and Wildenschild, 2004; Ustra et al., 2012; Vanhala, 1997). For example, Brown et al. (2004) attempted unsuccessfully to reproduce the reported high ϕ response associated with clay–toluene interactions despite conducting a series of laboratory experiments that closely mimicked those of Olhoeft (1985); instead finding a barely distinguishable ϕ response for clay containing samples contaminated with toluene.

These inconsistent previous findings encourage further research to determine whether or not the interactions of organic contaminants with clay minerals result in useful geoelectrical responses. In this paper, we focus on the potential application of CR as a tool for monitoring clay–ethanol interactions.

Ethanol is an emerging contaminant (Gomez and Alvarez, 2010) that poses potential risks to groundwater resources (Powers et al., 2001a) when accidental releases of large volumes occur during transportation (Spalding et al., 2011) or from storage facilities (McDowell et al., 2003). Ethanol contamination in the subsurface has recently become more likely as its production and use as a biofuel blend (EtOH blended with conventional gasoline) have increased exponentially (ITRC, 2011) as a result of regulatory stimuli in the USA to reduce air pollution and provide an alternative to petroleum. Potential adverse impacts of EtOH on groundwater include, (1) increases in aqueous phase BTEX (benzene, toluene, ethyl-benzene and xylene) compounds contained in gasoline (Powers et al., 2001b) due to cosolvency effects (Powers et al., 2001b; Da Silva and Alvarez, 2002; Corseuil et al., 2004; Stafford et al., 2009), (2) slower natural degradation of BTEX compounds (Corseuil et al., 1998; Freitas et al., 2011; Gomez and Alvarez, 2009, 2010; Mackay et al., 2006; Powers et al., 2001b; Ruiz-Aguilar et al., 2003) attributed to the preferential biodegradation of EtOH and associated rapid depletion of dissolved oxygen and other electron acceptors, and (3) methane production associated with anaerobic degradation of EtOH reaching the explosive limit level (Freitas et al., 2010; Nelson et al., 2010; Spalding et al., 2011). EtOH may also quickly become toxic to soil and aquifer microorganisms (Nelson et al., 2010), affecting their growth (Ingram, 1989; Nelson et al., 2010) and community structure (Cápiro et al., 2008; Ma et al., 2011).

In this paper, we report on CR signatures associated with clay–ethanol interactions. Our main objectives were to determine (a) the electrical properties of EtOH in a sand–clay medium, (b) if clay–organic reactions associated with EtOH enhance or suppress the CR response, and (c) whether CR signatures associated with clay–EtOH interactions are reversible when the EtOH is removed, thereby providing information on the persistence of clay–organic reactions.

2. Potential interactions in a clay–ethanol–water system

Clay mineral surfaces generally carry a net negative charge due to isomorphous substitutions of some electropositive elements of similar size but of lower valence (Van Olphen, 1977). This negative charge is generally compensated for by sorption of exchangeable cations in the interlayer and onto the external clay surfaces such that clay minerals, in their natural form, are hydrophilic (Yariv and Cross, 2002). In the type 2:1 clay minerals (i.e. those having 2 tetrahedral sheets on each side of an octahedral sheet (T–O–T)), water molecules can be readily adsorbed onto the existing exchangeable cations as part of the associated electrical double layer (EDL). The EDL is the most common model used to describe charge distribution at the mineral/water interface associated with chemical reactions between the surface sites and ions in water. The EDL includes (a) a Stern layer i.e. the layer between the mineral surface and the inner surface of the diffuse layer resulting from sorbed ions (counterions) directly to mineral surface, and (b) a diffuse layer i.e. a layer that extends beyond the Stern layer and includes an excess of counterions and a depletion of co-ions moving mostly freely. Two types of water may be distinguished from the water–cation interactions: type 1 whereby an inner or primary hydration shell is directly coordinated to the cation, and type 2 whereby an outer or secondary hydration shell is indirectly coordinated to the cation (Sposito et al., 1999; Theng, 1974). The outer hydration shell is less stable than the inner shell and, hence, more likely to be displaced by other competing compounds for the cation sites.

Various interactions are possible between organic molecules and the type 2:1 clay minerals including hydrogen bonding, cation–dipole interaction, coordination bonds, acid–base reactions, charge transfer and van der Waals forces (for a review see Kowalska et al., 1994; Lagaly et al., 2006; Yariv and Cross, 2002). Like water molecules, the adsorption of EtOH molecules can occur on the existing cation sites in clay. As water and EtOH are both polar compounds, they will essentially compete for the same cation sites in the clay structure (Dowdy and Mortland, 1967; Theng, 1974). German and Harding (1969) demonstrated adsorption of large amounts of EtOH, n-propanol and n-butanol on Ca^{2+} and Na^{+} of montmorillonite. Among these primary n-alcohols, EtOH has been shown to be capable of displacing water even in the inner hydration shell around cations such as Ca^{2+}, Cu^{2+} and Al^{3+} in clay (Dowdy and Mortland, 1967) though the ratio of EtOH to water does play a role in these reactions (Brindley and Hoffmann, 1962). The adsorption of EtOH by displacement of water is a favorable reaction that results in a gain of entropy by the system (Theng, 1974).

Competition for adsorption on available cation sites in the clay structure aside, water and EtOH molecules in solution show complex intermolecular interactions (Franks and Ives, 1966; Parke and Birch, 1999; Atamas and Atamas, 2009). These molecules are subject to different attractive forces such that multi-hydration layers may be formed around the EtOH molecules. This type of solvent–solute interaction also known as solvation (IUPAC, 2006) may impede the ionic mobility of the solution, thus affecting its conductivity. The reduction in solvated ionic mobility in water–sulfacetamine sodium mixtures has been associated with a rapid decrease in molar conductance (Bhat and Shetty, 2011). Personna et al. (2013) interpreted a significant non-linear decrease in conductivity