Research Paper

Swelling of compacted bentonite in organic solvents: Correlation of rate and extent of swelling with solvent properties

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ABSTRACT

The swelling of clay minerals within shale formations during oil and gas exploration, and within compacted bentonite barriers for radioactive waste containment, presents a number of challenges to operators. Whilst much work has been devoted to understanding the interlayer swelling properties of clay mineral crystals, significantly less has been devoted to understanding coupled pore and interlayer swelling in reactive shale/compacted clay minerals. Here we study the swelling of compacted clay mineral tablets on exposure to a range of organic solvents, selected so that the effect of key solvent properties such as dielectric constant, density, octanol-water partition coefficient, viscosity and surface tension can be correlated with the swelling observed. We use a novel non-contact swelling meter to carry out the swelling tests, allowing us to access information on rate of swelling. Short-term swelling rate showed the strongest correlation to the solvent octanol-water partition coefficient. In long term swelling, good correlation was found between total linear swelling and viscosity, and the octanol-water partition coefficient.

1. Introduction

Shale is a fine-grained sedimentary rock, containing significant quantities of clay minerals in addition to quartz, calcite, organic matter, cements and other minor minerals. Controls on shale swelling are of wide interest, from fundamental science to applied research. Shale swelling is problematic for the oil and gas exploration sector owing to the ubiquity of shale formations in sedimentary systems, with a significant proportion of conventional oil reservoirs capped, or sealed, by shale, as well as the growing exploitation of unconventional shale gas/oil reservoirs. Due to their high affinity for water (Santarelli and Carminati, 1995; Van Oort, 2003; Anderson et al., 2010), certain clay minerals swell and destabilise when in contact with water based drilling fluids, used for hole clearing, during wellbore drilling operations, costing the industry an estimated 1 billion $/year (Zeynali, 2012). The contribution of clay minerals to the overall swelling of shales contacted with aqueous fluids is of key interest.

Bentonite is an analogous material to the clay minerals found in many reactive shale formations (Komine and Ogata, 1994). Much work

has been undertaken on water absorption by compacted bentonite as it is used as a barrier material in radioactive waste containment (for a review, see Sellin and Leupin (2013)). However, for assessing shale swelling stability, emphasis has been on developing methods for long-term swelling pressures, on the order of days (Wang et al., 2012). This makes it difficult to compare data between methods due to variation in water content and wetting conditions. Experiments using as-received bentonite, however, show the same trends: swelling pressures increase rapidly at early stages of hydration and become stable with little variation over time (Komine and Ogata, 1994; Villar and Lloret, 2008; Komine et al., 2009; Wang et al., 2012). In oil and gas exploration and production compacted bentonite samples are also routinely tested to establish reactivity towards swelling upon contact with technical drilling fluids, typically using linear variable differential transformer (LVDT) contact measurements with the parameter of interest being the static endpoint of clay expansion and total amount of water absorbed (Zhang and Sun, 1999; Liu et al., 2004; de Carvalho Balaban et al., 2015), rather than the kinetics of swelling.

Fundamental work on clay mineral single crystals using XRD, quasi-

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Table 1
Physical properties of water and the organic solvents used in this study. (Jasper, 1972; Smallwood, 2012).

Solvent	Chemical Formula	Viscosity (25 °C, mPa.s)	Dipole moment (D)	Dielectric constant (20 °C)	Surface tension (mN/m)	Octanol-Water Partition Coefficient
Water		0.890	1.87	80.1	72.80	N/A
Methanol		0.6	1.7	32.6	22.6	−0.74
Ethanol		1.08	1.7	22.4	22.3	−0.3
Butanol		3.0	1.66	18.2	24.6	0.84
Heptanol		5.77	1.71	12.1	26.44	2.62
Decanol		11.79	1.6	8.1	28.12	4.57
Acetone		0.33	2.9	20.6	23.3	−0.24
Propan-2-ol		2.0	1.66	18.3	21.7	0.05
Hexane		0.31	0	1.9	18.4	4
Benzyl alcohol		5.47	1.7	13.1	36.8	1.05

elastic neutron scattering (QENS), inter alia, also focus on long term equilibrium, driven by the enthalpy of hydration of the interlayer cation and the balance of attraction of the negatively charged clay layers for the interlayer cations (Norrish, 1954; Olejnik et al., 1974; Sposito et al., 1999). For a given clay mineral (Johnston, 2017), cation exchange with ions of lower hydration enthalpies, or introducing molecules to chelate the hydrating cations, minimise the interlayer swelling (for example, Boek et al. (1995) and Suter et al. (2011)). Continual uptake of water, beyond crystalline water, moves the clay mineral into the osmotic swelling regime, which has generally been thought to be the driver of large-scale shale instability (see review by Anderson et al. (2010)).

However, recent studies (see review by Wilson and Wilson (2014)) suggest that relative permittivity of the flooding solvent system may be also be key in controlling the swelling of clays/shales since they show that highly illitic and kaolinitic shales may also be unstable. Wilson and Wilson (2014) concluded that the instability stems from an increased pore pressure which is driven by the diffuse double layer (DDL) of the clay minerals being of the same order as, or thicker than, the sizes of a large proportion of the pore spaces within these shales, leading to repulsive DDL overlap. If this conclusion holds true, since the Debye screening length derived in Poisson-Boltzmann, Debye-Huckel and DLVO theory (Verwey and Overbeek, 1955; Smalley, 2006) is proportional to the square-root of the dielectric constant of the solvent fluid, the relative permittivity of the bulk fluid may be exploited to minimise shale swelling. Whilst these theories (DLVO theory in particular) have been able to describe the final equilibrium swelling state, none are capable of describing the dynamic swelling rate of shales as a function of the imbibing solvent properties. Additionally, experiments studying the permeability change of soils with high clay content suggest interplay exists between solvent dipole moment, the dielectric constant and molecular weight, controlling the extent to which permeability increases within the compacted soil (Anderson et al., 1985).

In order to experimentally test these theories, it is necessary to look at a wide range of contacting fluid relative permittivity, which is hard to achieve with aqueous salts alone, since: (i) the range of permittivity is limited, (ii) they cause competing osmotic effects and (iii) controlling cation exchange becomes problematic (Anderson et al., 2010). Organic solvents, however, offer a wide range of dielectric constants and are regularly used to clean oilfield reservoir cores, though are rarely looked at from the perspective of bulk shale swelling. Early work on understanding clay crystal swelling used crystals equilibrated with organic solvents, focussing on equilibrium interlayer spacing (Barshad, 1952a, 1952b) with very few studies attempting to relate bulk swelling and solvent dielectric constant (Murray and Quirk, 1982). However, the data suggests that decreasing dielectric constant leads to a decrease in total swelling within both interlayer and bulk swelling regimes. These prior studies performed analysis based solely on equilibrium states and do not study the effect of dielectric constant on the early-stage dynamics of

swelling, which is increasingly becoming an important factor to consider in the oilfield applications of these solvents for example, through trying to inhibit clay accretion around the cutting tools of the drill string, known as "bit balling" (Anderson et al., 2010). Understanding shale swelling may also become critical during well abandonment operations (Vrålstad et al., 2019), and for increasing the understanding of hydrocarbon extraction from shale using solvents, which are currently used to dissolve the hydrocarbons but may additionally have an influence on the surrounding shale (DiStefano et al., 2019).

When considering the impact of clay swelling, solvent properties cannot be considered in isolation. Contrary to the view that clay mineral swelling underpins shale failure in well bores, Santarelli and Carminati (1995) showed that laboratory tests on shales are generally not representative of downhole conditions and any swelling observed is mainly because of capillary effects. In their studies, they showed that there was no difference between the effects of inhibitive KCl and non-inhibitive lignosulfonate muds. Schmitt et al. (1994) stated that when shales are unsaturated, formation of capillary pressures is inevitable and is directly affected by the pore size distribution and the moisture content of the shale, which needs to be considered when undertaking swelling experiments in the laboratory. This insight has led to the possibility of modelling the initial rate and end-point of swelling of these compacted materials to generate useful information on the void space and pore-water content of the samples with time (Mathias et al., 2017).

The study presented here explores the short term (⟨1h) swelling of compacted bentonite in organic solvents with a range of relative permittivity. The study uses a new non-contact linear swelling meter (Mathias et al., 2017; Love, 2019) which offers high resolution (60 scans per minute) and repeatable data sets (4 simultaneous measurements). To provide comparison, the long-term equilibrium swelling of the compacted bentonite tablets was assessed using the same solvents, and further compared to theoretical values of stable equilibrium swelling states calculated from DLVO theory. Results of these experiments yield fundamental understanding for the development of appropriate drilling fluids to a given shale type, as well as having potential application in core studies and materials science.

