A critical investigation of diffuse double layer changes in clay-electrolyte systems at high temperatures

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Abstract

The objective of this work was to explore the impact of temperature on shale swelling and explain it in terms of diffuse double layer mechanics: Debye–Hückel length alterations. This was made possible through the use of a newly developed thermal linear swelling test. Moreover, the combined impact of temperature, dielectric constant of water and ionic strength (ionic concentration) of salt solutions on Debye–Hückel length and resultant shale swelling and shrinkage were investigated. For dilute solutions, results showed that the product of temperature and dielectric constant of water ($T^*\varepsilon_r$) remained near constant for a wide range of temperature (25–90°C). Results suggest that the dielectric constant of water may have been reduced by both temperature and ionic strength of solution, all of which caused a greater reduction in Debye–Hückel length and subsequent shale shrinkage. As for saturated NaCl and CaCl$_2$ solutions, shale exhibited swelling behaviour at moderate temperatures followed by shale shrinkage thereafter. This could be attributed to the development of repulsive forces between alike ions within diffuse double layer. At higher temperatures, the contribution of dielectric constant of water on lowering Debye–Hückel length may have softened the repulsion action produced by ions.

Keywords: clay mineral, Debye–Hückel length, dielectric constant, ionic strength, shale swelling, electrical double layer

1. Introduction

Drilling and maintaining a stable wellbore in shale, which comprises >75% of drilled formations, is a challenging job for drilling engineers. Such a problem not only presents technical issues that may lead to total well abandonment, but also results in loss of time, resources and money. AL-Bazali *et al.* (2009) pointed out that nearly 90% of wellbore instability problems occur in troublesome shale formations and cost the drilling industry around $1 billion annually. Wellbore instability problems related to shale include, but not limited to, shale swelling, caving, sloughing, heaving, bit balling, pipe sticking, loss of circulation and difficulties in logging, running casing and cementing. Besides these downhole problems, clogging of surface flow lines and equipment could result after shale dispersion and disintegration.

Wellbore instability problems in shale is often attributed to clay swelling, although other factors such as bad drilling practices and distribution and orientation of *in situ* stresses could also be blamed for shale instability. The primary cause of clay swelling is associated with the hydrophilic and charged nature of clay surfaces that enables them to adsorb water and exchange cations with nearby aqueous solutions, which leads
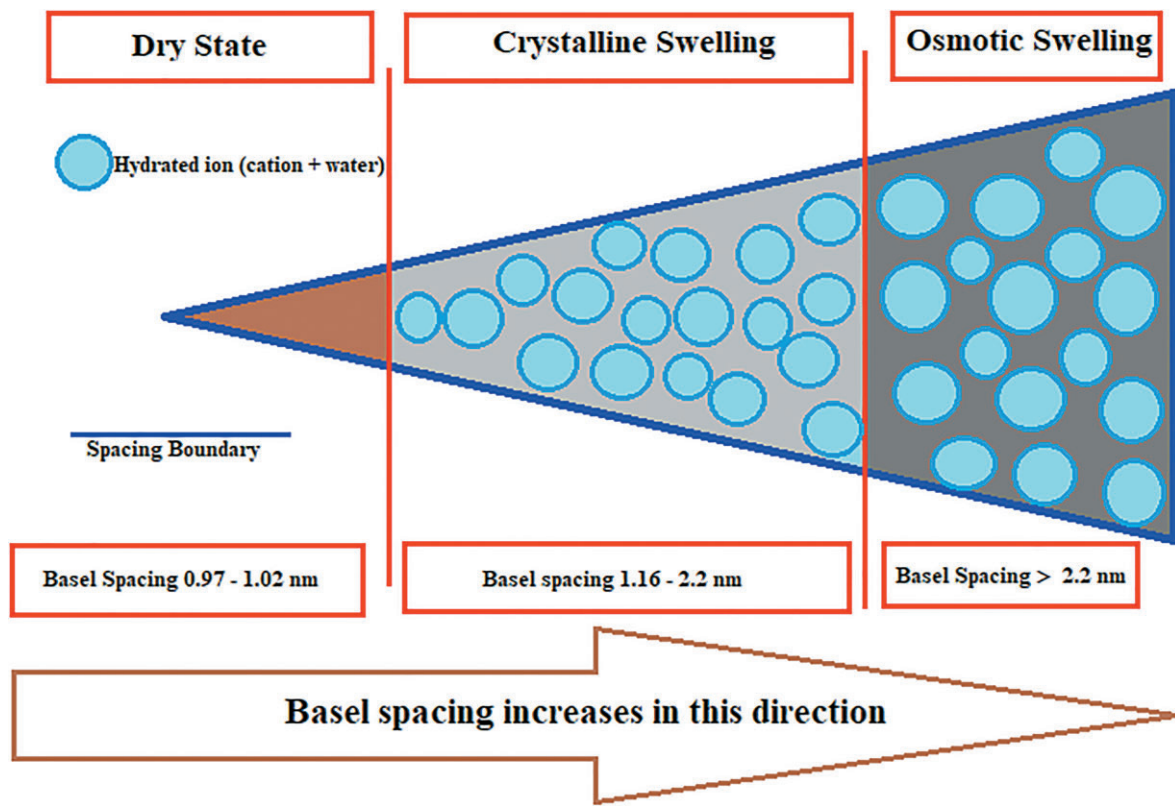
Figure 1. Crystalline swelling and osmotic swelling of clay minerals (1 Angstrom = 0.1 nm).

to volumetric expansion and subsequent clay swelling (Wilson & Wilson 2014). Since *in situ* shale is not allowed to volumetrically expand or freely swell, hydrational stresses develop and pore pressure builds up within the shale matrix due to water and ions adsorption, which eventually causes shale failure and collapse.

Clay swelling is classified into crystalline swelling and osmotic swelling. Crystalline swelling occurs due to adsorption of water molecules at interlayer separations of 10 to 22 Å while osmotic swelling occurs at interlayer separations >22 Å, as shown in figure 1.

While crystalline swelling, according to Low (1961), results from hydration of exchangeable cations of dry clay, osmotic swelling is caused by ionic concentrations imbalances between clay and aqueous solutions. Osmotic swelling is seen as a long-range interaction that mainly depends on ionic concentration, the type of exchangeable ion, pH of the pore water and clay mineralogical composition (Van Olphen 1986). It is thought that osmotic swelling takes place within the diffuse double layer of negatively charged clay surfaces and functions within a specific space known as Debye–Hückel or electrostatic screening length (κ^{-1}) (Smith *et al.* 2016; Prelesnik *et al.* 2021; AL-Bazali 2021a). The quantity of cations and water in the diffuse double layer determines its thickness (κ^{-1}) and the resultant swelling and shrinkage status of clay as depicted in figure 2.

The presence of cations in the diffuse double layer reduces κ^{-1} (diffuse layer shrinkage), shields negative surface charge of interacting particles, and promotes particles attraction and stability. On the other hand, transport of water into the diffuse double layer increases κ^{-1}, exposes negative surface charges of nearby particles and causes particle repulsion, swelling and instability (Stillinger & Kirkwood 1960). The Debye–Hückel length (κ^{-1}) for a monovalent electrolyte, for electrolytes and colloidal suspensions, is given by

$$\kappa^{-1} = \sqrt{\frac{\varepsilon_r \varepsilon_0 k_B T}{2 N_A e^2 I}}, \qquad (1)$$

where

ε_r	Dielectric constant of water = (78.5 at 298 K);
ε_0	Permittivity of free space = 8.85E-12 $C^2/(J\,m^{-1})$;
k_B	Boltzmann constant = 1.38E-23 $(J\,K^{-1})$;
T	Absolute temperature in Kelvin (K);
N_A	Avogadro number = 6.02E23 $(1/mol^{-1})$;
e	Elementary charge = 1.6E-19 C;
I	Ionic strength of the electrolyte in molar units (M or $mol\,l^{-1}$) and is given by:

$$I = \frac{1}{2} \sum_i m_i z_i^2; \qquad (2)$$

Z   Valance of ion $(Na^+ = 1; Cl^- = 1; Ca^{+2} = 2; Mg^{+2} = 2)$;
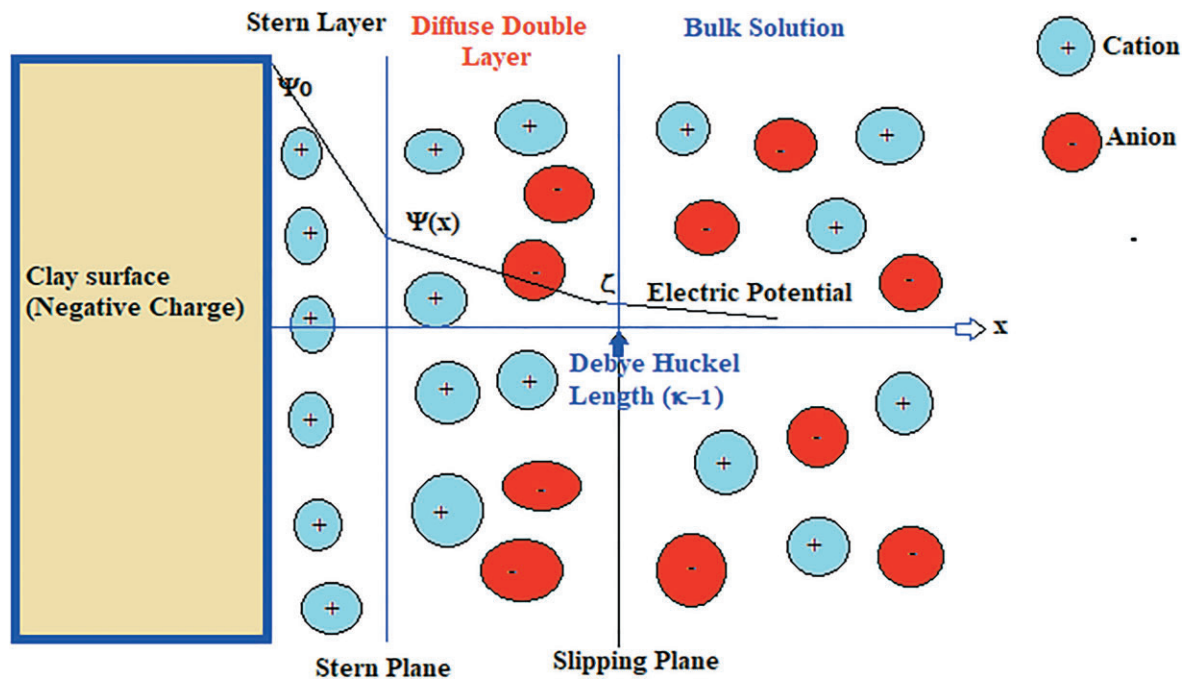m_i Molality of the ith ion in $(mol\,l^{-1})$.

