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Journal of Contaminant Hydrology 80 (2005) 1–17

JOURNAL OF

Contaminant
Hydrology

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The impact of additives found in industrial formulations of TCE on the wettability of sandstone

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Received 13 July 2004; received in revised form 21 June 2005; accepted 5 July 2005

Available online 15 August 2005

Abstract

The wettability of aquifer rocks is a key physical parameter which exerts an important control on the transport, residual trapping, distribution and eventual fate of chlorinated hydrocarbon solvents (CHSs) released into the subsurface. Typically chlorinated solvents are assumed to be non-wetting in water saturated rocks and unconsolidated sediments. However industrially formulated solvent products are often combined with basic additives such as alkylamines to improve their performance; and the mineral surfaces of aquifer rocks and sediments usually possess a range of acid and hydrogen-bonding adsorption sites. The presence of these sites provides a mechanism whereby the basic additives in CHSs can be adsorbed at the solvent phase/solid phase interface. Given the amphiphilic molecular structure of these additives, this may result in changes in the wetting conditions of the solid phase. The aim of this study was therefore to test this conjecture for two classes of additives (alkylamines and quaternary ammonium salts) that are often encountered in industrial solvent formulations. Wettability assessments were made on sandstone cores by means of measurements of spontaneous and forced water drainage and spontaneous and forced water imbibition and through contact angle measurements on a smooth quartz surface. No solvent/additive combination produced solvent wetting conditions, though dodecylamine and octadecylamine significantly reduced the water wetting preference of sandstone which frequently resulted in neutral wetting conditions. The large volume of spontaneous water drainage observed in wettability experiments involving cetyltrimethylammonium bromide and octadecyltrimethylammonium bromide, suggested that the sandstone cores in these tests remained strongly water wetting. However

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equilibrium static contact angles of around 60° were measured on quartz suggesting that the sandstone surfaces should be close to neutral wetting conditions. This paradox was finally resolved by noting that contact between the solvent mixture and water in the sandstone core resulted in a final solvent phase which had an extremely low interfacial tension. It is therefore suspected that the observed spontaneous drainage of solvent from the core was driven by gravitational and buoyancy forces rather than strong water wetting conditions. Finally it was noted that the mobilisation of iron oxide coatings from the sandstone surface had a considerable influence in reducing the interfacial tension and in the formation and stabilisation of TCE/water emulsions.

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Keywords: Wettability; Chlorinated solvents; Basic additives; Sandstone

1. Introduction

Chlorinated hydrocarbon solvents (CHSs) have been widely used in a variety of industrial and cleaning processes since the 1930s and are now, as a result, amongst the most common and insidious of groundwater contaminants (Lohman, 2002; Mackay and Cherry, 1989). This situation has arisen principally because of frequent spillage, leakage from underground storage tanks, disposal to ground by industrial users, and their unique physicochemical properties (Kueper et al., 2003; Mackay and Cherry, 1989; Mercer and Cohen, 1990).

The CHS properties of most interest in contaminant hydrogeology are their high densities, low viscosities and immiscibility with water. CHSs are part of a group of organic liquids referred to as dense non-aqueous phase liquids or DNAPLs. DNAPLs are characterised by densities greater than that of water and immiscibility with water. When a CHS DNAPL enters the subsurface, the combination of its high density and low viscosity creates rapid, gravity driven downward migration as a separate phase through both the unsaturated and saturated zones (Huling and Weaver, 1991; Kueper et al., 2003). However as a necessary pre-condition for entry into the saturated zone, the capillary pressure – this being the difference in hydrostatic pressures between the wetting and non-wetting phases – has to be greater than the entry pressure of the aquifer rock or sediment. The inequality expressing this condition is written as:

$$P_{NW} > P_W + \frac{2\gamma \cos \theta}{r} \quad (1)$$

Where P is pressure, the subscripts NW and W refer to the non-wetting and wetting phases respectively; γ is the interfacial tension at the interface between the wetting and non-wetting liquids; θ is the contact angle the angle made by the fluid/fluid interface at the three phase contact line and r is the pore throat radius (Kueper and McWhorter, 1991). The contact angle is an important parameter as it expresses the wetting preference of the solid phase in competition with a separate fluid phase.

CHSs are immiscible with water and air; their solubilities, however, are several orders of magnitude greater than the maximum allowable concentrations in drinking water. Despite this their solubilities are sufficiently low as to signify that residually trapped CHS

DNAPL is only slowly depleted by dissolution. As such these contaminants remain a persistent source of groundwater contamination for decades (Poulsen and Kueper, 1992).

A number of studies (Barranco et al., 1997; Rugge and Ahlert, 1993; She and Sleep, 1998) have measured the physicochemical properties of chlorinated solvents such as IFT. In general these studies used laboratory grade solvents. Many of the solvents used in industrial applications are, however, formulated with additives to augment end use solvent performance (Archer, 1996). The precise nature of these additives and stabilisers depends on the designated end use of the solvent product. Additives include: antioxidants that help prevent the formation of oxidation products; corrosion inhibitors in degreasing solvents in order to deactivate metal surfaces and thus prevent corrosion; chelating agents to complex metals such as aluminium which can rapidly degrade TCE and PCE; acid acceptors which chemically neutralise trace amounts of acid formed during degreasing operations; surfactants which are used in TCE to help remove Fe_2O_3 and water during lens grinding and even perfumes (Archer, 1996; Dudman, 1999; Jackson and Dwarakanath, 1999). Many of these additives have the potential to adsorb at the various fluid/fluid fluid/solid interfaces in aqueous/solvent/solid systems, affecting interfacial properties and hence the wettability of such systems (Rosen, 1989).