2. Experimental methods

2.1. Materials

The Wyoming Bentonite GDM, purchased from Steetley Bentonite & Absorbents Ltd., Retford, U.K., contains >95% dioctahedral sodium-montmorillonite smectite clay mineral, with a cation exchange capacity of 0.7 meq/g (Meeten, 1994). The XRD pattern of the bentonite is provided in the supplementary information. The bentonite was sieved to remove particles >150 μm, but otherwise was used as received. The BET surface area was determined by the nitrogen gas adsorption isotherm
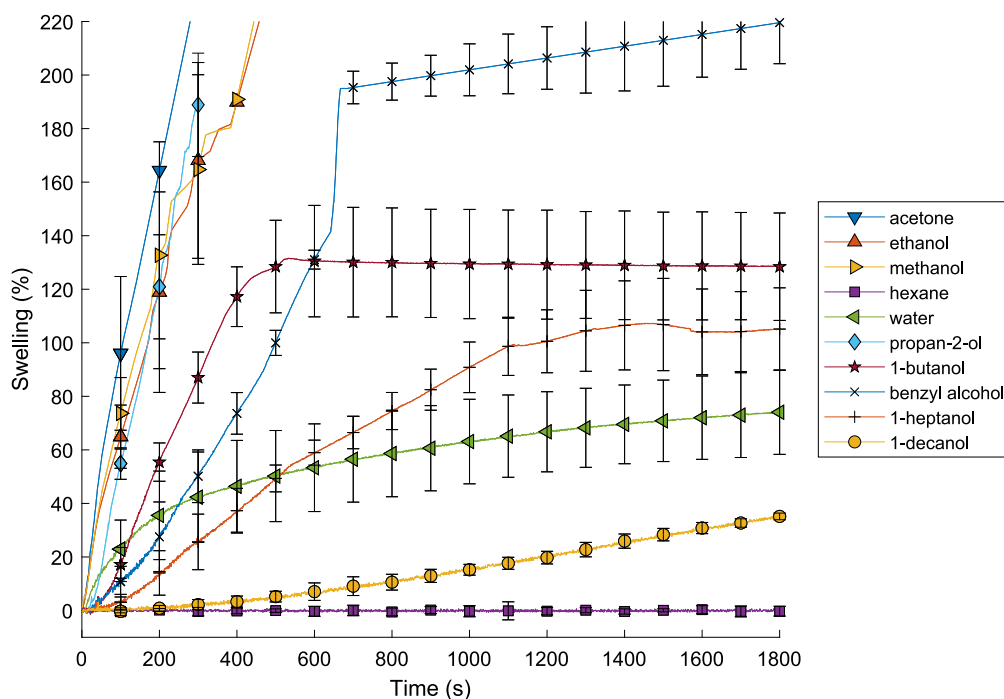
Fig. 1. Linear swelling behaviour of bentonite tablets in various organic solvents via NC-LDM with 60 readings/min frequency. Error bars show in experiment variation between tested clay tablets. Swelling >220% could not be recorded as it was outwith the measurement range of the sensor (acetone, ethanol, methanol, propan-2-ol).

method to be 30.33 m^2/g (Ratcliffe et al., 2009).

Organic solvents were laboratory reagent-grade and used as obtained from Sigma-Aldrich. Table 1 shows the physical properties of the solvents used, with water included for comparison. A set of linear alcohols were chosen to investigate the effect swelling behaviour with respect to methylene group chain length. Acetone, hexane and benzyl alcohol were also chosen due to their particular dipole moments, viscosity and surface tension.

2.2. Clay tablet preparation

Compacted bentonite tablets of 20 mm diameter and 3.8 mm thickness were prepared by applying a uniaxial pressure of 63 MPa, a pressure similar to that seen in North Sea oilfields (Wilson and Wilson, 2014), for 2 min to 2.5 g of the as received bentonite powder (stored in a closed container in the laboratort with no additional control of humidity) with a 20 mm clean tablet die and a hydraulic press. Upon removing the tablets from the press, the mass was again taken to ensure no clay remained stuck to the tablet die; the average mass was found to be 2.5 g ± 0.0025 g (Love, 2019). The tablets were used within 30 min of preparation, and four clay tablets were used in each test.

2.3. Swelling measurements

2.3.1. Non-contact linear displacement meter

In this study, a novel non-contact linear displacement meter (NC-LDM), based on induction sensors is used to investigate the uniaxial swelling behaviour of compacted clay tablets (Erdogan, 2016). The data from the sensors (giving 1.2% variation in reading at maximum distance) was collected and processed via customised data-acquisition software in LabVIEW® (Elliott et al., 2007). Short-term swelling tests were performed using 200 ml of the designated solvent at room temperature (20–22 °C) and pressure. The experiment was run for a maximum of 30 min, or until the maximum swelling range of the instrument was reached (approximately 8 mm). The data was normalised to the initial tablet height, and an average swelling curve was calculated

for each solvent. Data was excluded from tablets with obvious cracking, as this was due to imperfections in tablet preparation, not solvent effects (no more than one tablet per solvent was required to be excluded, giving a minimum *n* = 3 per solvent).

2.3.2. Long-term (equilibrium) swelling tests

The overall equilibrium swelling behaviour of clay tablets in the solvents was examined by a simple volumetric method. Clay tablets were placed into flat bottom vials with 20 ml of solvent and left at room temperature (20–22 °C). The change in gel height was recorded every five min in the first hour, every hour in the next 8 h, and every 24 h thereafter. Overall equilibrium swelling was recorded at the point where no further clay expansion was observed between consecutive measurements. All experiments were carried out simultaneously.

2.4. Swelling calculations

In addition to the experimental measurements, long-term equilibrium swelling distances have been calculated using DLVO theory. In this work, the equilibrium distance between two basal clay surfaces has been calculated via deriving the minimum in the pair potential (V(*r*)):

$$V(r) = V_{att}(r) + V_{rep}(r)$$

where $V_{att}(r)$ represents the attraction between adjacent basal surfaces due to London dispersion forces, $V_{rep}(r)$ represents the electrostatic repulsion between like-charged clay basal surfaces, and *r* is the interplanar basal separation. In our calculations, $V_{att}(r)$ has been evaluated as:

$$V_{att}(r) = -\frac{A}{12\pi r^2}$$

where *A* is the Hamaker constant, which represents the strength of the dispersion forces between the sheets.

The electrostatic repulsion between the clay basal surfaces has been calculated as:
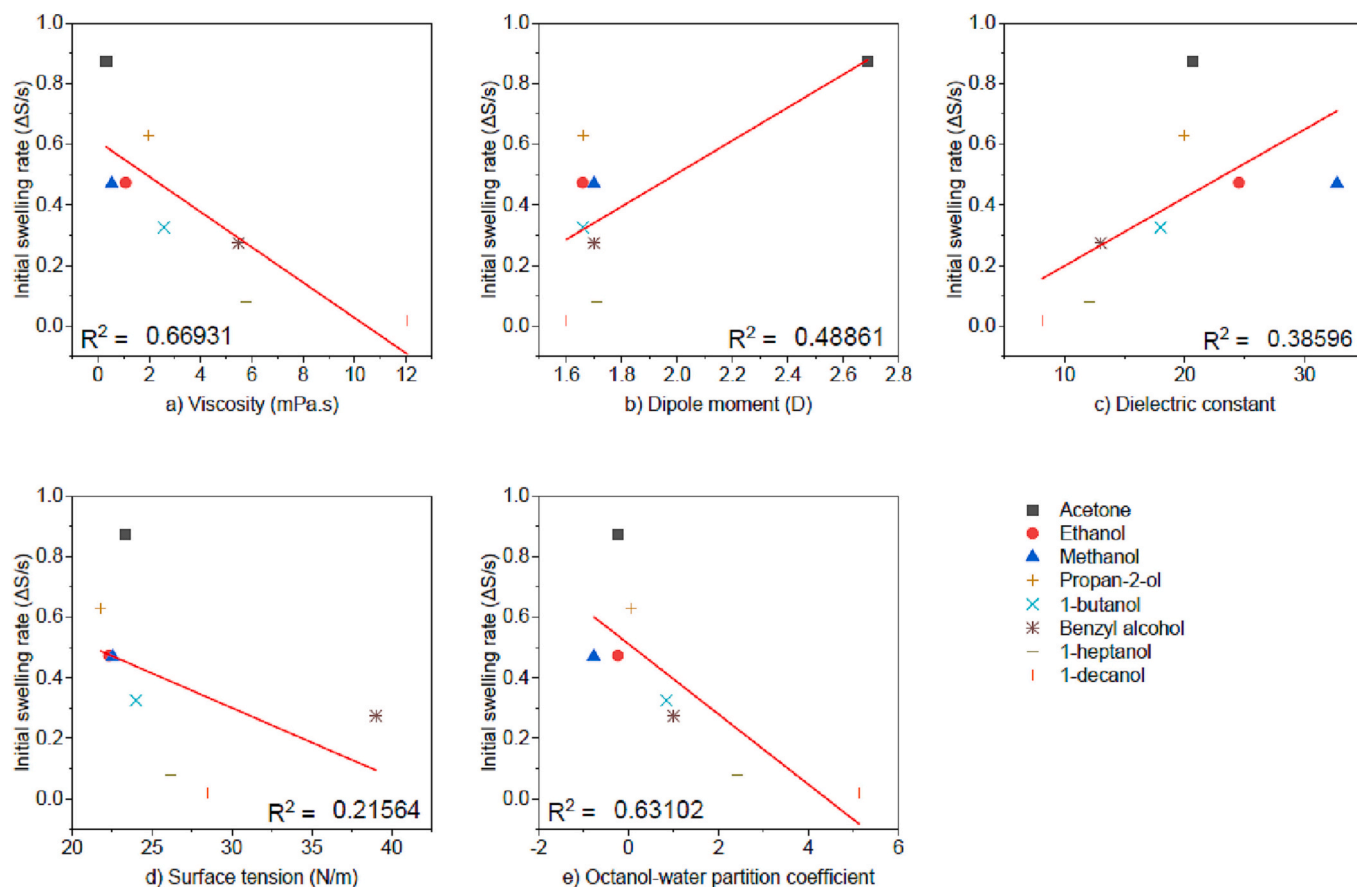
Fig. 2. Correlations of the linear swelling rate of compacted bentonite tablets with: a) viscosity, b) dipole moment, c) dielectric constant, d) surface tension and e) octanol-water partition coefficient of the designated solvent. Water and hexane are omitted as water is not an organic solvent and hexane shows no swelling.