Figure 2. Debye–Hückel length within the diffuse double layer.

As stated previously, macroscopic shale swelling and shrinkage are highly linked to microscopic changes in Debye–Hückel length in a diffuse double layer of clay. Therefore, understanding the factors that affect this length could shed more light on the swelling behaviour of clay and may provide practical solutions to wellbore instability in shale formations. Many researchers have studied clay swelling behaviour as a function of ionic concentration of both shale's pore fluid and interacting aqueous solutions (Madsen & Müller-Vonmoos 1989; van Oort *et al.* 1996; Chenevert & Pernot 1998; van Oort 2003; Zhang *et al.* 2004; Bharat & Sridharan 2015; Gao *et al.* 2016; Aftab *et al.* 2017; Rana *et al.* 2020). These studies have focused on the isothermal impact of ionic concentration on clay swelling and the development of Debye–Hückel length, and completely ignored the direct and indirect impact of temperature on clay swelling and Debye–Hückel length. Other studies have assumed that the effects of temperature on Debye–Hückel length will be counteracted by the effects of dielectric constant of water since it is inversely proportional to temperature (Mitchell & Soga 2005; Schwank *et al.* 2006). In other words, while higher temperatures should increase Debye–Hückel length as per equation (1), higher temperatures also decrease dielectric constant of water that in turn decreases Debye–Hückel length. Malmberg & Maryott (1956) developed an empirical equation that calculated dielectric constant of water over temperature range of 0.1 to 99°C, as shown in Table 1.

They concluded that variations of dielectric constant of water with temperature could be substantial and should not be overlooked. I believe that temperature not only affects the development of Debye–Hückel length directly, but also both the dielectric constant of water and ionic strength of solution, both of which affect Debye–Hückel length, as shown in equation (1). The contributions of the impact of temperature, dielectric constant of water and ionic strength on Debye–Hückel length and clay swelling at elevated temperatures may not be equally shared, and one factor may dominate the total impact at certain temperature and ionic concentration. Therefore, neglecting the impact of temperature and dielectric constant of water at higher temperature may not be scientifically wise. It is recommended to account for the direct impact of temperature and consequent impact of dielectric constant of water and ionic strength of solution when analysing Debye–Hückel length progress and clay swelling development at elevated temperatures.

A critical investigation of the direct and consequent impact of temperature on changes in Debye–Hückel length (diffuse double layer thickness) is provided here. The impact of temperature on dielectric constant of water and ionic strength of aqueous solutions used will be closely monitored to better understand the full impact of temperature on the development of Debye–Hückel length. The notion of neglecting the impact of temperature on Debye–Hückel length will be tested. This was made possible through a newly developed thermo-linear swelling experimental methodology.

Table 1. Dielectric constant of water (ε_r) at various temperatures, after Malmberg & Maryott (1956)

Temperature (°C)	0.1	5	10	25	40	50	70	80	90
ε_r	87.7	85.703	83.832	78.304	73.151	69.910	63.857	61.027	58.319

Table 2. Mineralogical composition of shale

X-ray diffraction	Shale (w/w%)
quartz mineral	15.2
feldspar mineral	4.1
calcite mineral	1.7
dolomite mineral	1.8
pyrite mineral	1.4
siderite mineral	1.5
Overall clay minerals	74.37
chlorite clay	3.5
kaolinite clay	6.8
illite clay	7.49
smectite clay	22.4
mixed layer clay	34.18

2. Material and methods

2.1. Shale core

A shale core (2.5 inches by 6 feet), obtained from a Kuwaiti oil field, was used in this experimental work. Cautious steps were taken to lessen shale core exposure to air during coring, handling, storing and transporting. Direct interaction of air with shale could change its native properties; i.e. water activity and water content (Chenevert & Amanullah 2001). The X-ray diffraction technique was conducted by an independent commercial testing facility located in the USA to obtain the mineralogical composition of shale, as shown in Table 2.

Adsorption isotherm methodology was used to determine the water activity of native shale where cubical shale samples of dimensions (0.75" × 0.75" × 0.50") were cut out of the native shale core and placed in several desiccators of different water activities. A complete explanation of procedures used to measure water activity, water content, cation exchange capacity (CEC), porosity and permeability of shale is given in (Al-Bazali *et al.* 2008). Table 3 shows the physical, chemical and petrophysical properties of shale.

2.2. Thermal linear swelling test

The objective of this work is to explore the impact of temperature on shale swelling and explain it in terms of diffuse double layer mechanics; Debye–Hückel length alterations. The call for neglecting the impact of temperature and dielectric constant of water on Debye–Hückel length will be challenged and an alternative approach will be presented. Moreover, the combined impact of temperature, dielectric constant of water and ionic strength (ionic concentration) of salt solutions on Debye–Hückel length and resultant shale swelling and shrinkage will be investigated. The experimental procedure is conducted as follows:

- Prepare 5, 12 and 20% by weight sodium chloride (NaCl) and calcium chloride ($CaCl_2$) solutions. The corresponding water activities of these solutions can be obtained from figure 3.
- Cut shale samples of size ($0.75 \times 0.75 \times 0.5$) from the native core to run linear swelling tests.
- Insert a shale sample inside a high temperature plastic bag and place it between a movable anvil and stationary anvil of a standard linear swelling device. The plastic bag can endure temperature up to 250°C without being damaged.
- Pour a 35 ml volume of 5% w/w NaCl solution in the plastic bag and firmly seal it after the air is completely squeezed out.
- Place the swelling device (containing shale sample and 5% NaCl solution) inside an oven for temperature control purposes. Make sure that all parts of the swelling device and cables are insulated using polystyrene to avoid temperature damage.
- Set the oven to the desired test temperature (25 to 90°C) and open the plastic bag allowing the applied heat to communicate with the shale sample and 5% NaCl solution. Seal the oven door to prevent heat dissipation. (Temperatures <25°C were not included in this study since wellbore instability and shale swelling problems usually occur at temperatures >25°C beneath the
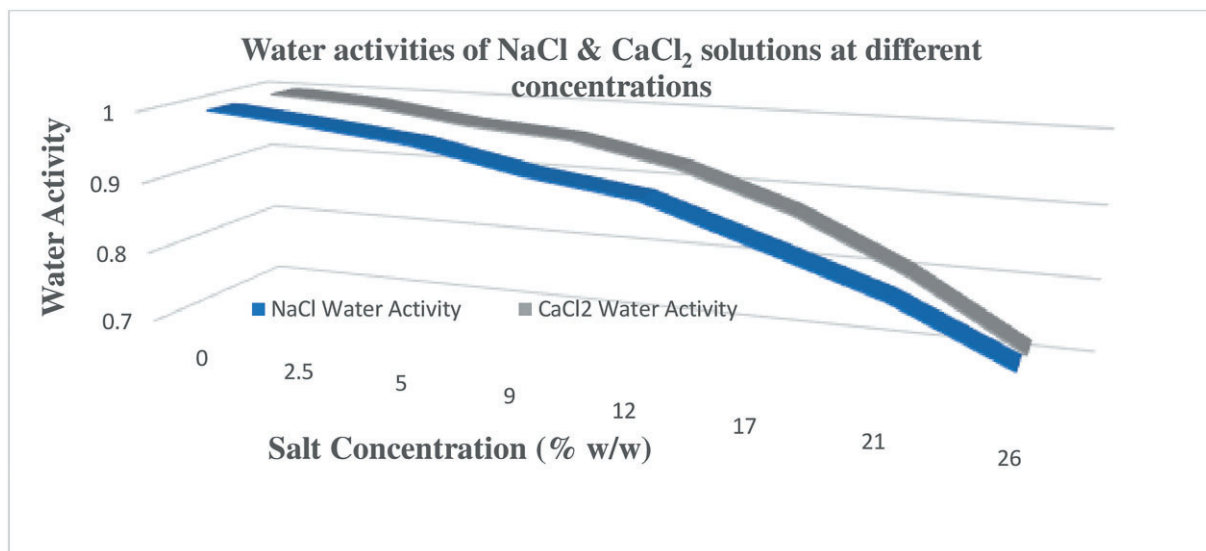
Table 3. Physical, chemical and petrophysical properties of shale

Property	Water content (%)	Water activity	Porosity (%)	Permeability (nD)	CEC (ml. eq/100 gm)
Shale	10.09	0.96	12.8	3.7	24.7

Figure 3. Water activities of NaCl and CaCl$_2$ solutions at different concentrations (%w/w).

Earth's surface. Also, a temperature of 25°C was chosen as a starting point because acceptable laboratory conditions are normally taken to be 25°C and 1 atm.)

- Using a stop watch, monitor time dependent swelling/shrinkage of shale sample by dividing increase or decrease in shale sample's length, shown as displacement readings, by the original sample length. Each test lasts for 24 hours (1440 minutes). Many studies confirm that up to 95% of shale swelling, in the laboratory, takes place within the first 24 hours, after which it slows down considerably (Zhang *et al.* 2004; AL-Bazali *et al.* 2005; AL-Bazali *et al.* 2008).
- Plot the linear swelling (%) of the shale sample versus time (minutes) on a semi-log plot.
- Repeat this procedure using 12 and 20% NaCl solutions and 5, 12 and 20% CaCl$_2$ solutions.
- Repeat this procedure using saturated NaCl and CaCl$_2$ solutions.

3. Results and discussion

3.1. *Impact of temperature on Debye–Hückel length* (κ^{-1}): *dilute solutions*

Equation (1) states that an increase in temperature leads to an increase in (κ^{-1}). In these experiments, the shale's volumetric changes represent changes in (κ^{-1}) within a diffuse double layer where shale swelling indicates the expansion of spacing distance between clay platelets (increase in κ^{-1}) and shale shrinkage points to a reduction in spacing distance between clay platelets (decrease in κ^{-1}). Figure 4 shows the shale's volumetric changes (swelling) when it was exposed to a dilute NaCl solution of 5% w/w concentrations at 25, 50 and 90 °C.

