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Impact of surfactant-induced wettability alterations on DNAPL invasion in quartz and iron oxide-coated sand systems

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ABSTRACT

Dense non-aqueous phase liquids (DNAPLs) present in the subsurface may contain surface active compounds that impact DNAPL migration and distribution. While a number of studies have revealed the role surface active compounds play in altering the wettability of quartz sand, few have considered the implications for other minerals common to contaminated sites. This study extends understanding of DNAPL/surfactant wettability to iron oxide surfaces. Specifically, quartz and iron oxide-coated sands in a tetrachloroethene (PCE)/water system containing the organic base (an organic molecule that acts as a base) dodecylamine (DDA) were compared at a variety of scales. Wettability of the minerals' surfaces, and the impact of wettability on capillary resistance to DNAPL entry, were assessed as a function of pH through: (i) advancing and receding contact angles, (ii) primary drainage capillary pressure–saturation experiments, and (iii) small, two-dimensional, flow cell experiments. The work revealed that, at neutral pH and under identical boundary capillary pressures, DNAPL invaded quartz sand but not iron oxide-coated sand; however, at low pH, DNAPL invaded both sands equally. These differences were demonstrated to be due to wettability alterations associated with the strength of attractive forces between DDA and the mineral surface, dictated by the isolectric point of the minerals and system pH. Observed differences in DNAPL invasion behavior were consistent with measured intrinsic contact angles and P_c–S relationships, the latter requiring scaling by the operative contact angle inside the porous medium for a meaningful comparison. This study suggests that the distribution of minerals (and, more specifically, their isoelectric points), as well as the aqueous phase pH at a given site, may have a significant impact on the DNAPL source zone architecture.

1. Introduction

Dense Non-Aqueous Phase Liquids (DNAPLs) released to the subsurface often pose a significant risk to the surrounding environment and populace. Although much effort has been made in recent years to limit the risks associated with DNAPL contaminated sites, a lack of knowledge in several key areas frequently hinders remediation efforts (National Research Council, 2005). One such area is the impact of wettability on DNAPL source zone architecture and remediation efficiency (Powers et al., 1996; Dwarakanath et al., 2002). Wettability is defined as the tendency of one fluid to preferentially spread over a solid surface in the presence of another fluid (National Research Council, 2005). For the purposes of this study 'wettability' refers to the contact angle (θ) measured through the aqueous phase, 'advancing contact angle' refers to NAPL advancing over the solid surface and 'receding contact angle' refers to NAPL receding over the solid surface. A system with an advancing contact angle of $0° < \theta < 70°$ is typically considered water-wetting, $70° < \theta < 120°$ is intermediate wetting and $120° < \theta < 180°$ is NAPL-wetting (Powers et al., 1996).

The subsurface has been typically assumed to be water-wetting (Mayer and Hassanizadeh, 2005), where the aqueous phase preferentially coats the soil grains in the saturated zone

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and DNAPL occupies the larger pore bodies (Mayer and Hassanizadeh, 2005). However, intermediate and NAPL-wetting systems are not uncommon. For example, engineered wettability alterations in petroleum reservoirs are used to increase petroleum yield (Mercer and Cohen, 1990) and numerous coal tar and creosote contaminated sites have been identified as NAPL-wetting (Birak and Miller, 2009). In the laboratory, both neat solvents (Ryder and Demond, 2008) and solvents containing surface active chemicals have been demonstrated to act as the wetting fluid on quartz in the presence of water (Demond et al., 1994; Lord et al., 2000; Harrold et al., 2001, 2005; Hsu and Demond, 2007). Chlorinated solvents often contain surface active chemicals that improve their working efficiency (e.g., anti-oxidants and fabric softeners) and may also contain significant amounts of entrained grease, both of which may affect the solvent's interfacial properties (Jackson and Dwarakanath, 1999; Nellis et al., 2009; Yoon et al., 2009). Consequently, a variety of natural and anthropogenic surface active chemicals may be present in NAPLs at impacted sites (Jackson and Dwarakanath, 1999; Zheng et al., 2001; Dou et al., 2008; Nellis et al., 2009; Yoon et al., 2009). Under these circumstances, assuming a water–wet system may be inappropriate, with consequences including incorrect dissolution rate predictions (Bradford et al., 2000) or inaccurate conceptual models of fluid distribution potentially impacting remediation efficiency (e.g., waterflooding may be less effective than anticipated).