$$V_{rep}(r) = \frac{64Nk_BT}{\kappa}\gamma^2 exp(-\kappa r)$$

where k_B is the Boltzmann constant, T is the temperature of the system and N is the concentration of 1:1 salt ions in the bulk liquid phase (in units of m^{-3}). In our notation, κ is the inverse Debye screening length, which describes how well the electric field generated by the charged clay surface permeates through space and is given by (for a 1:1 electrolyte):

$$\kappa^2 = \frac{Ne^2}{\varepsilon_0\varepsilon_r k_B T}$$

where e is the elementary electron charge, ε_0 is the vacuum permittivity and ε_r is the relative permittivity of the medium in the interlayer (i.e. the key differentiation between the tested solvent species). γ is a constant related to the surface potential of the clay and is given by:

$$\gamma = tanh\left(\frac{e\psi_0}{2k_BT}\right)$$

where ψ_0 is the electrostatic surface potential of the clay. In turn, ψ_0 is calculated from the surface charge density of the clay (σ) by inverting the non-linear Grahame equation, which in its original form is given as:

$$\sigma = \sqrt{8N\varepsilon_0\varepsilon_r k_B T}sinh\left(\frac{e\psi_0}{2k_BT}\right)$$

All calculations have been analysed at a temperature of 298 K using a Hamaker constant of $A = 2.25 \times 10^{-20}$ J, as calculated by Helmy (Helmy, 1998). We have calculated the surface charge density of the clay using the {xyz} unit cell parameters of Viani et al. (Viani et al., 2002) and assuming there to be one isomorphic substitution per unit cell. This

corresponds to an Arizona type montmorillonite (SAz-1) with a surface charge density of $-0.34C/m^2$ and a cation exchange capacity of approximately 120 meq/100 g. To calculate the overall swelling ratio, the final equilibrium swelling separation is compared to a z unit cell spacing given as 12.4 Å. This initial z spacing corresponds to the monolayer hydrated state of sodium montmorillonite. Finally, the ionic strength (1:1 electrolyte concentration) is fitted to match the overall swelling displacement of water. The swelling properties of all other solvents are then calculated by varying the relative permittivity in the calculations, to match that of the bulk solvent of interest.

3. Results

3.1. Short term swelling tests

Fig. 1 presents the short-term initial swelling behaviour of bentonite tablets in water and organic solvents over a 30-min period. No swelling was observed for hexane. In contrast, very rapid swelling was observed for acetone, methanol, ethanol and propan-2-ol with the tablets swelling to the limit of the device's measurement capabilities within 5 min. Fastest swelling was observed in acetone, where the clay tablets swelled to the measuring limit within 2 min. The slowest swelling was observed in 1-decanol.

After swelling in different solvents, the physical appearance of the clay tablet differed, with select cases presented in Fig. S1. Following exposure to water, the clay tablets formed a coherent structure, but were noticeably tacky to touch. In contrast, when the tablets were exposed to methanol and all other organic solvents (with the exception of hexane) the tablets became more friable, though less tacky to touch. For hexane the tablets did not appear dry, though surface discolouration was noted,
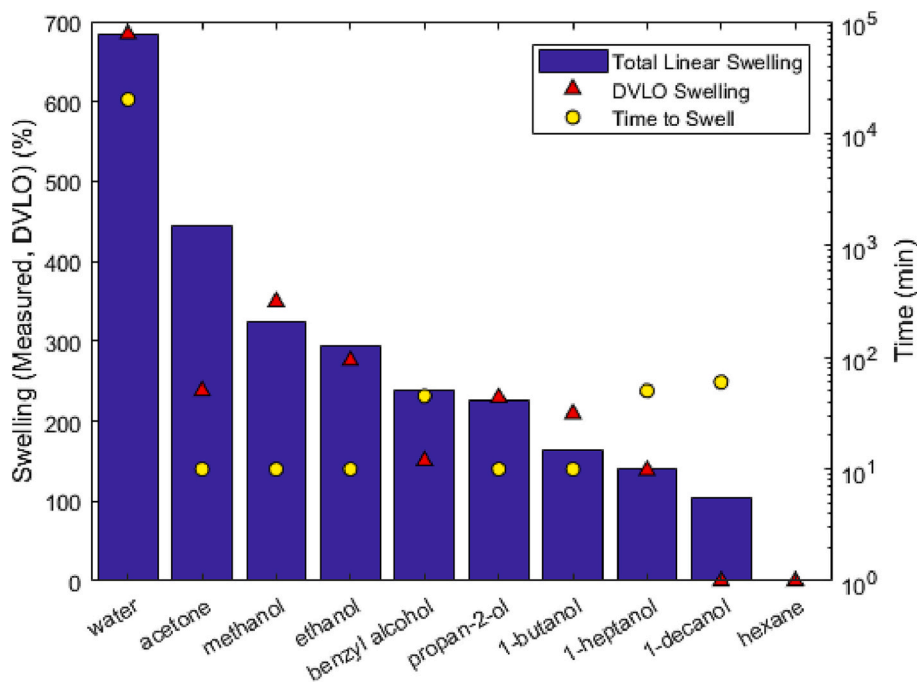
Fig. 3. Blue bars give results of equilibrium long term swelling tests of compressed bentonite tablets in organic solvents. Water swelling included as a reference point. Red triangle markers represent the theoretical DLVO calculated % equilibrium total linear swelling, yellow circular markers indicate the experimental time taken to reach equilibrium swelling. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
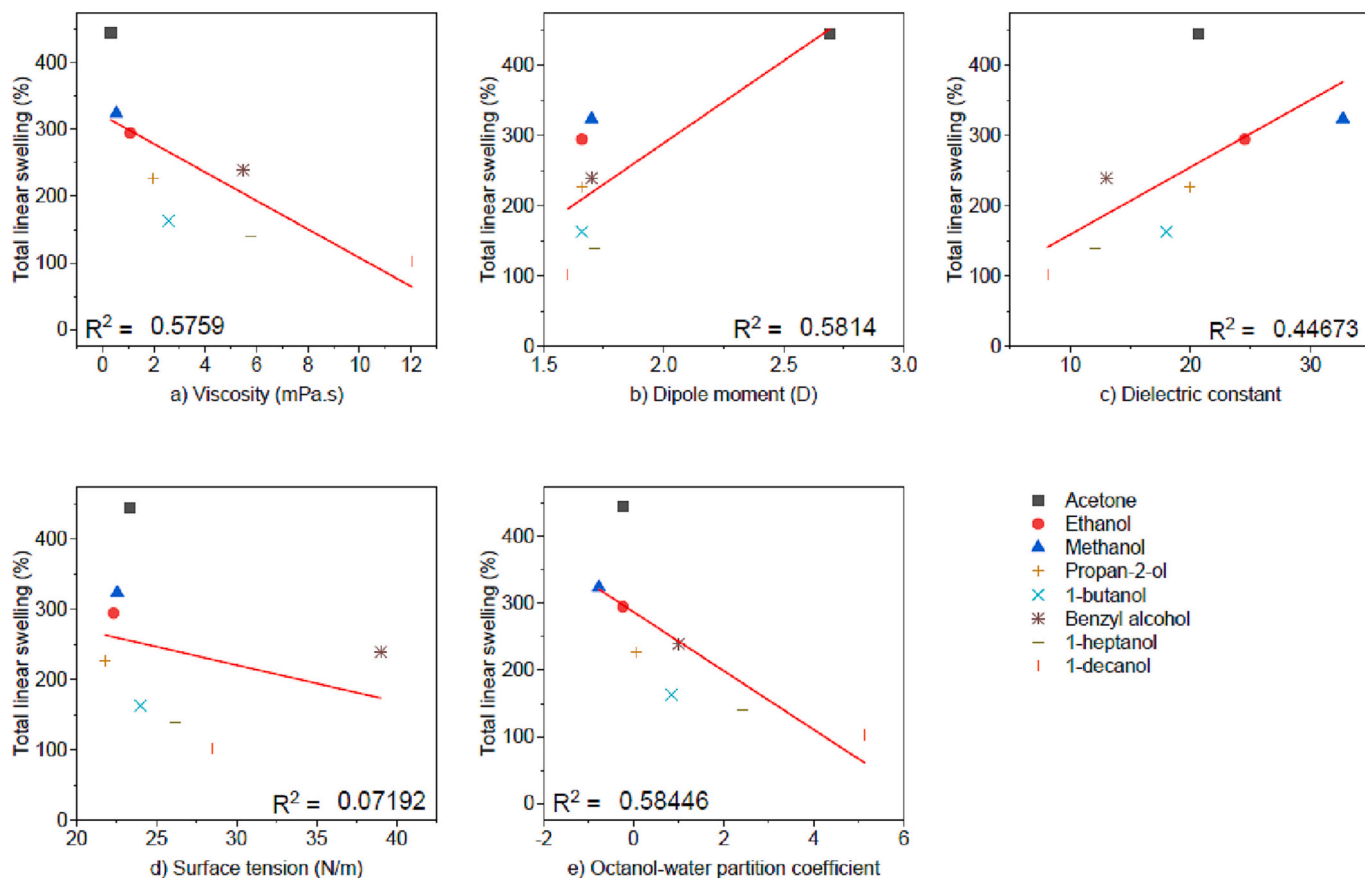