It can be seen from figure 4 that shale swelled when it interacted with 5% w/w NaCl solution at all temperatures. Shale swelling may be attributed to osmotic flow of water into shale by chemical osmosis and activation of clay sites by temperature (Al-Bazali *et al.* 2005; Schembre & Kovscek 2005; Hansen *et al.* 2012; Akinwunmi *et al.* 2019). The swelling of shale could be partially attributed to osmotic flow of water into shale since the water activity of shale ($a_w = 0.96$) is less than that of 5% w/w NaCl solution ($a_w = 0.97$). In addition, high temperature could have caused thermal swelling through the mobilization of clay platelets and detachment from clay surfaces. Figure 5 shows a schematic that explains the phenomenon of clay site (platelet) activation by temperature.

More importantly, shale swelling increased slightly as temperature increased from 25 to 90 °C despite the presumed impact of temperature on (κ^{-1}) as stated by equation (1). A closer look at equation (1) supports this increase since (κ^{-1}) is directly proportional to temperature; however, the measured swelling increase does not reflect the direct proportional relationship between (κ^{-1}) and a temperature where one would expect a more appreciable increase in (κ^{-1}) as temperatures increase. The thermo-swelling may have been offset by a thermal decrease in dielectric constant of water. In other words, the increase in (κ^{-1}) due to higher temperatures could have been counterpoised by a decrease in (κ^{-1}) due to a decrease in dielectric constant of water when temperature increased, as supported by Table 1. It is possible that when temperature increased, water molecules became energized and moved more vigorously in the solution, making it more difficult for them to align in the direction of applied electric field generated by their dipole's interactions with the dissociated ions. Thermal agitation of water molecules and consequent randomness in their alignment with the applied
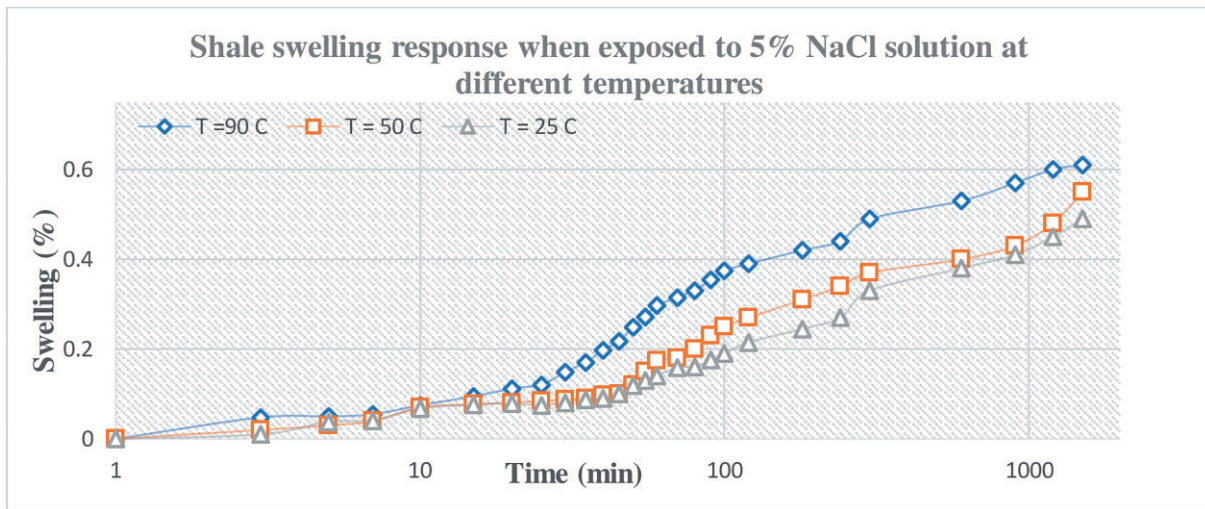
Figure 4. Shale's volumetric changes (swelling) when it was exposed to NaCl solution of 5% w/w concentration at 25, 50 and 90°C.
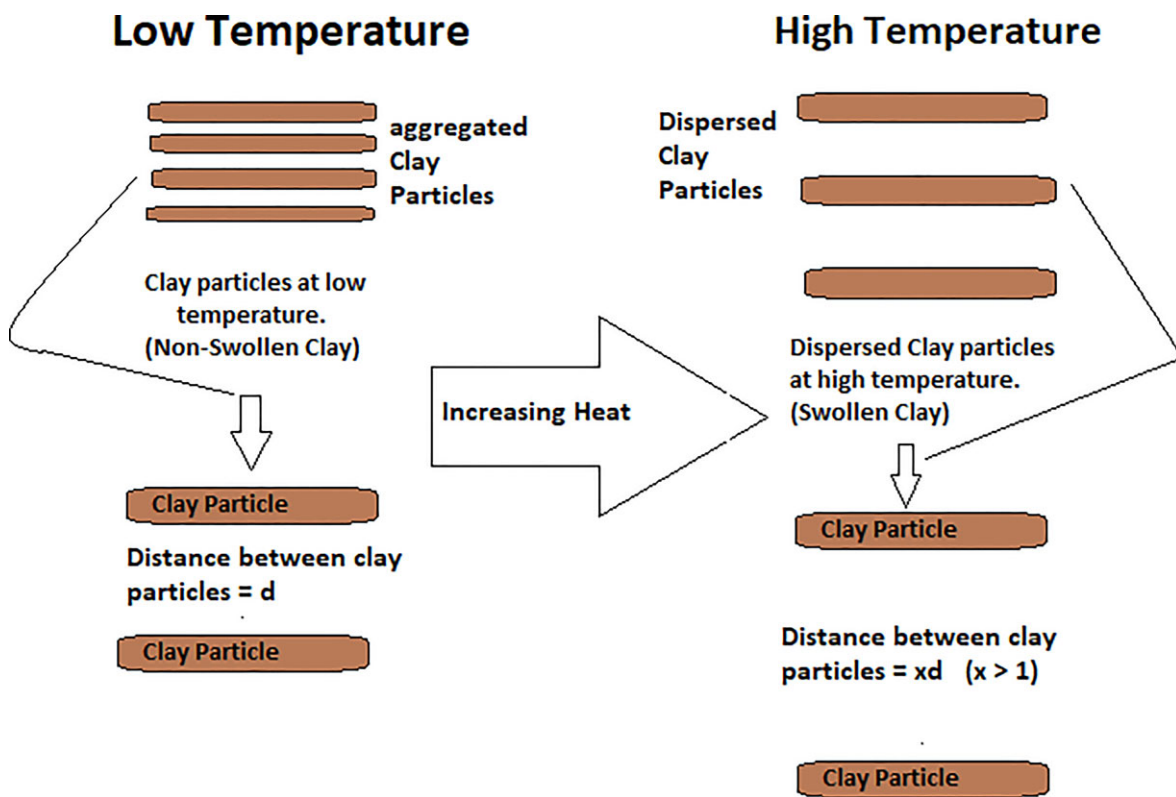

Figure 5. Activation of clay sites (platelets) by temperature.

electric field may have increased due to temperature and this may have reduced water molecule polarization and the dielectric constant. Figure 6 shows the dissociation of Na^+ and Cl^- ions in solution and the resultant electric field in the presence of polarized water molecules.

To examine this further, the effect of chemical osmosis was eliminated by exposing shale to NaCl solution of the same water activity ($a_w = 0.96$) as shown in figure 7. This was done by adding 6.5% w/w NaCl to deionized water.

It can be clearly seen that in the absence of an osmotic potential gradient, shale swelling was negligible even at higher temperatures. This may support the notion that the impact of temperature on Debye–Hückel length is negligible in the presence of dilute solutions, because an increase in temperature results in a decrease in dielectric constant of water that causes a reduction in Debye–Hückel length. Similar results were obtained when shale was exposed to 5 and 8% $CaCl_2$ solutions at different temperatures as shown in
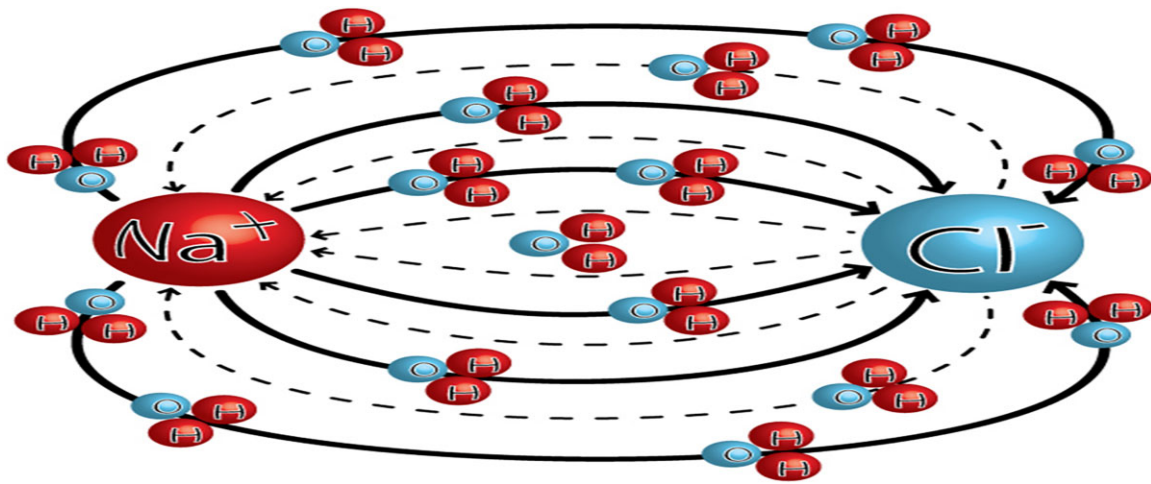
Figure 6. Dissociation of Na$^+$ and Cl$^-$ ions in solution and the resultant electric field in the presence of polarized water molecules.
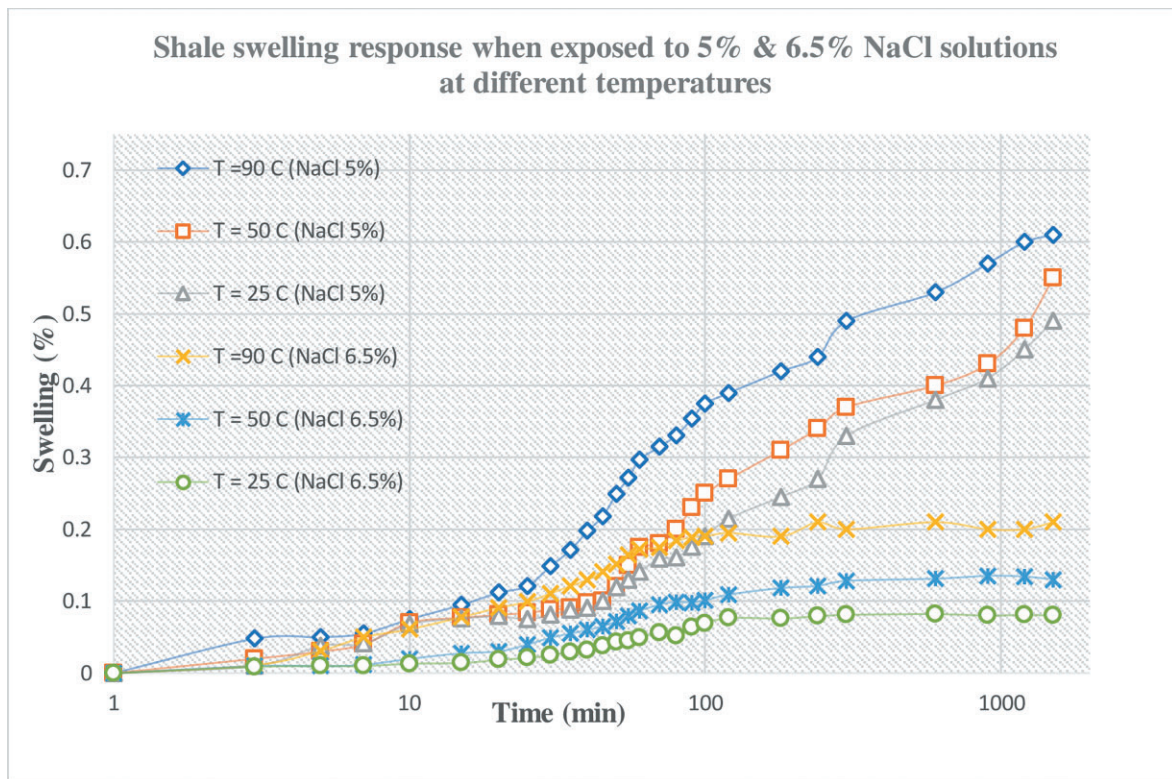