Considerable work has been completed studying the impact of typical NAPL constituents on wettability, in particular associated with crude oil/petroleum systems (Thomas et al., 1993; Powers and Tamblin, 1995; Buckley and Liu, 1998; Roy and McGill, 1998; Zheng and Powers, 1999; Buckley and Lord, 2003). In both the contaminated subsurface and petroleum reservoirs wettability alterations occur as a result of (i) precipitation of high molecular weight compounds onto the soil, and (ii) acid/base reactions between organic compounds and the electrical charge developed on the soil surface (Zheng et al., 2001). For example, Zheng and Powers (1999) correlated organic base concentrations in a variety of field NAPLs to soil wettability. At low pH, NAPLs with relatively high organic base concentrations preferentially wet quartz sand while NAPLs with low organic base concentrations did not wet the quartz sand.

Zheng and Powers (1999) postulated that pH was an important contributing factor to wettability alterations. At a sufficiently low pH, an organic base protonates, developing a positive charge (e.g., for dodecylamine (DDA) this occurs at pH 10.6). Meanwhile, as pH increases to the isoelectric point of the solid, the net surface charge of the solid surface transitions from positive to negative (Singh and Uehara, 1999). For example, quartz possesses a net negative charge above its isoelectric point at pH 2 (Sposito, 1989) and becomes increasingly negative as pH increases further. Thus, in the range $2<\mathrm{pH}<10.6$, there is an electrostatic attraction between the negative quartz surface and positive charge of DDA. In general, wettability alterations are therefore expected for soils in the presence of NAPLs containing an organic base at pH values above the solid isoelectric point and below the pH at which the organic base loses its positive charge (Zheng and Powers, 1999).

A number of studies have focused specifically on wettability alterations related to surface active chemicals contained in chlorinated solvents (Demond et al., 1994; Powers and Tamblin, 1995; Powers et al., 1996; Lord et al., 1997, 2000; Harrold et al., 2001; Abriola et al., 2005; Harrold et al., 2005; Lord et al., 2005; Hsu and Demond, 2007). These results are consistent with the study of Zheng and Powers (1999) in that wettability alterations are functions of the concentration of cationic organic base in aqueous solution and the density of negatively charged sites on the solid surface. The concentration of cationic organic base in aqueous solution is, in turn, inversely proportional to the solution's pH. As the solution becomes more acidic, organic base will partition out of the NAPL and into the aqueous phase and will develop a predominantly cationic charge. This pH dependent partitioning is due to the higher aqueous solubility of the organic base when it possesses a cationic charge.

Most of the cited studies examined the wettability of solvents containing surface active chemicals with quartz as the solid surface. Although quartz is a very common subsurface material, there are many other typical subsurface minerals exhibiting different isoelectric points (Sposito, 1989) (Table 1). For example, the isoelectric point of hematite and goethite ranges between pH of 6 and 8, a substantially higher pH than quartz (Parks, 1965). Therefore, at neutral pH quartz is expected to exhibit a larger net negative surface charge than iron oxide. Organic bases, which are positively

Table 1
Common soil minerals and points of zero charge.

Name	Ubiquity in Soils[a]	Environment[a]	Isoelectric Point
Quartz	Ubiquitous	Nearly all soils and parent materials	2[b]
Hematite and goethite	Ubiquitous	Well-drained, near surface soil	6–10[c]
Feldspars	Rare to common	Wide variety of igneous and metamorphic rocks	2–2.4[a]
Gibbsite	Common	Old, stable soils or feldspar pseudomorphs	8–9[a]
Kaolinite	Ubiquitous	Desilication of 2:1 lays/feldspathic	4–5[a]
Calcite	Common	Arid soils	9.5[a]
Hydroxy-interlayered vermiculite	Ubiquitous	Acid, highly weathered soil surface horizons	P[a,d]
Muscovite	Common	Granitic and high-grade metamorphic rocks	P[a,d]

[a] (Feldman et al., 2008).
[b] (Cornell and Schwetmann, 2003).
[c] (Parks, 1965).
[d] Indicates that the soil maintains a permanent negative charge at all pH values.