Fig. 4. Correlations of the total linear swelling of bentonite tablets with: a) viscosity, b) dipole moment c) dielectric constant, d) surface tension e) octanol-water partition co-efficient of the designated solvent. Water and hexane are omitted as water is not an organic solvent and hexane shows no swelling.

suggesting some hexane wetting of the surface.

The results of short-term swelling tests were correlated with various solvent properties: dielectric constant; surface tension; viscosity and octanol-water partition coefficient. As some of the rapidly swelling tablets reached the maximum displacement of the NC-LDM within the 30 min limit of our experiments, the absolute swelling percentage of tablets could not be measured in all instances. Therefore, we compare the initial swelling *rate* of each tablet against the bulk properties of each solvent. The swelling rate vs solvent property correlations were only applied for the bulk properties of the organic solvents, since swelling in water did not show linear behaviour. Fig. 2 presents the effects of bulk solvent parameters on the linear swelling rate of bentonite tablets obtained in short-term swelling tests.

Fig. 2a shows that swelling rate shows reasonable correlation with the viscosity of the solvent. Swelling rate is minimal in high viscosity 1-decanol and increases non-linearly with decreasing viscosity. Swelling rate is also highest in acetone, which has the lowest viscosity. Fig. 2b shows that if the acetone were removed, no correlation would exist with dipole moment, but that a higher dipole moment may contribute to a higher initial swelling rate. In Fig. 2c, it can be observed that there is a trend of swelling rate with increasing dielectric constant, though low overall correlation. Fig. 2d shows that there are also no clear overall correlations of surface tension with clay swelling rate, though linear alcohols alone show some trend, and, also, when the solvents are divided into two groups as water miscible (acetone, methanol, ethanol, propan-2-ol and 1-butanol) and water immiscible (1-heptanol, 1-decanol and benzyl alcohol), there seems to be two distinct relationships.

As there seemed to be a correlation between water miscibility and swelling, the octanol-water partition coefficient was also chosen to assess correlation (Sangster, 1997); this is shown in Fig. 2e. It can be seen that the fit of the trend-line is reasonable, with water miscible solvents (with a low octanol-water partition coefficient) giving the highest swelling, and immiscible solvents (with a higher octanol-water partition coefficient) giving lower swelling values. This agrees with Green et al. (1983), who looked at the correlation of octanol-water co-efficient with the swelling of a number of clay mineral rich soils. Finally, it is noteworthy that acetone appears to be an outlier in all the cases studied, possibly owing to its chemical reactivity rather than physical solvent properties alone. Indeed, if acetone is omitted from the correlations, the fit improves for all but dipole moment, where the correlation disappears entirely ($R^2 = 0.04$).

3.2. Long term swelling tests

The results of equilibrium swelling tests of bentonite tablets in organic solvents are shown in Fig. 3. Tablets were fully immersed into the designated solvents and the linear expansion was recorded periodically until swelling ceased. As the readings were recorded manually at specific time intervals, the time at which swelling ceased (see Table S1) was recorded as the first time where the equilibrium swelling value was recorded. The equilibrium swelling states calculated using DLVO theory are presented in Fig. 3.

The correlations of viscosity were similar to the swelling rate correlations, as total swelling decreased with increasing viscosity in Fig. 4a. Fig. 4b shows apparently reasonable correlation of dipole moment and equilibrium swelling, although in a similar manner to initial swelling correlation, omitting acetone reduces the correlation (to $R^2 = 0.2$). Fig. 4c shows that equilibrium swelling of bentonite tablets increased with increasing dielectric constant although with an apparently poor correlation. Furthermore, the long-term swelling calculations using DLVO theory, which are dictated by solvent dielectric constant/relative permittivity, generally agree with measured swelling of bentonite, suggesting that such models may be useful in describing the final state of swelling in shale. Noteworthy here is that the equilibrium swelling of bentonite in acetone is not well predicted by DVLO theory, and also appears to be an outlier for the correlation with dielectric constant;

omitting it increases the correlation to $R^2 = 0.77$. Correlations of surface tension with swelling in Fig. 4d were similar to previous swelling rate correlations, and there was no discernible relationship (R^2 of 0.07). A good fit was seen between octanol-water partition coefficient and swelling, further suggesting that water miscibility is an important parameter to consider when assessing clay swelling (Fig. 4e), and again, omitting acetone improves the correlation.

4. Discussion

4.1. Correlation of swelling with solvent parameters

4.1.1. Short-term swelling

Viscosity showed reasonable correlation with the short-term swelling rate of bentonite tablets in the solvents tested ($R^2 = 0.67$), and higher ($R^2 = 0.72$) if acetone were discounted. The viscosity of the invading pore fluid has an essential role in formation of pore pressures in the compacted bentonite clay fabric. The faster the fluid is drawn into the pores, the higher the pore pressure becomes. Thus, solvents with lower viscosities are expected to lead to higher pore pressures and faster swelling rates at the initial stage (i.e. pore swelling) (Schmitt et al., 1994), a phenomenon also exploited during oil drilling whereby a higher viscosity fluid may provide greater shale stability (Van Oort, 2003). Dipole moment appears to correlate with initial swelling rate ($R^2 = 0.49$). However, much of the correlation comes from acetone and if it is excluded, the correlation drops significantly ($r^2 = 0.04$). Berkheiser and Mortland (1975) similarly showed a lack of correlation. Dielectric constant is an indication of how well the solvent can separate the charges present. There is low correlation between dielectric constant and initial swelling rate ($R^2 = 0.39$). Even though there seems to be a relationship between swelling rate and dielectric constant, it is assumed that the proportionality between swelling rate and dielectric constant is because the solvents with higher viscosity tend to have lower dielectric constants, since the initial stage of swelling is expected to be mostly pore swelling and only affected by capillary forces (Olejnik et al., 1974). Consequently, in a similar manner to viscosity, if acetone is removed due to its increased reactivity the correlation improves somewhat ($R^2 = 0.58$).

The lack of correlation ($R^2 = 0.22$) between surface tension and initial swelling rate is an unexpected finding as with increasing surface tension, capillary forces developed in the pores leading to pore swelling are expected to increase, according to the Laplace law.

$$\Delta P = \frac{2\gamma cos\theta}{r}$$

where: ΔP = pressure difference across the fluid interface (Pa); γ = surface tension of solvent (N/m); θ = contact angle (°); r = radius of pore (m).

This lack of correlation may suggest that additional factors must be considered when assessing short-term swelling rate. The strongest correlation was observed in the octanol-water partition co-efficient ($r^2 = 0.70$). As the compacted clay was not fully dry, this is perhaps due to the more water soluble solvents being transported into the, presumably, water wet micropores faster than the more hydrophobic solvents (Green et al., 1983).

4.1.2. Long-term swelling

Considering swelling organic solvents, a relationship was seen between dipole moment ($R^2 = 0.58$) and long-term swelling. However, in a similar manner to short-term swelling, the correlation is dominated by the presence of acetone which, if excluded, drops the correlation to $R^2 = 0.21$. It can be concluded though that some dipole moment was required for swelling, as no swelling was observed in hexane. Polar compounds compete with water to be adsorbed in the interlayer and replacement of water with larger molecules may cause higher interlayer expansions.
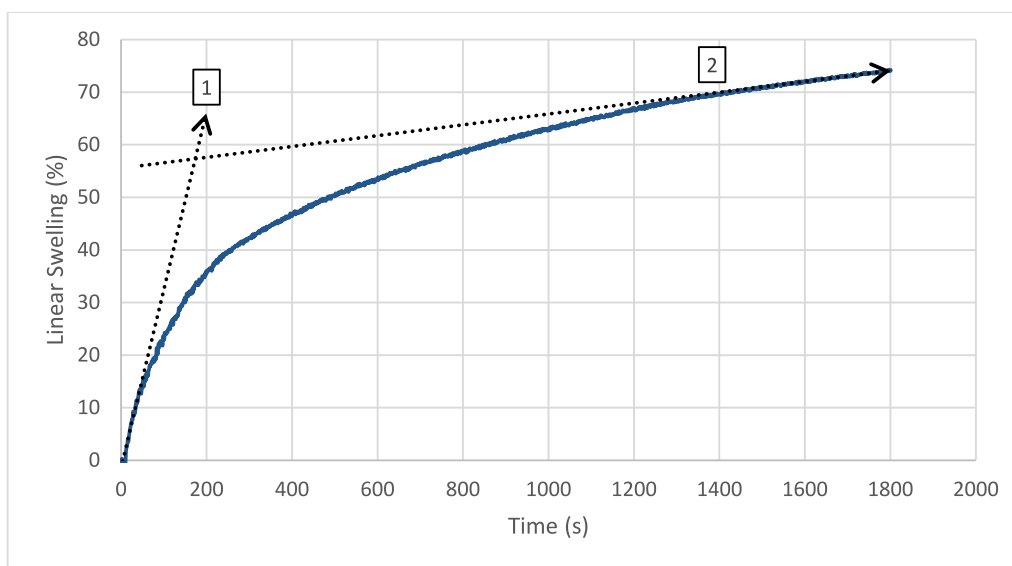
Fig. 5. Short-term swelling tests of bentonite tablets in water, showing the two main swelling regimes (1 and 2) discussed in the main text. Note that equilibrium swelling in this case has not been reached.