Figure 7. Shale's volumetric changes (swelling) when it was exposed to NaCl solutions of 5 and 6.5% w/w concentrations at 25, 50 and 90°C.

figure 8. Addition of 8% w/w CaCl$_2$ to deionized water yields a CaCl$_2$ solution of 0.96 water activity, which matches that of shale.

Thus, it is fair to state that when shale interacts with dilute solutions, the impact of temperature on Debye–Hückel length and subsequent shale swelling, in the absence of chemical potential gradient, may be negligible due to the counteracting effect of dielectric water constant on Debye length. More precisely, the product of temperature and dielectric constant of water remains constant for dilute solutions.

Therefore, equation (1) may be rewritten as follows:

$$\kappa^{-1} = C\sqrt{\frac{1}{I}}, \qquad (3)$$

where C is a constant and is equal to

$$C = \sqrt{\frac{\varepsilon_0 K_B (T * \varepsilon_r)}{2N_A e^2}}, \qquad (4)$$
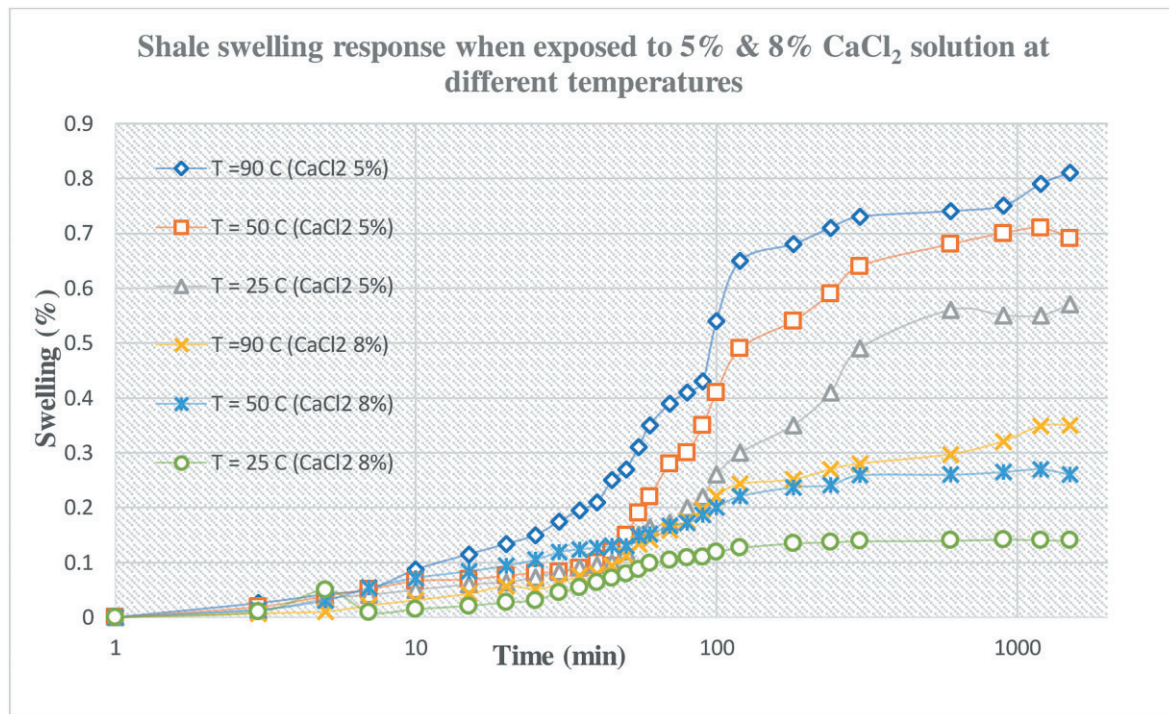
Figure 8. Shale's volumetric changes (swelling) when it was exposed to $CaCl_2$ solutions of 5 and 8% w/w concentrations at 25, 50 and 90°C.

where $(T^*\varepsilon_r)$ represents the product of the temperature and dielectric constant of water at any given temperature. Results obtained from thermo-swelling measurements confirmed this notion.

One must keep in mind that clay mobilization by heat may still play a part in shale swelling and its effect must not be mistaken for the impact of temperature on Debye length within the diffuse double layer. The previous argument may only hold true for dilute solutions in the absence of chemical potential gradient. Thus, it is essential to examine the impact of temperature on shale swelling and Debye length in the presence of concentrated solutions.

It has been observed, from figures 4, 7 and 8, that a 10-minute transition zone exists separating the two swelling regions. Low swelling occurs before this transition zone, whereas high swelling takes place afterwards (after 10 minutes). This could be attributed to many factors such as the transformation from crystalline to osmotic swelling regimes, heat transfer effects and shale sample texture. It is possible that crystalline swelling occurred first (before 10 minutes) and then followed by osmotic swelling. Depending on the d-space of the clay particle, many argue that clay swelling transpires in two separate manners; crystalline swelling and osmotic swelling (Rao *et al.* 2013; Chen *et al.* 2022). For clay particles, the d-space is acknowledged as the summation of the interlayer distance and the thickness of one clay layer. Crystalline swelling takes place when the d-space increases

from 10 to 22 Å while osmotic swelling takes over when the d-space goes beyond 22 Å.

3.2. *Impact of temperature on Debye–Hückel length (κ^{-1}): concentrated solutions*

The following analysis focuses on the percentage change of swelling or shrinkage of shale due to temperature when exposed to concentrated solutions. While the initial swelling or shrinkage of shale is controlled mainly by chemical osmosis, changes in swelling and shrinkage behaviour of shale, for a fixed ionic strength of solution as a function of temperature, will be investigated. The Debye–Hückel length and subsequent swelling or shrinkage of shale is different when concentrated solutions are involved as opposed to dilute solutions. In addition to the impact of temperature on Debye–Hückel length, ionic strength of solutions come into play and its effect could be profound. figures 9 and 10 show shale swelling/shrinkage response when exposed to NaCl and $CaCl_2$ solutions of different concentrations (ionic strength) for a wide range of temperatures (25 up to 90 °C).

Every bar on figures 9 and 10 represents the final swelling or shrinkage measurement of shale taken at 1500 minutes. Changes in swelling or shrinkage response of shale after 1500 minutes will be minimal and can therefore be neglected as seen in figures 11 and 12. It is noted from figures 11 and 12 that swelling or shrinkage of shale seems to equilibrate after 1000 minutes as it interacts with NaCl and $CaCl_2$ solutions.
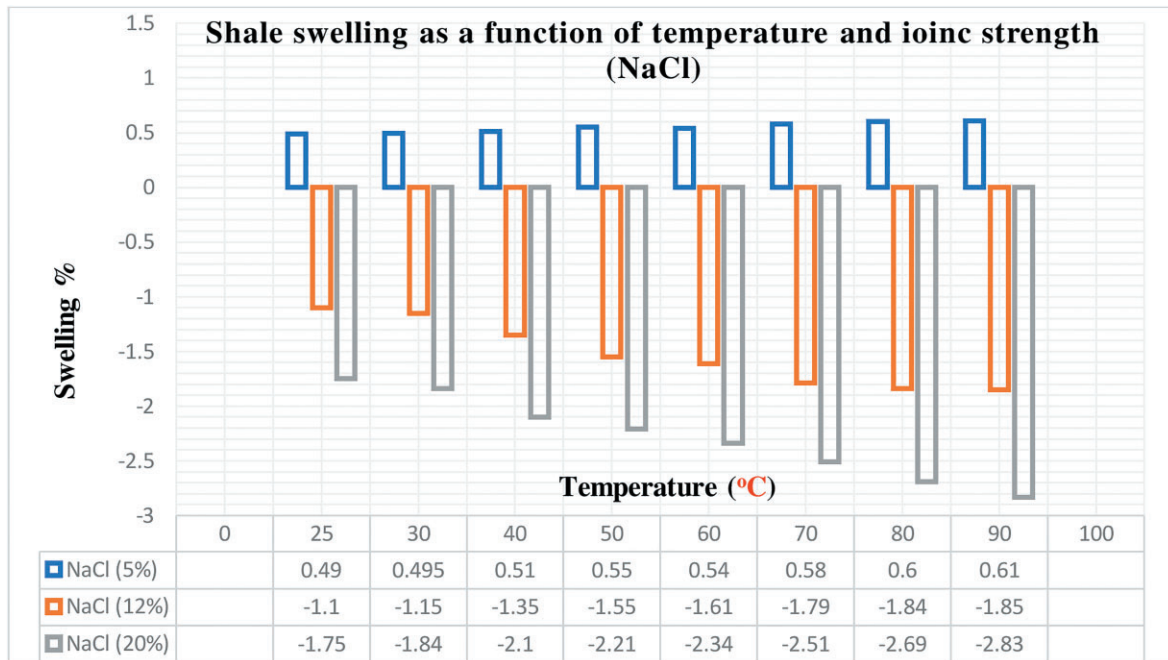
Shale swelling as a function of temperature and ioinc strength (NaCl)

	0	25	30	40	50	60	70	80	90	100
■ NaCl (5%)		0.49	0.495	0.51	0.55	0.54	0.58	0.6	0.61	
■ NaCl (12%)		-1.1	-1.15	-1.35	-1.55	-1.61	-1.79	-1.84	-1.85	
■ NaCl (20%)		-1.75	-1.84	-2.1	-2.21	-2.34	-2.51	-2.69	-2.83	

Figure 9. Shale swelling/shrinkage when exposed to 5, 12 and 20% w/w NaCl solutions at different temperatures.