Wetting conditions are characterised by the contact angle (see Fig. 1). For a water/organic liquid/solid system the contact angle (θ), measured, as shown in Fig. 1, through the aqueous phase, can be related to the interfacial tensions (γ) between the various liquid/liquid and liquid/solid pairs in the system by the following equation (Heimenz and Rajagopalan, 1997):

$$\cos\theta = \frac{\gamma_{so} - \gamma_{sw}}{\gamma_{ow}} \quad (2)$$

The subscripts s, o and w refer to the solid, organic liquid and water phases respectively. Ionised surface active materials are readily adsorbed to mineral surfaces by means of coulombic attractions between the ionic head group of the surfactant and

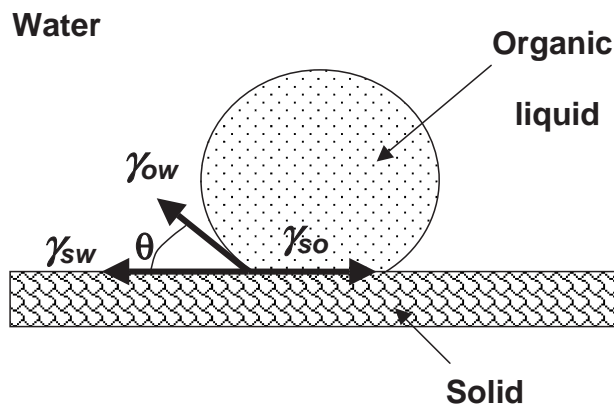


Fig. 1. Cartoon showing a non-wetting organic liquid drop on a mineral surface in the presence of water. The contact angle is the angle made by the water/organic liquid interface at the three phase contact line. γ_{sw} , γ_{ow} and γ_{so} are the solid/water, organic liquid/water and solid/organic liquid interfacial tensions respectively.

oppositely charged surface groups. This is the mechanism by which cationic surfactants are adsorbed to negatively charged quartz surfaces. As a result the hydrophobic tails are exposed to both the aqueous and organic liquid phases. This in turn leads to a reduction in γ_{so} and an increase in γ_{sw} . This has the effect of reducing $\cos \theta$ (the contact angle increases) in Eq. (2) even though there is a decrease in γ_{ow} (Rosen, 1989).

Pre-occupation with additives in NAPLs is not new. Several investigators have previously examined the extent to which additives in NAPLs can alter the wettability of porous media. Powers and Tamblin (1995) observed that dodecylamine in gasoline – at concentrations likely to be encountered in industrial products – was able to produce intermediate wetting conditions in sand. Demond et al. (1994) observed that cetyltrimethylammonium bromide adsorption to quartz surfaces had a major effect on wetting conditions in a water/xylene/quartz system. However, few investigators have considered the impact that additives in CHS DNAPLs may have upon wetting conditions in aquifer sediments and rocks. This should be an important area of concern given the routine use of surfactants in CHSs used in textiles finishing and dry-cleaning.

This report therefore emerges from our ongoing concern with chlorinated solvent contamination that is prevalent in the sandstone aquifers of the Midlands and North West regions of the United Kingdom (Lerner et al., 1993). In the past there has been a huge concentration of heavy industries – in these regions – using large quantities of CHSs in a variety of production processes. This report therefore seeks to examine the impact that four surface active additives, typical of those used in formulated products, have on the wettability of Permo–Triassic sandstone. *Inter alia* these impacts are examined as a function of additive concentration and the length of time that the sandstone is exposed to the solvent/additive mixture.

2. Methods and materials

Four additives were used in this the study: dodecylamine, octadecylamine, cetyltrimethylammonium bromide (CTAB) and octadecyltrimethylammonium bromide (OTMAB) (obtained from BDH, Poole, Dorset, UK). They were dissolved in TCE (purity: 99.5%; obtained from BDH, Poole, Dorset, UK), at three different concentrations (w/w) —0.1%, 0.05%, and 0.01%.

Sandstone wettability was assessed using the Amott method, which compares the ratios of spontaneous drainage and imbibition to forced drainage and imbibition (of the non-aqueous and aqueous phases) (Graue et al., 1999; Harrold et al., 2001; Tweheyo et al., 1999). In total 78 rock cores were used for this series of experiments. Replicate measurements were made for each of the surfactant concentrations. All the cores, which were 2.5 cm in length and 3.8 cm in diameter, were cut from one block of Permo–Triassic sandstone originating from the Cheshire Basin in the UK.