However, this replacement is unlikely to occur if the molecular size of the organic compound is larger than the interlayer spacing and the dipole is low unless entropic terms become important. Organic solvents may hydrogen bond with water or interact with water through dipole-dipole forces and can have a tendency to become solubilized in the tablet pore water and therefore cause bulk clay expansion (Green et al., 1983).

There was a correlation shown between dielectric constant and long-term swelling ($R^2 = 0.45$), which again increases when acetone is removed ($R^2 = 0.77$). Barshad (1952a, 1952b) explained the dependence of swelling on dielectric constant by suggesting that the absorbed liquid phase acts as a dielectric medium weakening the interlayer attractive forces of the crystal lattice. This action could be interpreted from Coulomb's law, that the greater the dielectric medium separating the charges, the weaker the interlayer attractive forces of the crystal lattice itself. Norrish (1954) made a deduction of swelling index described by $U\varepsilon/v^2$ in which U is the solvation energy and v is the valence of the interlayer cation, while ε is the dielectric constant of the interlayer liquid. For a given cation valence, swelling is increased with increased solvation energy and dielectric constant. Since these theories apply only for layer expansion phase of clay mineral swelling, the effects of pore swelling on total bulk swelling of clays should also be considered.

Increasing dipole moment of the solvent is expected to increase the ion-dipole interactions of the exchangeable cations in a clay interlayer and lead to development of diffuse layers. According to Onikata et al. (1999), since the driving force governing the intercalation of solvent molecules into the clay interlayer is primarily due to solvation of the interlayer cations then the electron donor ability of the solvents should be considered for correlation, rather than the dipole moment. However, these studies also reveal that there is also no direct correlation between layer expansion and electron donor ability. The lack of correlation seen between dipole moment and total swelling ($R^2 = 0.21$ upon exclusion of acetone) support the conclusion of Onikata et al. (1999).

No correlation was seen between surface tension and long-term swelling ($R^2 = 0.07$), and again the correlation seems influenced by the acetone outlier. If this outlier is excluded, the correlation drops further ($r^2 = 0.04$). The results can be interpreted as that the swelling at first is driven by capillary forces and mainly pore swelling, then interlayer swelling occurs and the dielectric constant of the medium becomes a determinant parameter. As a result, a combination of having lower

viscosity and higher dielectric constants leads to both more rapid swelling owing to capillarity and an overall greater final equilibrium swelling in acetone and methanol among the organic solvents. The apparent difference between the short term and the equilibrium swelling behaviour of water and polar organics might be explained by the following argument: At the initial swelling state, interlayer water is replaced by larger organic molecules, driven entropically, which lead to higher interlayer swelling. In the latter state, due to osmotic swelling, forming of double layers occurs and the influence of the dielectric constant arises. This is evidenced by the strong correlation observed between long-term swelling and the octanol-water partition coefficient ($R^2 = 0.58$, increasing to 0.76 upon exclusion of acetone).

4.2. Swelling of compacted bentonite tablets in water

In Fig. 5, it is seen that swelling of bentonite tablets in water occurs in two regimes as the slope of linear swelling changes after a point and remains lower until the end of the experiment. Note that the slope of the second regime did not change when the experiment time was extended. This shows that swelling of bentonite in water is dominated by differing effects depending on the extent of swelling and therefore the rate changes throughout.

Clay minerals are negatively charged particles and water molecules are attracted to the clay surfaces in multiple possible ways under normal circumstances. Clay tablets swell through a combination of capillary and chemical forces (Anderson et al., 2010). Water enters the pores via capillary forces and causes pore swelling, followed by water hydrating clay mineral surfaces. Cation hydration is important especially at low water contents, with hydration is strongly dependent on the size and the charge (or electronegativity) of the cation (Underwood et al., 2016). The reason why two different regimes operate can be interpreted as follows: The first regime is dominated by capillary forces and occurs as water enters the pores. Smaller pores fill immediately due to increased pore suction, (although tortuosity may slow this process), then larger pores. When pore saturation is completed, capillary forces are no longer effective and therefore swelling is dominated via adsorption and hydration forces described in Fig. 5, causing the swelling rate of the bentonite tablets to change.

As a clay tablet swells, the volume of the clay tablet increases but the mass of clay mineral in the tablet remains constant. This may be described as a change in porosity of the clay, and the porosity may be
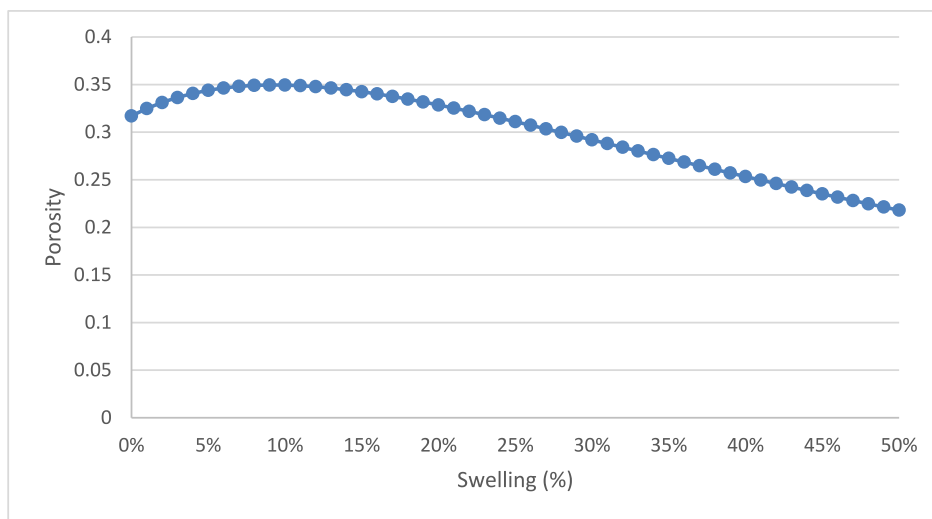
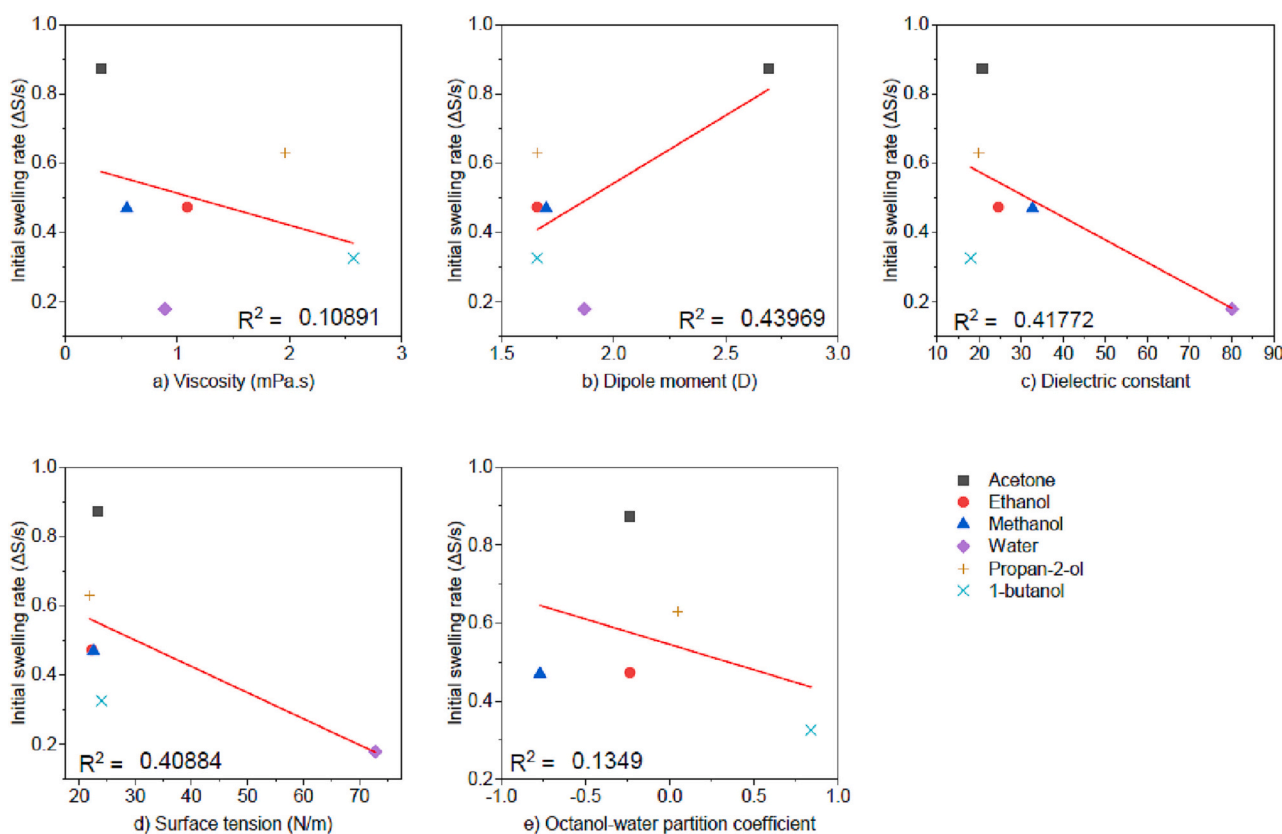**Fig. 6.** The calculated variation of interlayer porosity with swelling.