Shale swelling as a function of temperature and ioinc strength (CaCl$_2$)

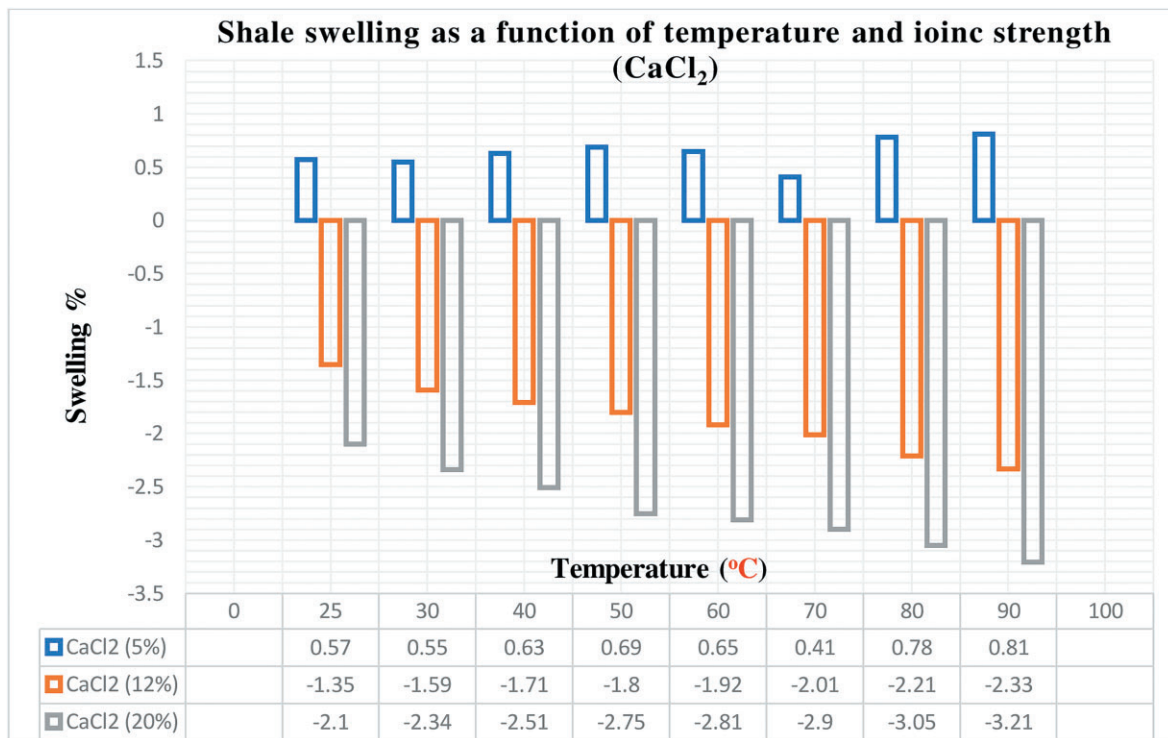|	0	25	30	40	50	60	70	80	90	100
■ CaCl2 (5%)		0.57	0.55	0.63	0.69	0.65	0.41	0.78	0.81	
■ CaCl2 (12%)		-1.35	-1.59	-1.71	-1.8	-1.92	-2.01	-2.21	-2.33	
■ CaCl2 (20%)		-2.1	-2.34	-2.51	-2.75	-2.81	-2.9	-3.05	-3.21	

Figure 10. Shale swelling/shrinkage when exposed to 5, 12 and 20% w/w CaCl$_2$ solutions at different temperatures.

AL-Bazali (2021b) found that when running linear swelling experiments, shale swelling or shrinkage will not change considerably after 1500 minutes where it might affect the final swelling outcome.

It can be seen from figures 9 and 10 that when shale interacted with 12 and 20% w/w NaCl and CaCl$_2$ solutions, the percentage change in shale shrinkage as temperature incrementally increased from 25 to 90°C is large and cannot be neglected. On the other hand, percentage change in shale swelling when shale interacted with 5% w/w NaCl and CaCl$_2$ solutions is minimal. Therefore, it is reasonable to assume that the effect of temperature on Debye–Hückel length and
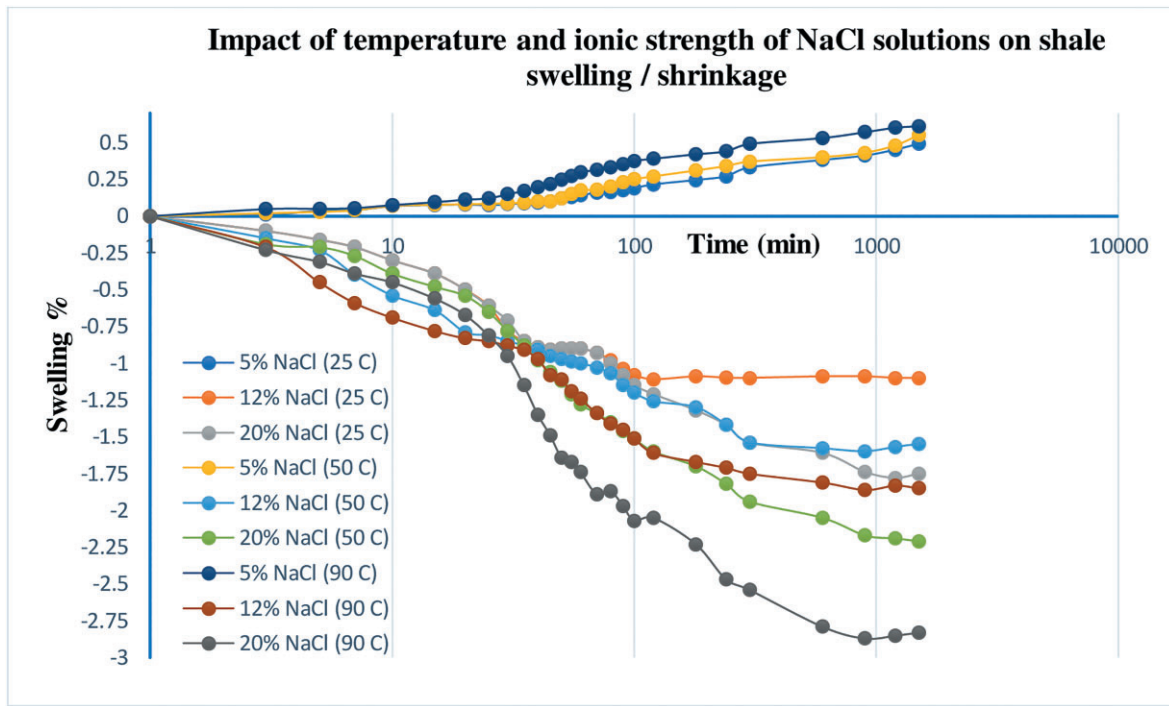
Figure 11. Swelling or shrinkage of shale seem to equilibrate after 1000 minutes as it interacted with NaCl solutions.
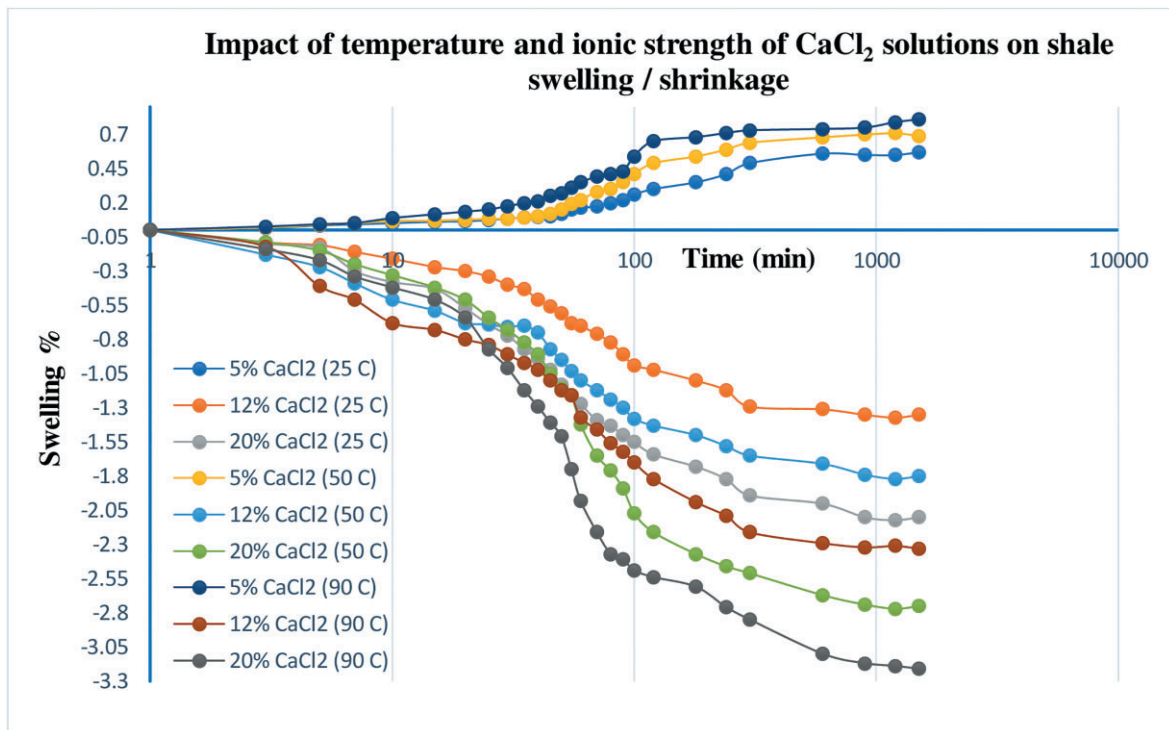