The sandstone cores were dried in an oven at 60 °C for 48 h and then re-saturated under vacuum for a period of at least 96 h with 2 mM sodium hydrogen carbonate solution. This was used to prevent any dissolution of carbonate cement at grain contact regions. Following this procedure cores were treated in one of two ways. Those cores in which the wettability was to be assessed immediately, i.e. without any prior exposure to the solvent

were placed in 100 ml jars containing a CHS/additive mixture for a period of two days to allow the spontaneous drainage of the aqueous phase in the core. The volume of expelled aqueous phase, which because of the density difference could be found, floating on the TCE, was measured using a Hamilton microlitre syringe. The cores were then placed together with their respective CHS/additive mixtures in 250 ml polycarbonate centrifuge tubes and centrifuged at incrementally increasing pressures until a capillary pressure of 68.95 MPa was reached. The volume of expelled aqueous phase was measured using a syringe. The reverse process consisted of a similar two stage procedure. The cores were immersed in 2 mM sodium hydrogen carbonate solution for two days to permit spontaneous imbibition of the aqueous phase and then centrifuged to a capillary pressure of 68.95 MPa. In order to allow the denser TCE to drain freely and to prevent its possible re-imbibition, each core was placed in a core holder that was constructed of sealed stainless steel tubing. This raised the core approximately 4 mm off the bottom of the tube. The volume of CHS expelled during this procedure was measured using a syringe.

Following saturation with the sodium bicarbonate solution, those cores whose wettability was to be assessed following a period of aging were placed in centrifuge tubes containing CHS/additive mixtures. They were centrifuged at a capillary pressure of 68.95 MPa, for a period of eight hours. This process forces solvent into the cores and brings the cores to the point of irreducible water saturation. The cores were subsequently removed from the centrifuge and stored in the CHS/additive mixture for an allotted period of time. The wettability of the cores was then determined using the previously described methods.

Results from these experiments are expressed as (a) the displacement-by-organic ratio δ_o , which is the ratio of water volume displaced by spontaneous organic imbibition alone, V_{wsp} to the total displaced by organic imbibition and centrifugal displacement, V_{wt} :

$$\delta_o = \frac{V_{wsp}}{V_{wt}} \quad (3)$$

and (b) the displacement-by-water (aqueous phase) ratio δ_w , which is the ratio of the organic phase volume displaced by spontaneous water imbibition, V_{osp} , to the total organic phase volume displaced by imbibition and centrifugal displacement, V_{ot} :

$$\delta_w = \frac{V_{osp}}{V_{ot}} \quad (4)$$

A preferentially water wetting core has a non zero δ_w value and a zero value for δ_o . An increasing water preference is demonstrated by δ_w values approaching 1. Conversely an organic wetting core has a non zero δ_o value and a zero δ_w . In the case of a neutrally wetting core both ratios are zero and two positive ratios indicate fractional wetting (Anderson, 1986a).

The interfacial tension (IFT) between TCE and the aqueous phase and the static contact angle of TCE on a quartz glass surface were measured by drop shape analysis (Del Rio and Neumann, 1997). A commercial instrument – the DSA 10 (*ex* Krüss GmbH, Germany) – was used to capture the shapes of pendant TCE drops suspended in aqueous solution (for interfacial tension measurements) and sessile TCE drops formed on a quartz glass surface in a bathing aqueous solution (for contact angle measurements), using a digital camera.

Once captured the profile was extracted and numerically fitted to the Young Laplace equation (Del Rio and Neumann, 1997) using dedicated computer software.

A detailed description of the experimental procedure used for the IFT measurements can be found in a previous publication (Harrold et al., 2003). It should, however, be noted that the IFT measurements were made by suspending a drop of TCE in double distilled water. The uncertainties in the IFT measurements are in the order of $\pm 0.2 \text{ mN m}^{-1}$.

Contact angle measurements were made using a quartz cuvette. The cuvette was cleaned in chromic acid and rinsed in copious amounts of distilled water prior to use. Following cleaning the cuvette was filled with double distilled water and placed in an environmental chamber whose temperature was maintained at $20 \pm 0.1 \text{ }^\circ\text{C}$ by a Grant recirculating water bath. A drop of the organic liquid of interest was carefully placed on the bottom of the cuvette using a syringe and the instrument set to acquire images of the evolving contact angle at 15 s intervals. Contact angles were calculated using the DSA 1 software supplied with the Drop Shape Analyser.

Goethite was used in a series of experiments in which the impact of iron oxide on the IFT of the solvent additive mixtures was investigated. 100 mg of powdered goethite was placed in 10 mL vials and 8 mL of the solvent/additive mixture was added, shaken manually for 10 s and then allowed to stand for 1 min. A sample of the solvent was subsequently removed from the vial and the IFT measured as detailed above.

3. Results and discussion

3.1. Wetting changes

The results from the core wettability tests are shown in Fig. 2. The data are presented as plots of the displacement-by-water ratios, δ_w , as a function of aging time, this being the length of time the cores were left at irreducible water saturation with the rest of the pore space occupied by TCE plus additive. There was no evidence, in any of the experiments, of spontaneous water drainage. Thus, since every core had a displacement-by-organic liquid ratio (δ_o) of 0 it is concluded that none of the solvent/additive combinations changed the wetting preference of the cores to solvent wetting. However it is apparent from the results that in a number of cases the cores display a much-reduced water wetting preference after aging. This is demonstrated by the size of the value obtained for δ_w . A value close to 1 indicates that the sandstone core is strongly water wetting. That is most of the water imbibition in these cores is spontaneous. On the other hand values close to zero indicate that much of the imbibition of water is by forced displacement. This latter condition is indicative of weak water or even neutral wetting conditions.