Fig. 7. Swelling rate vs a) viscosity, b) dipole moment, c) dielectric constant, d) surface tension and e) octanol-water partition coefficient; water miscible, including water.

calculated based on swelling data obtained. Appelo (2013) calculated the ratio of interlayer to total porosity for bentonite for a given dry density packing of the clay. This methodology may be used to calculate the theoretical interlayer porosity for different linear swelling percentage increases in water (shown in Fig. 6), based on both the thickness and diameter of the tablet increasing with time.

It can be seen that maximum interlayer porosity occurs at 9% swelling. Considering the data presented in Fig. 5, it would appear to be in agreement with the beginning of a change of swelling regime from capillary crystalline swelling to osmotic adsorption and hydration. This

particular analysis of interlayer porosity requires the presence of water, and as such cannot be used in its current form to interpret the swelling of bentonite tablets in other solvents, although the results presented in this study may give scope to produce a similar analysis of the linear alcohols in future.

4.3. Assessment of effect of water miscibility

As a good correlation was found with the octanol-water partition coefficient for swelling, it would appear that the water miscibility of the
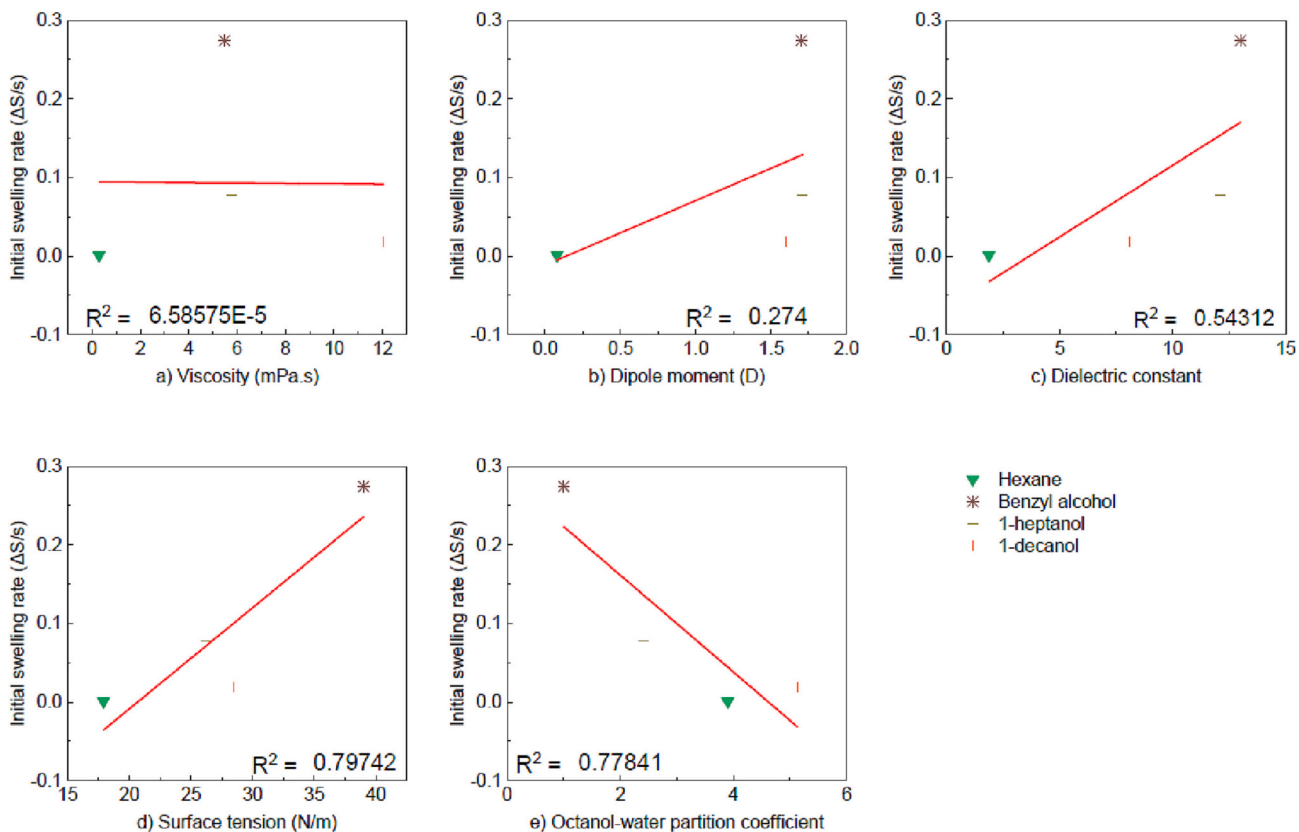
Fig. 8. Swelling rate vs a) viscosity, b) dipole moment, c) dielectric constant, d) surface tension and e) octanol-water partition coefficient; water immiscible, including hexane.

Fig. 9. Total linear swelling vs a) viscosity, b) dipole moment, c) dielectric constant, d) surface tension and e) octanol-water partition coefficient; water miscible, including water.