Figure 12. Swelling or shrinkage of shale seem to equilibrate after 1000 minutes as it interacted with CaCl$_2$ solutions.

consequent shale swelling/shrinkage is more severe when shale interacts with concentrated electrolytes than when it interacts with dilute electrolytes. As stated previously, temperature decreases dielectric constant of water, which lowers Debye–Hückel length. This is true for both concentrated and dilute solutions at elevated temperatures. For concentrated solutions however, dielectric constant of water may further be reduced by the presence of concentrated electrolytes and this leads to further reduction in Debye–Hückel length within a diffuse double layer. Seal *et al.* (2019) argued
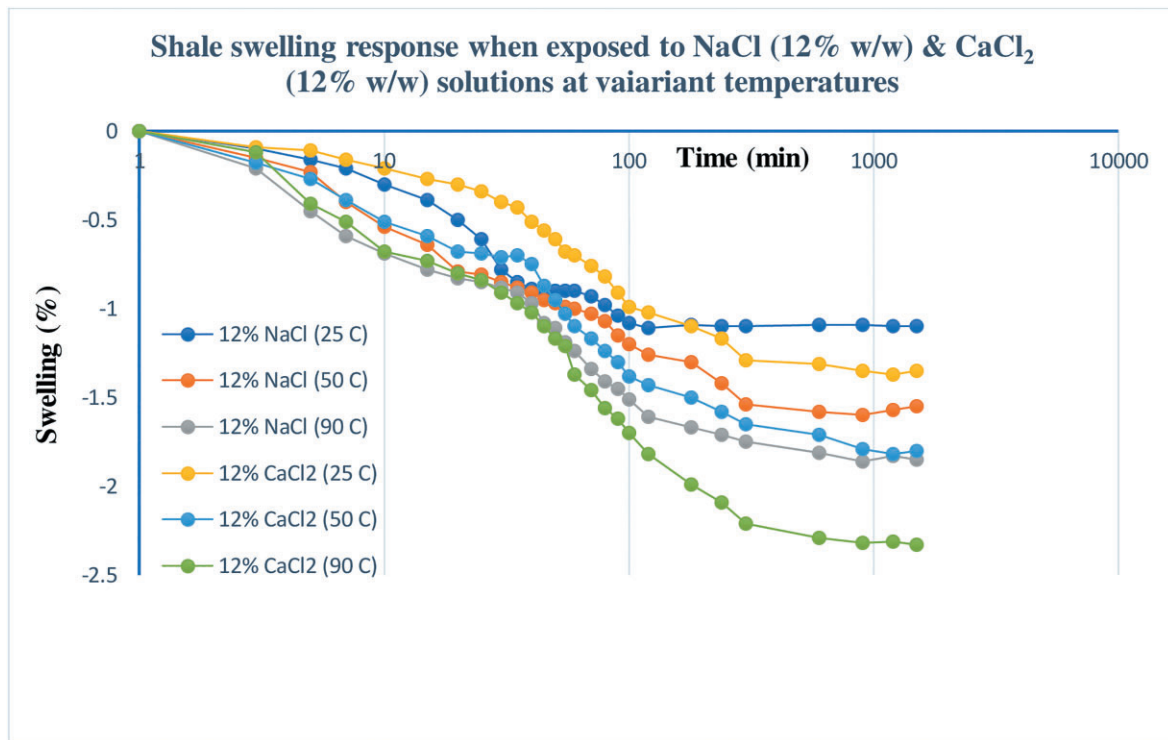
Figure 13. Shale swelling response when exposed to 12% w/w NaCl and CaCl$_2$ solutions at different temperatures.

that in the neighbourhood of an ion, water dipoles tend to align themselves along the electric field established by the ion rather than to the external field and consequently water molecules in the so-formed solvation shell will contribute less to the dielectric response than free water molecules, thus depressing the dielectric constant. In addition, an increase in ionic strength of electrolyte solution lowers the Debye–Hückel length as per equation (1). This is supported by figures 9 and 10 where the percentage increase in shale shrinkage is much higher when shale interacted with 12 and 20% w/w NaCl and CaCl$_2$ solutions than when it interacted with 5% w/w NaCl and CaCl$_2$ solutions. Thus, the combined impact of high temperature and ionic strength on dielectric constant of water leads to lowering Debye–Hückel length as shale interacts with concentrated solutions. In addition to the indirect impact of temperature and ionic strength on Debye–Hückel length through the reduction of dielectric constant of water, one must not discount the direct impact of temperature and ionic strength on Debye–Hückel length.

Equation (3) is not valid for shale interaction with concentrated solutions since the dielectric constant of water is affected by both temperature and ionic strength of electrolyte solutions. Thus, assuming that the product of temperature and dielectric constant of water remains constant may not hold true for the case of concentrated solutions. This is partly due to the impact of ionic strength on dielectric constant of

water. It was found that dielectric constant of water decreases as ionic strength of electrolyte solution increases and that all salts reduce the dielectric constant and shift the relaxation time of water (Hasted *et al.* 1948; Levy *et al.* 2012; Gavish & Promislow 2016). The following equation may be a better representation of Debye–Hückel length in the presence of concentrated solutions:

$$\kappa^{-1} = C\sqrt{\frac{\varepsilon_r(T, I) * T}{I}}, \qquad (5)$$

where C is a constant and equals to

$$C = \sqrt{\frac{\varepsilon_0 K_B}{2N_A e^2}}, \qquad (6)$$

and $\varepsilon_r(T, I)$ is the dielectric constant of water as a function of both temperature and ionic strength of electrolyte solution.

The ionic strength is also related to the valance of the ion as stated in equation (2). Multivalent ions such as calcium ions are expected to produce higher ionic strength solutions than monovalent ions such as sodium ions. Thus, multivalent ions should lower Debye–Hückel length and produce less shale swelling than monovalent ions. This is confirmed by figures 13 and 14 where 12 and 20% w/w calcium chloride solutions produced less shale swelling (more shrinkage) than 12 and 20% w/w sodium chloride
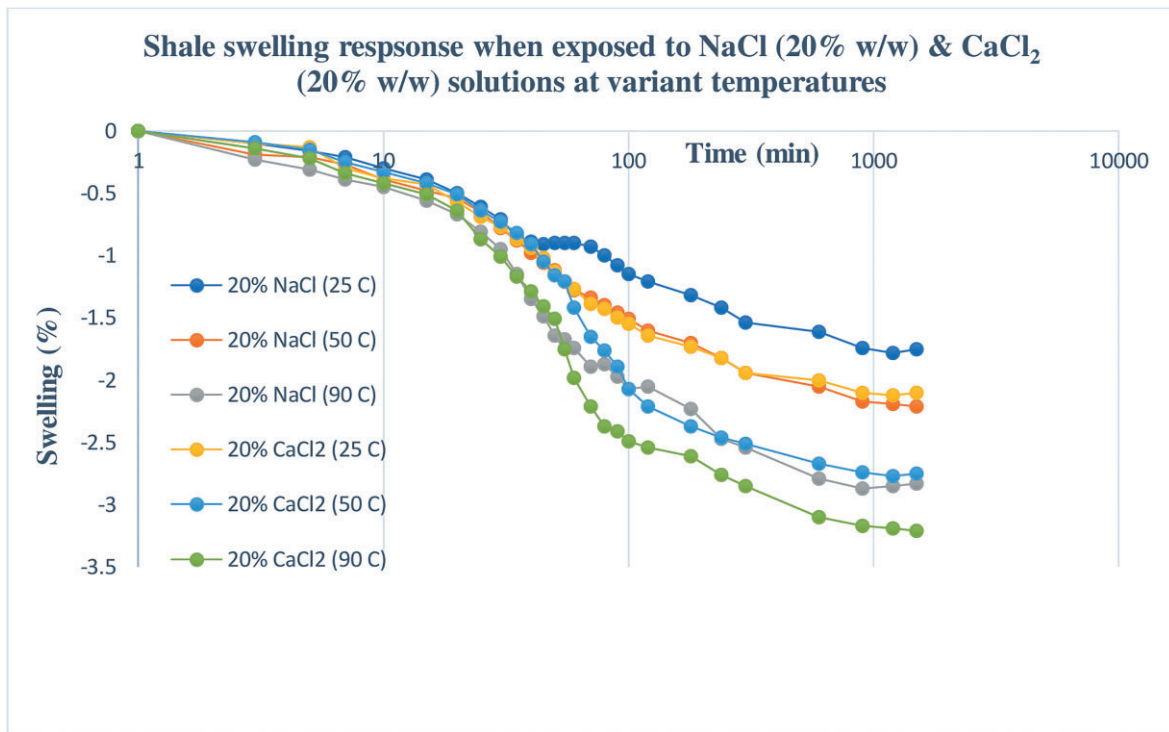
Figure 14. Shale swelling response when exposed to 12% w/w NaCl and CaCl$_2$ solutions at different temperatures.
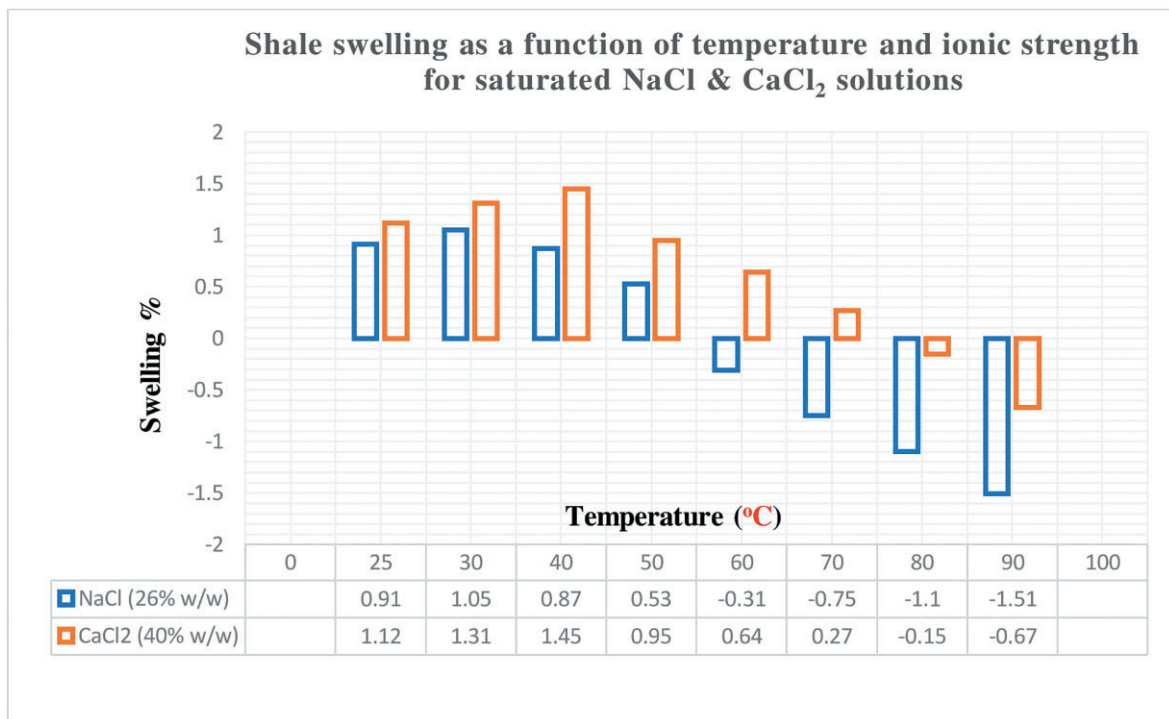
Figure 15. Shale swelling/shrinkage when exposed saturated NaCl and CaCl$_2$ solutions at different temperatures.