It is well to stress some important features of these plots. All the un-aged cores, where TCE contains 0.01% of the additive, exhibit a high δ_w value (Fig. 2). This indicates that almost all water imbibition is spontaneous. At low wetting phase saturation, as is the case at the end of the drainage runs in this series of experiments and where the water wetting preference of the rock is sufficiently strong, capillary forces will permit water – as the wetting fluid – to spontaneously imbibe into the cores. This process is driven by the favourable surface free energy change that occurs as the wetting fluid replaces the non-

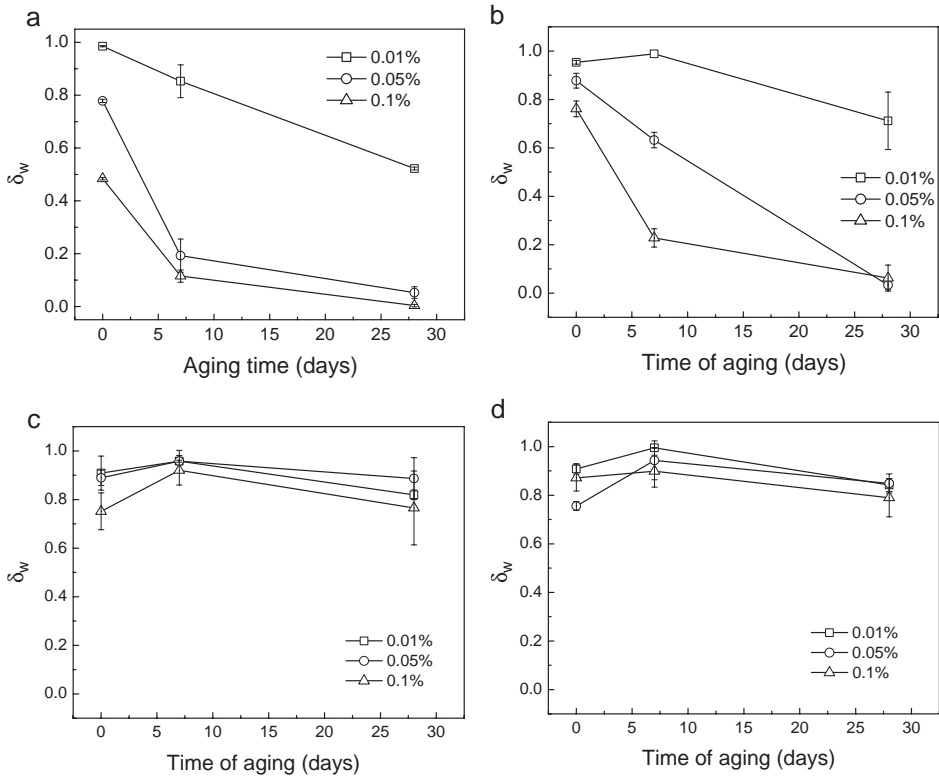


Fig. 2. Displacement by water ratios for sandstone cores exposed to TCE containing (a) dodecylamine, (b) octadecylamine, (c) CTAB and (d) OTMAB as a function of additive concentration and exposure time. The data point information on the plots indicates the % concentration of each additive.

wetting fluid. In those cases where the core has a strong wetting preference the wetting fluid is rapidly imbibed due to the large decrease in the surface free energy. Therefore cores with a high δ_w essentially demonstrate a strong water wetting preference, which is driven by a large decrease in surface free energy (Anderson, 1986b, 1987).

The data obtained for the TCE with 0.1% additive are shown in Fig. 3. An extremely interesting contrast is noted between the behaviour of the TCE/alkylamine compound solutions and the TCE/quaternary ammonium compound solutions. Both alkylamine compounds would appear to play a dominant role in the enormous reduction in the wetting preference of the sandstone cores to neutral wetting conditions even after a short period of exposure to the TCE/additive solution. It may be recalled that neutral wetting conditions are demonstrated by both δ_o and δ_w having values of zero. Comparison with the data obtained for lab grade TCE, which contains a small amount of triethylamine as a stabiliser, suggests that these wetting changes are due to the presence of the alkylamine compounds. Moreover as might be anticipated, the magnitude of the wetting changes is related to both additive concentration and length of ageing period. In both cases an increase in either results in a more pronounced change towards neutral wetting.

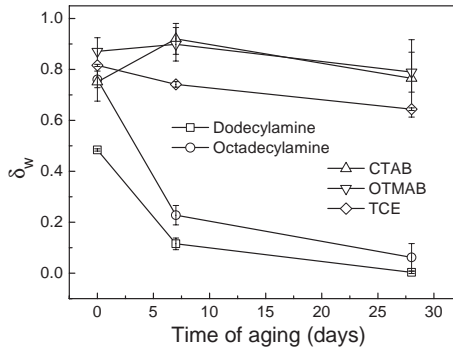


Fig. 3. The relationship between the displacement by water ratio and exposure time for a variety of TCE samples containing 0.1% of (□) dodecylamine, (○) octadecylamine, (△) CTAB and (▽) OTMAB plus (◇) TCE which only contains triethylamine stabiliser.