Fig. 10. Total linear swelling vs a) viscosity, b) dipole moment, c) dielectric constant, d) surface tension and e) octanol-water partition coefficient; water immiscible, including hexane.
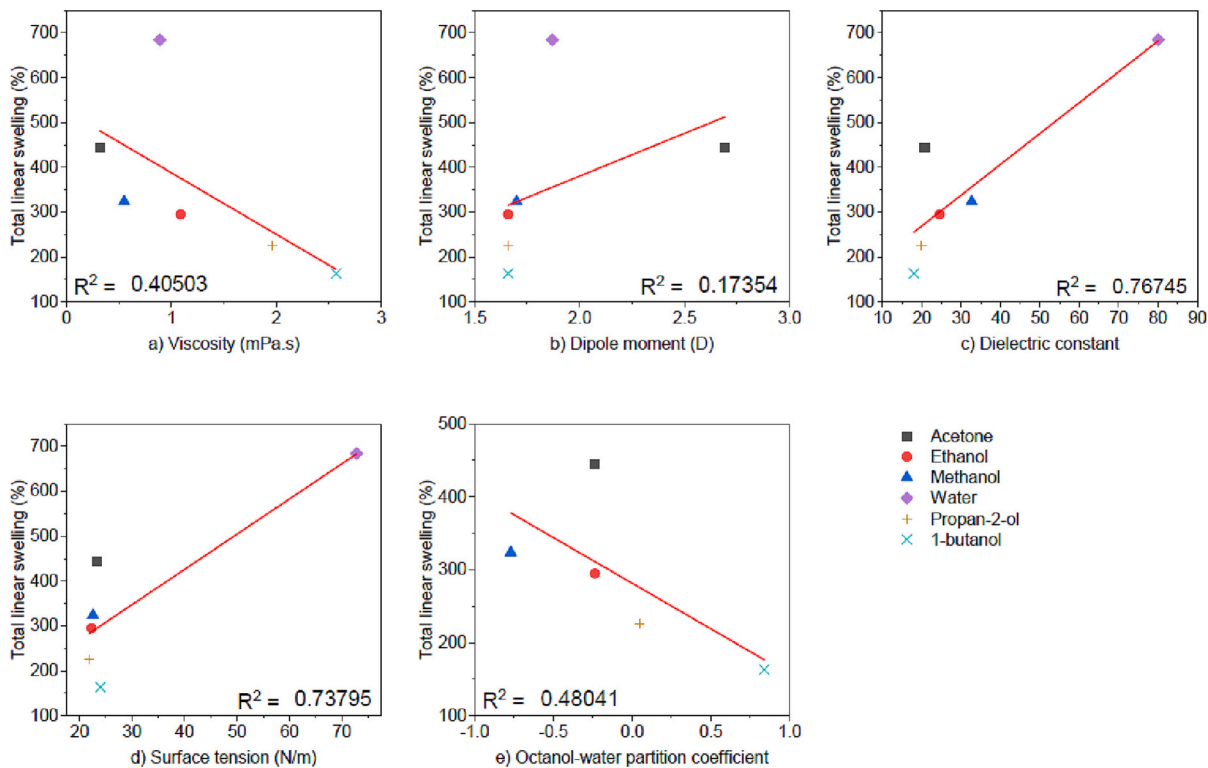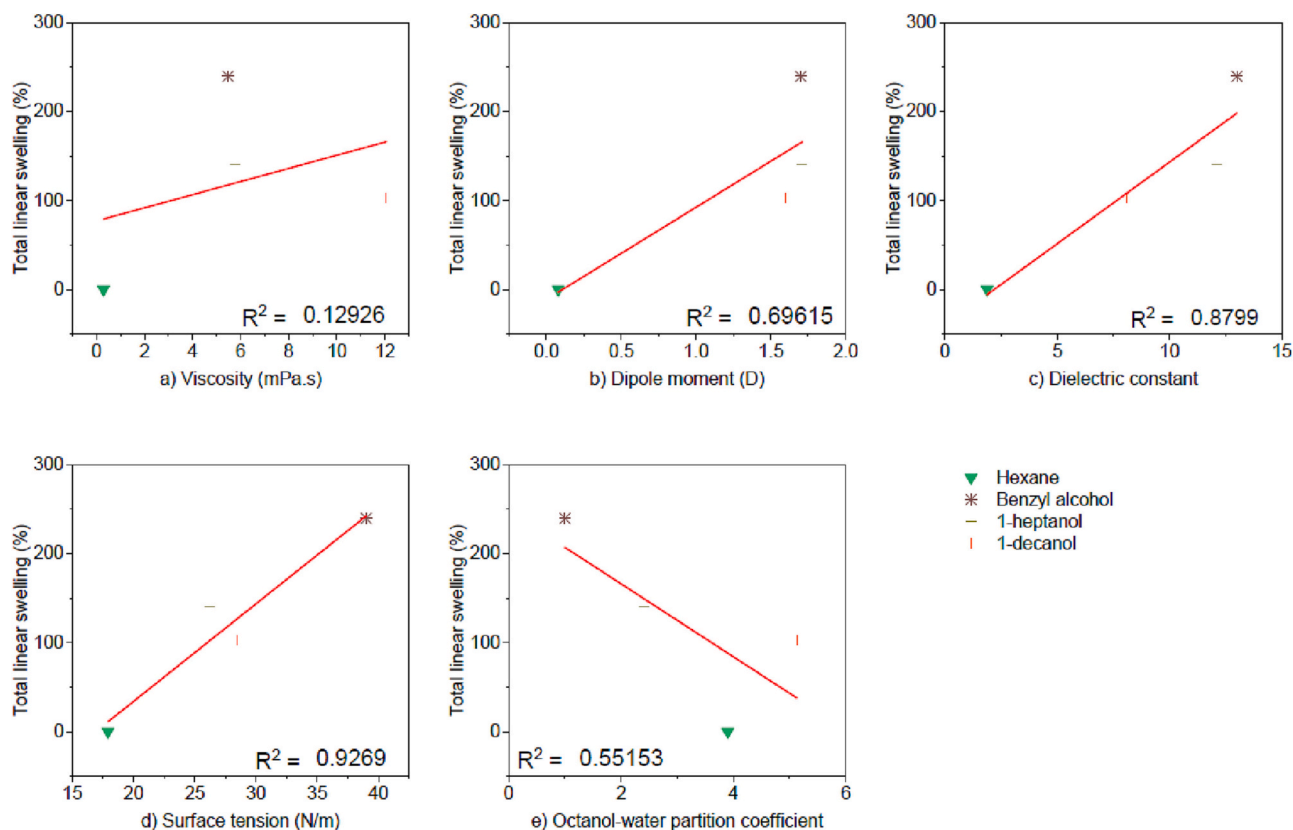
solvent may have a substantial effect on the swelling of a clay mineral tablet. The solvents were therefore characterised by their water miscibility. The swelling rate and total linear swelling were plotted against the solvent parameters and separated by water miscibility, and the R^2 value for correlation separated by water miscibility was obtained. These results are shown in Figs. 7–10.

Considering the effect of miscibility upon swelling rate correlations in Figs. 7a and 8a, and Figs. 7b and 8b, the water miscibility has an effect on how viscosity and surface tension affect the swelling rate of the bentonite tablets. The octanol-water partition coefficient can be considered to be a measure of water miscibility (Sangster, 1997). Looking at the correlation coefficient between the octanol-water partition coefficient and each of the solvent parameters considered, viscosity, dipole moment and surface tension are parameters with a correlation coefficient of <0.5, suggesting that the value of these parameters for each solvent does not linearly depend on their water miscibility (Table S2). As it can be shown that these variables are linearly independent, it follows that water miscibility may be considered as an additional variable that affects the swelling when viscosity and surface tension are studied.

Viscosity and surface tension are variables that affect the capillary force that promotes the ingress of fluid into the pores. It would be expected that as the viscosity increases the rate of swelling would decrease, and as surface tension increases, the rate of swelling would increase. For water immiscible solvents, viscosity does not affect swelling, and surface tension affects swelling as predicted by the Laplace law. However, when considering water miscible solvents, surface tension does not have a great effect on swelling; this instead increases with the rate dependant on another constant. The influence of viscosity on swelling rate also changes when water miscible solvents are considered; the trend here matches the predicted behaviour. If hexane is disregarded (as no swelling is seen), the swelling behaviour is as predicted when

viscosity is considered throughout the whole series of solvents.

When the total linear swelling is considered as a function of solvent parameters separated by water miscibility the division between water miscible and immiscible solvents is less clear. The parameters may be divided by water miscibility, and upon doing so an improvement in the fit of the dielectric constant and the surface tension is seen. As discussed previously, an increased dielectric constant is expected to lead to an increase in swelling, Given that the dielectric constant is expected to influence the interlayer swelling most strongly, it may be expected that miscible vs immiscible solvents may have differing effects owing to the ease of their entering the interlayer. Surface tension correlation also appears significantly improved when solvents are separated into miscible and immiscible, and one of the most notable improvements is the transformation from a negative gradient (unexpected) to a positive gradient (expected).

4.4. Correlation of total linear swelling for alcohol series

On closer examination of the viscosity and octanol-water partition coefficient correlations with total linear swelling, the series of alcohols show a good correlation if a logarithmic fit is used, shown in Fig. 9.

Viscosity (Fig. 11a) and water solubility (and hence octanol-water partition coefficient, Fig. 11b) are predicted to vary with chain length. Chain length of polar alcohol molecules directly affects the total linear swelling. In addition, carbon chain length for the alcohol series may also be plotted against total linear swelling, and again give good correlation. This is shown in Fig. 11c.