solutions at 25, 50 and 90°C. AL-Bazali (2022) argued that multivalent ions induce lesser screening length (κ^{-1}) than monovalent ions because they are more effective at shielding particle surface charge and screening electrostatic forces.

3.3. Impact of temperature on Debye–Hückel length (κ^{-1}): saturated solutions

Changes in Debye–Hückel length and resultant swelling when shale interacted with concentrated NaCl and CaCl$_2$ solutions were examined as shown in figure 15.

Table 4. Mineralogical composition of Pierre shale

X-ray diffraction	Shale (w/w%)
quartz mineral	21.3
feldspar mineral	6.1
calcite mineral	2.1
dolomite mineral	5.9
pyrite mineral	1.9
siderite mineral	0.9
Overall clay minerals	61.8
chlorite clay	2.45
kaolinite clay	6.8
illite clay	11.75
smectite clay	10.5
mixed layer clay	30.3

It can be seen from figure 15 that when shale interacted with saturated NaCl solutions, it experienced swelling for a temperature range of 25 to 50°C and then it shrank thereafter for temperatures higher than 60°C. As for saturated $CaCl_2$ solutions, shale swelling continued up 70°C, after which it

shrank. This is counterintuitive since ionic strength is inversely proportional to Debye–Hückel length and one would expect shale to always shrink in response to higher electrolyte concentrations at all temperatures. Increasing electrolyte concentration, especially at saturation levels, within the diffuse double layer may have produced extreme electrostatic repulsion between identical ions that could have enlarged the diffuse double layer thickness. It is possible that the electrostatic repulsive forces that developed between alike cations may have overcome their effect on shielding a nearby charged clay surface. At higher temperatures, excessive thermal reduction in dielectric constant of water may have contributed to shale shrinkage by offsetting some of the swelling encouraged by the repulsive forces generated by similar ions and thus reducing the Debye–Hückel length within the diffuse double layer. When compared to NaCl, the different swelling and shrinkage onset and magnitude produced by saturated $CaCl_2$ may be attributed to the divalent calcium ion that further reduces the ionic strength and resultant Debye–Hückel length.
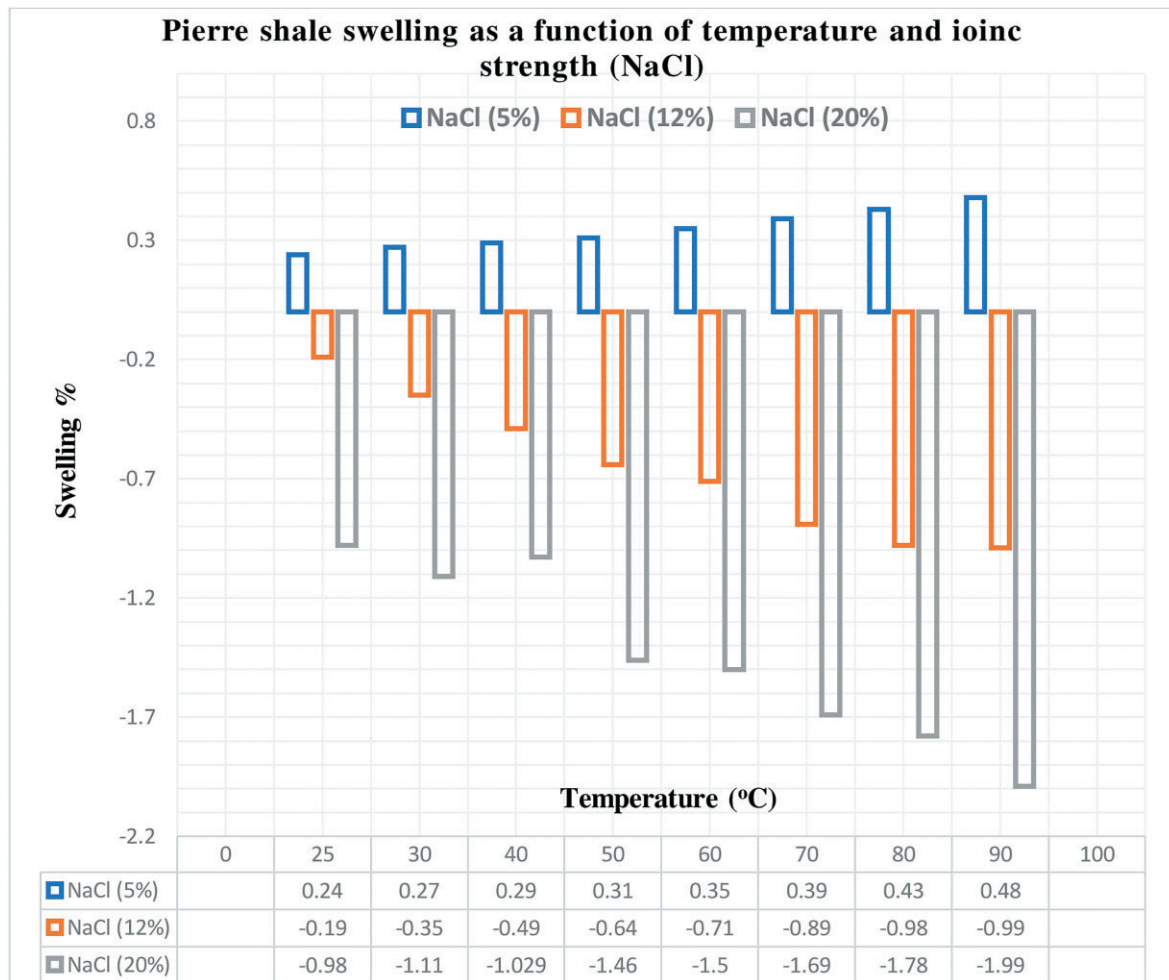
Pierre shale swelling as a function of temperature and ioinc strength (NaCl)

	0	25	30	40	50	60	70	80	90	100
NaCl (5%)		0.24	0.27	0.29	0.31	0.35	0.39	0.43	0.48	
NaCl (12%)		-0.19	-0.35	-0.49	-0.64	-0.71	-0.89	-0.98	-0.99	
NaCl (20%)		-0.98	-1.11	-1.029	-1.46	-1.5	-1.69	-1.78	-1.99	

Figure 16. Pierre shale swelling/shrinkage when exposed to 5, 12 and 20% w/w NaCl solutions at different temperatures.

3.4. Mineralogical composition perspective

To investigate the effect of mineralogical composition on shale swelling at high temperatures, the thermal linear swelling test was conducted on an outcrop Pierre shale. The minerals make up of Pierre shale can be seen in Table 4. Figure 16 shows Pierre shale swelling/shrinkage when exposed to 5, 12 and 20% w/w NaCl solutions at different temperatures. Comparing figure 9 with figure 16 reveals that Pierre shale's shrinkage/swelling behaviour followed that of our shale when exposed to NaCl solutions of 5, 12 and 20% w/w at different temperatures. While the magnitude of Pierre shale's shrinkage/swelling is less than that of our original shale, the shrinkage/swelling trend followed the same direction. One can conclude that the type and amount of minerals, especially clay minerals, may affect the magnitude of shrinkage/swelling behaviour of shale. It is important to notice that our original shale has 22.4% smectite clay and 34.18% mixed layer clay while Pierre shale has 10.5% smectite clay and 30.3% mixed layer clay. Smectite and mixed layer clays are classified by many as sensitive clays since they have shrinkage and swelling tendencies when exposed to aqueous solutions.

3.5. Water activity consideration

It is important to mention that temperature also affects water activity of both shale and salt solutions which could contribute to Debye–Hückel length changes and consequent swelling/shrinkage of shale. Kouzel (1982) showed that water activity of NaCl solutions increased with temperature especially when ionic concentration exceeded 10%. The introduction of heat seems to increase the electrical double layer separation distance causing a sparser Boltzmann's distribution of cations away from the negatively charged clay surfaces (Zhang *et al.* 2017). The increase in water activity may be attributed to the fact that thermal energy gained by shale's pore fluid or ionic solution may have surpassed chemical energy binding water molecules to ions, which may have increased the free energy of water molecules leading to higher water activity. The role of water activity plays a major part in determining osmotic water flow direction in the presence of a chemical potential gradient as per the following equation:

$$\pi = -\frac{RT}{V_m} ln \left[\frac{a_{w1}}{a_{w2}} \right], \tag{7}$$

where

π Osmotic pressure = m l-t^{-2};
R Gas law constant = 8.314×10^3 kg m^{-2} s^{-2} K^{-1} mol^{-1};
T Absolute temperature = T;
V_m Molar volume of water, 0.018 m^3 mol^{-1};
a_{w1} and a_{w2} Water activities of shale and salt solution, respectively.