As shown in Fig. 2a and b for solutions with additive concentrations of 0.05% and 0.1%, after 28 days ageing, little spontaneous imbibition occurs in any of the cores. Indeed in the case of dodecylamine, this change to neutral wettability is rapidly completed at both concentrations as evidenced by the low value for δ_w after 7 days (Fig. 2a). A similar pattern is demonstrated by the cores containing 0.1% octadecylamine; however the change at a concentration of 0.05% is less rapid and more linear (Fig. 2b). Of the two alkylamine compounds it can be seen that wettability changes are more pronounced in the dodecylamine exposed cores than the octadecylamine cores. It is conjectured that this is related to differences in the molecular size of the two amines. Dada and Wenzel (1991) have suggested that differences in the structure and size of adsorbed surfactant monomers can lead to different packing efficiencies on a solid substrate. A lower packing efficiency for the larger octadecylamine molecule is likely to create less pronounced changes in wettability when compared with the greater packing efficiency of the smaller dodecylamine molecules.

The adsorption of alkylamine surfactants to the sandstone surface is driven principally by acid–base interactions. At neutral and slightly acidic pH values the alkylamines used in this study are almost totally protonated — pK_a for dodecylamine is reported to be 10.63 (Quast, 2000). Under the same pH conditions the silicate sandstone surface is negatively charged. Thus alkylammonium cations will be attracted to the oppositely charged surface through electrostatic interactions (Chernyshova et al., 2000).

Ernstsson and Larsson (2000), using a series of basic test molecules, including octadecylamine, recognised that there are a variety of adsorption sites on the surfaces of iron oxide coated quartz. They suggested that the initially strong adsorption of long chain alkylamines onto quartz was due to the presence of iron and/or iron hydrous oxides, which presumably act as Lewis acid sites. A second group of strong adsorption sites were considered to be geminal hydroxyl groups, which are located at the corners and edges of quartz crystals. Finally they identified hydrogen bonding to surface hydroxyl groups as the principal mechanism for the weaker adsorption seen at higher surface coverages. These hydrogen bonding sites represent the bulk of the available adsorption sites. The results obtained suggested that the adsorbed layer of octadecylamine chains forms a closely packed monolayer.

Quast (2000) has reviewed the work of investigators whose interest was the adsorption of 12-carbon atom collectors on haematite as a prelude to mineral flotation. It was reported that the amount of dodecylamine adsorbed was greater than could be accounted for by ionic interactions alone. Chernyshova et al. (2000) have investigated dodecylamine adsorption onto a quartz. They concluded that at bulk concentrations lower than the critical hemi-micelle (*cmc*) concentration, the protonated amine head-group is hydrogen bonded to the oxygen atoms present in the surface silanol (SiOH) groups. Surface coverage is fairly sparse and the hydrocarbon chains adopt a chaotic orientation. Above the *cmc* un-ionised amine molecules are hydrogen bonded to surface silanol groups and protonated amine molecules are attached to de-protonated silanol groups. As a consequence monolayer patches of well-oriented and densely packed adsorbed amine species form and the surface becomes very hydrophobic. Finally at even higher concentrations bulk precipitation of un-ionised amine molecules was noted. It therefore seems a sustainable conjecture that alkylamine adsorption from TCE solution to the sandstone surface is responsible for the change in wetting conditions.

3.2. Changes in interfacial tensions: alkylamines

The Gibbs adsorption isotherm describes the functional relationship between surface/interfacial tension and bulk solute concentration for systems where the solute is either preferentially adsorbed at the interface, thereby creating a surface excess concentration of solute, or negatively adsorbed thereby producing surface depletion (Hunter, 1993). The interfacial activity of the amine additives at the TCE/water interface under conditions where the pH of the aqueous phase is neutral to slightly acidic should produce a marked decrease in interfacial tension. The removal of amine additives from the bulk TCE phase by adsorption should lead to a corresponding increase in the interfacial tension of the TCE/aqueous system. A number of investigators have demonstrated the validity of this proposition (Liu et al., 1992; Paterson et al., 1999; Paterson et al., 2000) and previously we have reported that the removal of modest amounts of triethylamine from TCE is responsible for an increase in the water/TCE IFT (Harrold et al., 2003). Therefore to test this conjecture, for our systems, a series of IFT measurements were made using distilled water and TCE containing octadecylamine before and after TCE had been exposed to sandstone. The tests were repeated to ensure data consistency.

The results obtained in this series of measurements are shown in Fig. 4a. Somewhat counter-intuitively those TCE/octadecylamine mixtures which have been displaced from the core by the forced and spontaneous imbibition of water have lower IFTs than those samples which have not been in contact with the cores. It is presumed that the adsorption of the amine compound is responsible for the wetting changes noted. There is plenty of evidence in the literature that amine adsorption from oils to sand (Powers and Tamblin, 1995) and sandstone (Kowalewski et al., 2002) alters wettability with respect to the hydrocarbon liquids. Adsorption of the amine from TCE must reduce the bulk amine concentration and thus should give rise to an increase in IFT. Yet we are confronted with the paradox that the TCE draining from the cores, following exposure to the sandstone cores, has reduced IFT values.