4.5. Influence of density on swelling rate of water miscible solvents

It has been seen that, although general correlations may be made between the swelling rate of bentonite tablets and the solvent
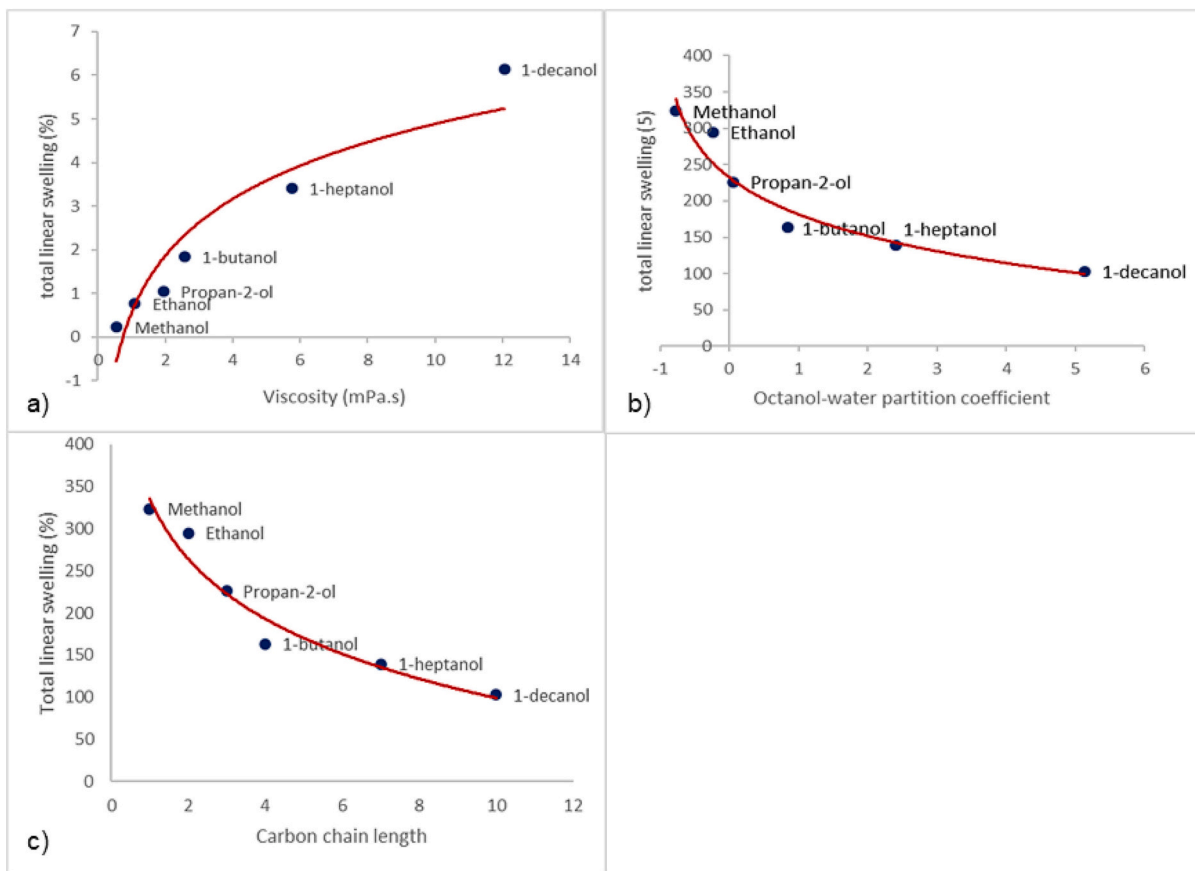
Fig. 11. a) Correlation of total linear swelling with viscosity for alcohol series. $R^2 = 0.93$ b) Correlation of total linear swelling with octanol-water partition coefficient for alcohol series. $R^2 = 0.93$ c) Correlation of carbon chain length with total linear swelling. $R^2 = 0.95$.
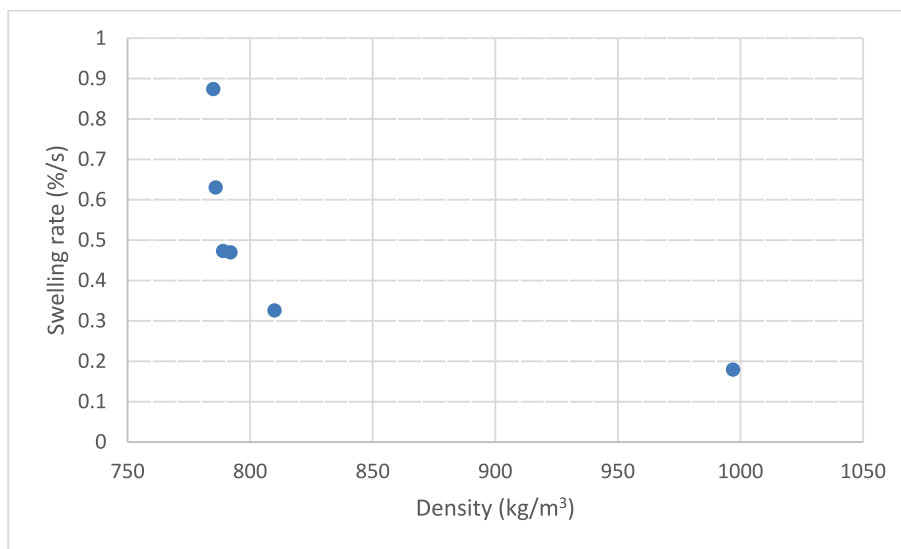

Fig. 12. Swelling rate data vs density for water miscible solvents.

parameters considered for water miscible solvents, there are no parameters that predict the ordering of swelling rate for the water miscible solvents. A study was therefore conducted to assess a wide range of parameters to assess whether a single parameter may predict the swelling of bentonite tablets in water miscible solvents. A relationship was found between density and swelling rate for the water miscible solvents (Fig. 12).

There are several possible hypotheses as to why this correlation may be good. The natural moisture content of the bentonite tablets was measured using TGA, and found to be 10.4%, although most of this is expected to be in the interlayer at this level of hydration. Upon hydration in solvent, the solvent will mix with the internal water in the clay tablet. Appelo (2013) states that most of the porosity of a clay tablet will come from interlayer porosity when the dry density of the clay tablet is

above 1.8 kg/m³, which is the case for the tablets prepared in this study. Martin (1960) states that, when the moisture content of a montmorillonite is <0.7 g H₂O per gram of clay, that the density of water in the clay is 1.4 kg/m³. The lower density of the solvent may cause improved mixing with the water, allowing the solvent to enter the interlayer more efficiently. Alternatively, the lower density may be due to the molecular ordering. The packing of the molecules in the very small interlayers may be more efficient, allowing more of the solvent to enter and increase swelling. Modelling has shown that, as the concentration of acetone or ethanol increases in an solvent/water mixture near the surface of a layered double hydroxide (LDH), that the acetone moves progressively near to the LDH surface (Erastova et al., 2017). It can be shown that initially the concentration of water and solvent may be in the ratio of 1:1 in the clay tablet, subsequently increasing as the swelling continues. Erastova et al. (2017) show that, at a 1:1 concentration, the hydrogen bonding between the solvent/water mixture is greatly reduced compared to the pure water system. This may disrupt the bonding between the clay layers, causing more rapid initial swelling. As swelling continues, the proportion of solvent increases, and it would be expected that the hydrogen bonding becomes further reduced, promoting further swelling. Another alternative may be that the shape of the molecule allows efficient solvation of the sodium ions in the interlayer of the bentonite. It has been shown that acetone may solvate sodium ions in a similar manner to water (Howie and Wardell, 2003). The mixture of acetone and water therefore in the interlayer may promote swelling. These hypotheses are contrary to the mechanism put forward to explain the shape of the plot of bentonite tablet swelling in water (Fig. 5), as considering the graph of swelling rate vs time (Fig. 1), it can be seen that the water miscible solvents swell more rapidly than water (and the water immiscible solvents), so a different process may be occurring.

4.6. Overall influences of solvent parameters on swelling behaviour

4.6.1. Short-term swelling

- Considering solvent parameters alone, viscosity and octanol-water partition coefficient gives the best correlation with initial swelling rate for the solvents investigated.
- Separating the solvents into water miscible and immiscible, surface tension gives the best correlation with initial swelling rate for water immiscible solvents, and dipole moment for the water miscible solvents.
- Solvent density can be used as a predictor of short-term swelling rate for water miscible solvents, although the correlation is not linear.

4.6.2. Long-term swelling

- Considering solvent parameters alone, octanol-water partition coefficient gives the best correlation with total swelling for the solvents tested.
- When the solvents are separated into water miscible and immiscible, surface tension gives the best correlation with total swelling for immiscible solvents, and dielectric constant correlation is much improved upon separation of immiscible and miscible solvents.
- For the series of linear alcohols tested, carbon chain length predicts the ordering of total swelling, although the relationship is not linear.

5. Conclusions

The present study is an investigation into bulk swelling of a compacted shale analogue using a novel non-contact displacement meter. Time dependent short term swelling tests and equilibrium long term swelling tests were performed in a range of organic solvents in order to compare the bulk swelling behaviour of bentonite tablets in the varying time-scale regimes.

Swelling tests of bentonite tablets in water showed that there are two

regimes occurring in water swelling indicating that different forces are dominating the swelling in different times. It is assumed that the first regime is due to capillary swelling when water enters the pores and the second regime is due to interlayer expansion due to water-clay interactions.

In line with EDL theory the dielectric constant of the solvent was a key determinant for swelling of smectite clays. In both short and equilibrium swelling tests, linear swelling rate and total linear swelling of bentonite tablets increased with increasing dielectric constant. It was also seen that below a specific value of dielectric constant, (approximately 50–60) the swelling behaviour of smectite tablets change. Equilibrium swelling and swelling rate of bentonite tablets decreased with increasing viscosity of the medium, therefore pore swelling has substantial effects on bulk swelling of bentonites. There are no clear correlations of the dipole moment, yet it was seen that having a dipole moment larger than zero is essential for swelling. In addition, good correlation with the octanol-water partition coefficient shows that water miscibility has a strong effect on interlayer swelling rate. Good correlation between the swelling rate of bentonite tablets in water miscible solvents and density of the solvents was found, and hypotheses were put forward to explain this. Extremely good correlation was found between total linear swelling and viscosity, octanol-water partition coefficient and chain length for the alcohol solvents considered.

In general, swelling behaviour of compacted clay tablets is time dependent due to the domination of different swelling components in different time periods. At any time of swelling action, several of these components might act simultaneously and their combined influence determines macroscopic effects of swelling. This work has ramifications for drilling fluid design, pre-treatment of cores for flooding experiments and compacted bentonite storage systems, among others. Future work will extend to looking at other salt and water soluble oligomer reactivity with whole bentonite tablets.

CRediT authorship contribution statement

Ali Reza Erdogan: Conceptualization, Methodology, Writing – original draft. **Anna C. Whitford:** Methodology, Writing – review & editing. **Thomas R. Underwood:** Validation, Writing – review & editing. **Catriona Sellick:** Validation, Writing – review & editing. **Radhika Patel:** Conceptualization, Methodology, Writing – review & editing. **Neal T. Skipper:** Conceptualization, Supervision. **H. Christopher Greenwell:** Conceptualization, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.clay.2023.107000.

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