4. Conclusions

The impact of temperature and ionic strength on Debye–Hückel length alterations was investigated using a newly developed thermal linear swelling test where shale interacted with dilute, concentrated and saturated NaCl and CaCl$_2$ solutions at different temperatures. The impact of temperature and ionic strength on dielectric constant of water, which is often ignored when examining Debye length changes and swelling behaviour of clay, was also investigated in the presence of dilute, concentrated and saturated NaCl and CaCl$_2$ solutions.

For dilute solutions, it was found that the impact of temperature on Debye–Hückel length was negligible because an increase in temperature resulted in a decrease in dielectric constant of water, which caused a reduction in Debye–Hückel length. This was supported by thermo-swelling experiments where shale swelling increased slightly as temperature increased from 25 to 90 °C in the presence of dilute NaCl and CaCl$_2$ solutions. The increase in (κ^{-1}) due to higher temperatures could have been possibly counterpoised by a decrease in (κ^{-1}) due to a decrease in dielectric constant of water as temperature increased.

When shale interacted with 12 and 20% w/w NaCl and CaCl$_2$ solutions, the percentage change in shale shrinkage as temperature incrementally increased from 25 to 90°C is large and cannot be neglected. Therefore, it is reasonable to assume that the effect of temperature on Debye–Hückel length and consequent shale swelling/shrinkage is more severe when shale interacts with concentrated electrolytes than when it interacts with dilute electrolytes. The combined impact of high temperature and ionic strength on dielectric constant of water leads to excessive lowering of Debye–Hückel length as shale interacts with concentrated solutions.

As for saturated NaCl and CaCl$_2$ solutions, shale exhibited swelling behaviour at moderate temperatures (up to 50°C for NaCl and up to 70°C for CaCl$_2$) followed by shale shrinkage thereafter. This could be attributed to the development of repulsive forces between alike ions with the diffuse double layer, which may have overcome their electrostatic screening effect on charged clay surfaces. At higher temperatures, the contribution of dielectric constant of water on lowering Debye–Hückel length may have softened the repulsion action produced by ions.

Last, the effect of ionic valance on Debye–Hückel length was investigated. It was shown that 12 and 20% w/w calcium chloride solutions produced less shale swelling (more shrinkage) than 12 and 20% w/w sodium chloride solutions at 25, 50 and 90°C.

Funding and compliance with ethical standards

Moreover, the author has no relevant financial or non-financial interests to disclose.

Conflict of interest statement. None declared.

Availability of data and material

All data generated or analysed during this study are included in this article.

References

Aftab, A., Ismail, A.R. & Ibupoto, Z.H., 2017. Enhancing the rheological properties and shale inhibition behavior of water-based mud using nanosilica, multi-walled carbon nanotube, and graphene nanoplatelet. *Egyptian Journal of petroleum*, **26**, 291–299.

Akinwunmi, B., Sun, L., Hirvi, J.T., Kasa, S. & Pakkanen, T.A., 2019. Influence of temperature on the swelling pressure of bentonite clay. *Chemical Physics*, **516**, 177–181.

Al-Bazali, T., 2021a. Insight on the inhibitive property of potassium ion on the stability of shale: a diffuse double-layer thickness $(\kappa-1)$ perspective. *Journal of Petroleum Exploration and Production Technology*, **11**, 2709–2723.

Al-Bazali, T., 2021b. On the stability of shale: the role of zeta potential (ζ) and Debye Hückel length $(\kappa-1)$ on shale swelling. *Petroleum Science and Technology*, **39**, 1008–1026.

AL-Bazali, T., 2022. Insight into Debye–Hückel length $(\kappa-1)$: smart gravimetric and swelling techniques reveals discrepancy of diffuse double layer theory at high ionic concentrations. *Journal of Petroleum Exploration and Production Technology*, **12**, 461–471.

Al-Bazali, T.M., Zhang, J., Chenevert, M.E. & Sharma, M.M, 2005. A Rapid, Rigsite Deployable, Electrochemical Test for Evaluating the Membrane Potential of Shales. SPE-96098, *SPE Annual Technical Conference and Exhibition*, Dallas, Texas. OnePetro.

Al-Bazali, T.M., Zhang, J., Chenevert, M.E. & Sharma, M.M., 2008. An experimental investigation on the impact of diffusion osmosis, chemical osmosis, and capillary suction on shale alteration. *Journal of Porous Media*, **11**, 719–731.

Al-Bazali, T.M., Zhang, J., Wolfe, C., Chenevert, M.E. & Sharma, M.M., 2009. Wellbore instability of directional wells in laminated and naturally fractured shales. *Journal of Porous Media*, **12**, 119–130.

Bharat, T.V. & Sridharan, A., 2015. A critical appraisal of Debye length in clay-electrolyte systems. *Clays and Clay Minerals*, **63**, 43–50.

Chenevert, M.E. & Pernot, V., 1998. Control of shale swelling pressures using inhibitive water-base muds. In *SPE annual technical conference and exhibition*. OnePetro.

Chenevert, M E. & Amanullah, M., 2001. Shale preservation and testing techniques for borehole-stability studies. *SPE Drilling & Completion*, **16**, 146–149.

Chen, W.L., Grabowski, R.C. & Goel, S., 2022. Clay swelling: role of cations in stabilizing/destabilizing mechanisms. *ACS omega*, **7**, 3185–3191.

Gao, C., Miska, S.Z., Yu, M., Ozbayoglu, E.M. & Takach, N.E., 2016. Effective enhancement of wellbore stability in shales with new families of nanoparticles. In *SPE Deepwater Drilling and Completions Conference*. OnePetro.

Gavish, N. & Promislow, K., 2016. Dependence of the dielectric constant of electrolyte solutions on ionic concentration: a microfield approach. *Physical Review E*, **94**, 012611.

Hansen, E.L., Hemmen, H., Fonseca, D.D.M., Coutant, C., Knudsen, K.D., Plivelic, T.S., Bonn, D. & Fossum, J.O., 2012. Swelling transition of a clay induced by heating. *Scientific Reports*, **2**, 1–4.

Hasted, J.B., Ritson, D.M. & Collie, C.H., 1948. Dielectric properties of aqueous ionic solutions. Parts I and II. *The Journal of Chemical Physics*, **16**, 1–21.

Kouzel, B., 1982. Easy brine flash estimates. In *SPE Oilfield and Geothermal Chemistry Symposium*. SPE-10627, Dallas, Texas, OnePetro.

Levy, A., Andelman, D. & Orland, H., 2012. Dielectric constant of ionic solutions: a field-theory approach. *Physical Review Letters*, **108**, 227801.

Low, P. F., 1961. Physical chemistry of clay-water interaction. *Advances in Agronomy*, **13**, 269–327.

Madsen, F.T. & Müller-Vonmoos, M., 1989. The swelling behaviour of clays. *Applied Clay Science*, **4**, 143–156.

Malmberg, C.G. & Maryott, A.A., 1956. Dielectric constant of water from 0 to 100 C. *Journal of Research of the National Bureau of Standards*, **56**, 1–8.

Mitchell, J.K. & Soga, K., 2005. *Fundamentals of Soil Behavior, Vol.* **3**. New York: John Wiley & Sons.

Prelesnik, J.L., Alberstein, R.G., Zhang, S., Pyles, H., Baker, D., Pfaendtner, J. & Mundy, C.J., 2021. Ion-dependent protein–surface interactions from intrinsic solvent response. *Proceedings of the National Academy of Sciences of the United States of America*, **118**.

Rana, A., Khan, I., Ali, S., Saleh, T.A. & Khan, S.A., 2020. Controlling shale swelling and fluid loss properties of water-based drilling mud via ultrasonic impregnated SWCNTs/PVP nanocomposites. *Energy & Fuels*, **34**, 9515–9523.

Rao, S.M., Thyagaraj, T. & Rao, P.R., 2013. Crystalline and osmotic swelling of an expansive clay inundated with sodium chloride solutions. *Geotechnical and Geological Engineering*, **31**, 1399–1404.

Schembre, J.M. & Kovscek, A.R., 2005. Mechanism of formation damage at elevated temperature. *Journal of Energy Resources Technology*, **127**, 171–180.

Schwank, M., Green, T.R., Maïzler, C., Benedickter, H. & Fluhler, H., 2006. Laboratory characterization of a commercial capacitance sensor for estimating permittivity and inferring soil water content. *Vadose Zone Journal*, **5**, 1048–1064.

Seal, S., Doblhoff-Dier, K. & Meyer, J., 2019. Dielectric decrement for aqueous NaCl solutions: effect of ionic charge scaling in nonpolarizable water force fields. *The Journal of Physical Chemistry B*, **123**, 9912–9921.

Smith, A.M., Lee, A.A. & Perkin, S., 2016. The electrostatic screening length in concentrated electrolytes increases with concentration. *The Journal of Physical Chemistry Letters*, **7**, 2157–2163.

Stillinger, F.H., Jr. & Kirkwood, J. G, 1960. Theory of the diffuse double layer. *The Journal of Chemical Physics*, **33**, 1282–1290.

Van Olphen, H., 1986. *An Introduction to Clay Colloid Chemistry*, 1977. National Academy of Sciences, Washington, DC.

van Oort, E., 2003. On the physical and chemical stability of shales. *Journal of Petroleum Science and Engineering*, **38**, 213–235.

van Oort, E., Hale, A.H., Mody, F.K. & Roy, S., 1996. Transport in shales and the design of improved water-based shale drilling fluids. *SPE Drilling & Completion*, **11**, 137–146.

Wilson, M.J. & Wilson, L., 2014. Clay mineralogy and shale instability: an alternative conceptual analysis. *Clay Minerals*, **49**, 127–145.

Zhang, J., Chenevert, M.E., AL-Bazali, T. & Sharma, M.M, 2004. A new gravimetric-swelling test for evaluating water and ion uptake in shales. In *SPE annual technical conference and exhibition*. OnePetro.

Zhang, C., Pathegama Gamage, R., Perera, M.S. A. & Zhao, J., 2017. Characteristics of clay-abundant shale formations: use of CO_2 for production enhancement. *Energies*, **10**, 1887.