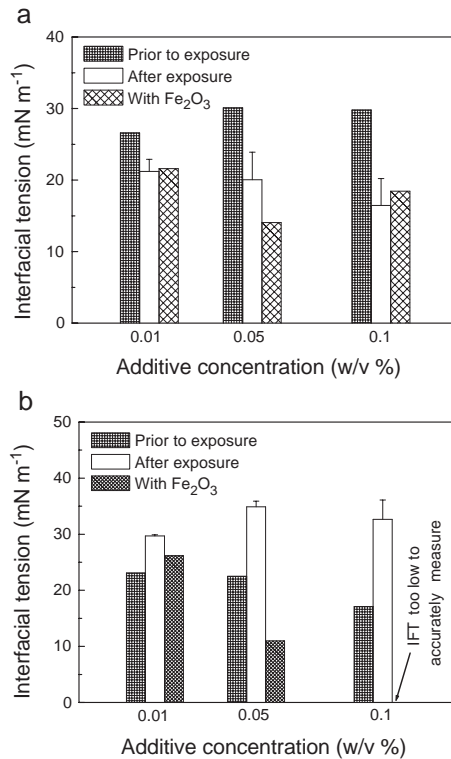


Fig. 4. The effect of TCE exposure to the sandstone cores and to goethite (Fe_2O_3) on the water/TCE IFT. Data in (a) were obtained for octadecylamine and (b) CTAB.

It was observed during the course of the experiments that TCE draining from the cores had undergone a colour change — from clear to a rust brown, which suggested that iron oxide particles had been removed from the mineral surfaces of the cores. In order to test the hypothesis that the presence of iron oxide in the solvent, presumably bound to alkylammonium ions/alkylamine molecules, could be responsible for the reductions in IFT, a series of IFT measurements were made using a TCE/octadecylamine mixture that had been exposed to goethite. As Fig. 4a demonstrates the IFT values are depressed by the presence of iron oxides.

The mechanism by which the iron was removed from the surface of the cores was not investigated; however it is possible that amine molecules acting as organic ligands can remove iron oxide particles. Stumm and Sulzberger (1992) report that Fe(II) can be adsorbed to particle surfaces through complexation with surface hydroxyl groups which enhances its oxidation to Fe(III). Subsequent reductive dissolution of iron(III) oxides/hydrous oxides can occur through interactions with organic ligands. It is worth noting that the oxidation of iron(II) to iron(III) is accompanied by the binding of the reactive compounds and conversely the dissolution of the iron(III) oxides/hydrous oxides results in the release of the complexed substances (Stumm and Sulzberger, 1992; Zachara et al., 1995).

The mechanism responsible for the reduction in IFT was not investigated. However it is well documented that alkylamine compounds like dodecylamine are used in mineral flotation processes (Quast, 2000). The objective in these schemes is to alter the surface properties of mineral grains such that they are preferentially adsorbed at the air/water interface (Hunter, 1993). Long chain un-ionised amine molecules are not expected to show any surface activity (Rosen, 1989) and therefore are not expected to provide a reduction in interfacial tension. However un-ionised amine molecules can be adsorbed by iron oxide (Quast, 2000) which enables them to be attached to the air/water interface. It is therefore conjectured that the removal of iron oxide particles by un-ionised amine molecules is responsible for some or even all of the reduction in water/TCE IFT.

This question of the impact that particles may play in enhancing the reduction in IFT in oil/water surfactant systems has been investigated – in a somewhat different way – by Masliyeh and co-workers (Wang et al., 2004). They measured the IFT between hexadecane, which contained dodecylamine and aqueous suspension of kaolinite. It was clear that the presence of dodecylamine in the hexadecane phase was responsible for the reductions in the IFT against pure water. However the presence of the kaolinite particles – suspended in the aqueous phase – resulted in significantly larger decreases in IFT. The authors conjectured that this was due to the presence of a negatively charged cloud on the water side of the interface – provided by the kaolinite – which augmented the adsorption of dodecylammonium ions at the interface through a reduction in electrostatic head group repulsion (Wang et al., 2004).

Whatever the exact mechanism responsible for the reduction in IFT in the octadecylamine/water/sandstone systems the available literature evidence would seem to indicate that the presence of particles can have a dramatic effect upon IFT values. Thus in these systems it seems likely that though the alkylamine solutes present in TCE are adsorbed from solution to sandstone mineral surfaces which alters the wetting behaviour of those surfaces. The solutes may also aid in the removal of iron oxide coatings which subsequently results in a decrease in IFT.

3.3. Changes in interfacial tensions: quaternary ammonium compounds

Both quaternary ammonium compounds used in these experiments are cationic and should readily be adsorbed at the negatively charged surface of the quartz in a similar manner to the alkylamines. It appears, however, from Figs. 2c,d and 3 that there is no substantive change in the wetting behaviour of the sandstone cores following their exposure to these particular solvent samples.

The mechanism of CTAB adsorption onto silicate surfaces is not entirely clear. It has been suggested that at low concentrations the positively charged heads of the CTAB ions are adsorbed to the negatively charged sites on the silica surface, with their non-polar tails arranged parallel to the surface. With increasing concentration, the tails of the adsorbed ions are orientated into the solution thus increasing the number of available active sites. When these sites eventually become exhausted it is then possible that adsorption of the CTAB ions proceeds on the tails of the previously adsorbed ions. This creates a second adsorbed layer where the charged heads are oriented toward the solution (Atkin et al., 2000; Churaev et al., 2000). Such an adsorption pattern could be responsible for the

apparent lack of wetting changes in the cores, as a surface covered in a double layer of molecules with the outer layer having its head groups oriented into the liquid would be hydrophilic. However Demond et al. (1994) suggest that the formation of this bilayer does not necessarily lead to a uniquely hydrophilic surface. They noted that in a system composed of water, quartz, CTAB and xylene that if the top layer of sorbed CTAB molecules is disturbed then xylene may spread on the exposed non-polar tails of the first layer of CTAB molecules, their charged heads having been adsorbed to the quartz surface. In this case they noted that the instability of the top layer appeared to be related to drop size and hence suggested that a sufficiently high gravitational force was required to disrupt the bilayer.

One way of testing the removal of CTAB from solution is by measuring the IFT of TCE against water. As with the octadecylamine, if CTAB is adsorbed to the silica surface and thereby removed from bulk solution, there should be an increase in the IFT of a TCE/aqueous system. Fig. 4b demonstrates that IFT of the TCE/aqueous system does indeed increase significantly following exposure to the sandstone in the core experiments. Interestingly however the introduction of goethite into the TCE/water/CTAB system, in two out of three cases, actually produces a significantly marked reduction in IFT. It would therefore seem likely that in the sandstone core wettability experiments CTAB is lost from TCE but CTAB can interact with iron oxide in such a way that the TCE/water IFT is significantly reduced.

The loss of CTAB from TCE can be accounted for in two ways. It is possible that CTAB has been adsorbed at the liquid/solid interface as a bilayer in which case the wetting behaviour of the sandstone would not be altered. Alternatively the loss could be accounted for by the transfer of CTAB from TCE to the aqueous phase. To probe these systems further and in order to ascertain whether we should expect to see a wetting change the static contact angle of TCE/CTAB drops were measured on quartz in the presence of water. The contact angle was measured as a function of time. The data obtained from these experiments are shown in Fig. 5.

The data clearly reveal that when a drop is placed on the quartz surface, the drop begins to spread and the contact angle quickly attains its maximum value. Subsequently the drop

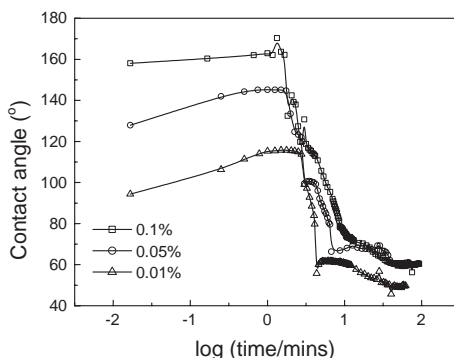


Fig. 5. Comparison of the evolution of contact angles for TCE containing cetyltrimethylammonium bromide at three different concentrations.

contracts as the forces of cohesion overcome the adhesive forces and the spreading coefficient becomes negative. The changes in the contact angle are readily explained. The initial formation of the TCE drop, containing CTAB, on the quartz surface is characterised by the rapid migration to and adsorption of surfactant unimers at the TCE/aqueous phase interface, with the positively charged heads orientated into the aqueous phase and the hydrophobic tails located within the body of the TCE drop. When the drop contacts the quartz surface the surfactant unimers present at the three phase boundary line quickly start to adsorb to the surface causing the drop to rapidly spread. However due to partitioning of the CTAB into the aqueous phase where it is more soluble and the preference of the surface for surfactant monomers over solvent molecules the solvent starts to retract until an equilibrium contact angle is reached.

This behaviour is in direct contrast to the TCE mixtures containing the amines which are more soluble in the solvent phase. In this case the initial and equilibrium contact angles are very similar (40– 60° depending on concentration).

The initial contact angle, maximum contact angle and the start of the contraction of the TCE/CTAB drop are related to the surfactant concentration. However it appears that the final contact angle is perhaps less dependent on the surfactant concentration. Both the 0.1% and 0.05% CTAB solutions have effectively the same final contact angle, while the least concentrated solution (0.01%) is about 10° lower. This behaviour may be explained by recalling that CTAB molecules can change their orientation with coverage and at low densities the CTAB alkyl chains may lie parallel to the surface while at higher densities they are forced into a more perpendicular orientation. Therefore at lower coverage, the hydrophobic tails cover a greater area per molecule than at higher coverage, resulting in a disproportionately large change in contact angle at lower surface densities and smaller changes in contact angle as coverage increases (Demond et al., 1994).

It is noticeable that the displacement-by-water ratio increases for both the CTAB and OTMAB samples after a period of seven days aging, suggesting that the cores have become more water wetting. Yet the contact angle data obtained for a similarly aged quartz slide (data shown in Fig. 6) suggest that the cores should display neutral wetting characteristics. The data reveal that the final contact angle for the CTA exposed quartz surface was 80° after an aging period of seven days compared with 60° for an un-aged surface.

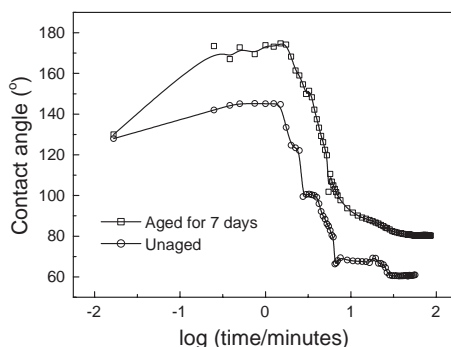


Fig. 6. Comparison of the evolution of contact angles, (□) on a quartz surface aged for seven days and (○) an un-aged surface, for TCE containing 0.05% cetyltrimethylammonium bromide.

There is clearly some difficulty in trying to reconcile the contact angle data with the displacement by water ratios. It is, of course, entirely possible that the differences could be ascribed to the presence on the sandstone surface of iron oxide coatings. Indeed, it is possible that the surface charge of the iron oxide is positive. However, it should be assumed that since the aqueous phase is 2 mM sodium hydrogen carbonate, the pH is sufficiently high for the surface charge to be negative. We would therefore expect CTAB to be adsorbed to anionic sites on both the quartz and iron oxide coatings.

A possible explanation for the wetting data shown in Figs. 2c,d and 3 could be as follows. If the contact angles in the core are close to 90° there is no clear wetting preference or, at best, a very weak water wetting preference. Under these conditions capillary forces would not be expected to dominate fluid distributions in the sandstone cores. For instance a weak water wetting preference in the system would not be expected to result in any significant spontaneous water imbibition and forced drainage of the TCE. Thus the only plausible explanation is that the IFT is suppressed to such an extent that the density difference between the two fluids allows for the drainage of the TCE from the core due to gravity.

The IFT of the TCE which initially contained CTAB and which had drained from the cores, was around 35 mNm^{-1} (Fig. 4b), which is clearly not low enough to allow gravity drainage. However, these IFT values were measured against distilled water. To replicate the test conditions more faithfully the IFT was subsequently measured against aqueous phase that was displaced from the core. In this case the IFT measured was too small (below 1 mNm^{-1}) to accurately measure it. With IFT values of this magnitude there will be drainage of solvent from the cores due to the relative gravitational forces. These extremely low IFTs may also help to explain why we observe such a large advancing angle for the CTAB containing solvent on a quartz surface, but no spontaneous imbibition of the solvent into the core. If a significant interfacial energy does not exist between the two fluid pairs at a pore throat then there is no driving force to draw the solvent into pore. In the case of the octadecylamine/TCE mixtures the IFT is not suppressed so spectacularly; but low IFT values of $11 - 17 \text{ mNm}^{-1}$ were recorded for the various mixtures.

3.4. Emulsion formation

Finally one unexpected observation was the ease by which TCE/water emulsions were formed in the presence of iron oxide. The emulsions formed are examples of Pickering emulsions. Pickering emulsions are water/oil emulsions stabilised by the presence of solid particles that are much smaller than the dispersed immiscible liquid drops in the continuous liquid phase (Binks, 2002). These solid particles stabilise emulsions by surrounding the dispersed phase droplets. Drop coalescence requires the removal of the stabilising particles from the interface to the continuous phase. If neither immiscible liquid phase preferentially wets the particles then the contact angle is in the region of 90° and removal from the interface carries a huge free energy penalty. This is the origin of the emulsion stability. Fig. 7 shows a TCE in water emulsion stabilised by goethite and octadecylamine. It is quite probable that octadecylamine has been adsorbed to the mineral surface thereby altering its contact angle. The surface is slightly water wetting which means that the goethite particles tend to have a larger degree of interaction with water at



Fig. 7. Photograph showing the distribution of goethite in water/TCE/additive systems. The bottle on the left contains CTAB as an additive and the one on the right contains octadecylamine.

the expense of their exposure to TCE. This results in the formation of TCE drops in water at the continuous phase.

Emulsion formation was also noted in the core wettability experiments. The aqueous phase that drained from the cores as it was replaced by TCE containing either CTAB or OTMAB during the initial aging step appeared to be an emulsion. No emulsions were formed when the alkylamine compounds were used. Clearly emulsion formation, low interfacial tensions and reduced wetting preferences point to significant problems in delineating industrially formulated TCE DNAPL fate and behaviour in sandstone aquifers.

4. Conclusions

The impact that two alkylamine compounds and two quaternary ammonium salts have upon the wetting properties of TCE was investigated. Both dodecylamine and octadecylamine reduce the wetting preference of sandstone from strongly water wetting to near neutral wetting conditions. In contradistinction the quaternary ammonium compounds investigated had little apparent impact upon wetting. Measurements of TCE plus additive/water interfacial tensions provided evidence that the interfacial tension can change after TCE has been exposed to sandstone in the presence of water. There was some evidence to suggest that these changes were the result of the detachment of iron oxide particles from the sandstone surface. In some cases this gave rise to emulsion formation and substantial decreases in interfacial tension. It would seem clear that the role that additives might play in TCE DNAPL transport and fate in the sub-surface environment can be substantially attenuated through interactions between the additives and mineral surfaces.

Acknowledgements

This work forms part of a wide ranging study into the behaviour of chlorinated hydrocarbon solvents in the Triassic Sandstone aquifers of the UK. Funding for the project

was provided by the Engineering and Physical Sciences Research Council (Grant Number GR/R55153/01).

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