A critical examination of diffuse double layer alterations in clay-electrolyte systems at elevated temperatures

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Research Article

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Posted Date: March 7th, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1387966/v1>

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A critical examination of diffuse double layer alterations in clay-electrolyte systems at elevated 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 our newly developed thermo linear swelling test. Moreover, 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 was investigated.

For dilute solutions, results showed that the product of temperature and dielectric constant of water ($T^*\epsilon_r$) remained near constant for a wide range of temperature (25C – 90C). When shale interacted with 12% and 20% w/w NaCl and CaCl₂ solutions, the % change in shale shrinkage as temperature incrementally increased from 25C to 90C is quite large and cannot be neglected. Results suggests that 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 CaCl₂ solutions, shale exhibited swelling behavior at moderate temperatures (up to 50C for NaCl and up to 70C for CaCl₂) followed by shale shrinkage thereafter. This could be attributed to the development of repulsive forces between alike ions with 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 soften 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 over 75% of drilled formations, is a challenging job to drilling engineers. Such 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 [1] pointed 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 the above-mentioned downhole problems, clogging of surface flow lines and equipment could result subsequent to shale dispersion and disintegration.

Wellbore instability problems in shale is often attributed to clay swelling, although other factors such as bad drilling practises 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 to volumetric expansion and subsequent clay swelling [2]. Since in situ shale is not allowed to volumetrically expand or freely swell, hydrational stresses develop and pore pressure builds up within 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 Å to 22 Å while osmotic swelling occurs at interlayer separations greater than 22 Å, as shown in Fig. 1.

Fig. 1 Crystalline swelling and osmotic swelling of clay minerals, (1 Angstrom = 0.1 nm).

While crystalline swelling 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 [3]. 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}) [4-6]. The quantity of cations and water in the diffuse double layer determines its thickness (κ^{-1}) and resultant swelling and shrinkage status of clay as depicted in Fig. 2.

Fig. 2 Debye Hückel length within Diffuse double layer.

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 particles repulsion, swelling and instability [7]. The Debye Hückel length (κ^{-1}) for a monovalent electrolyte, for electrolytes and colloidal suspensions, is given by:

$$\kappa^{-1} = \sqrt{\frac{\epsilon_r \epsilon_0 k_B T}{2 N_A e^2 I}} \quad (1)$$

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)
k_B	Boltzmann constant = 1.38E-23 (J/K)
T	Absolute temperature in Kelvins (K)
N_A	Avogadro number = 6.02E23 (1/mols)
e	Elementary charge = 1.6E-19 C
I	Ionic strength of the electrolyte in molar units (M or mol/L) and is given by:

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

Z Valance of ion (Na⁺ = 1; Cl⁻ = 1; Ca⁺² = 2; Mg⁺² = 2)

m_i Molality of the i th ion in (mol/L)

As stated above, macroscopic shale swelling and shrinkage is highly linked to microscopic changes in Debye Hückel length within diffuse double layer of clay. Therefore, understanding the factors that impact 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 [8-16]. These studies have focused on the isothermal impact of ionic concentration on clay swelling and the development of Debye Hückel length and completely ignored 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 [17-18]. In other words, while higher temperatures should increase Debye Hückel length as per equation (1), higher temperatures also decrease dielectric constant of water which in turn decreases Debye Hückel length. Malmberg & Maryott [19] developed an empirical equation that calculated dielectric constant of water over temperature range of 0.1°C to 99°C, as shown in Table 1.

Table 1 Dielectric constant of water (ϵ_r) at various temperatures, *after Malmberg & Maryott [19]*.

Temp (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

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 impact the development of Debye Hückel length directly but also affects both dielectric constant of water and ionic strength of solution, both of which impact 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.

This work investigates the direct and consequent impact of temperature on changes in Debye Hückel length (diffuse double layer thickness) through thermo-linear swelling measurements of shale samples. The impact of temperature on dielectric constant of water and ionic strength of utilized aqueous solutions will be closely monitored in order 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 our newly developed thermo-linear swelling experimental methodology.

2. Material & 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 [20]. X-Ray Diffraction technique was conducted by an independent commercial testing facility located in the USA to obtain the mineralogical composition of our shale, shown in Table 2.

Table 2 Mineralogical composition of shale.

X-Ray Diffraction	Shale w/w %
Quartz	15.2
Feldspar	4.1
Calcite	1.7
Dolomite	1.8
Pyrite	1.4
Siderite	1.5
Total Clay	74.3
<i>Chlorite</i>	3.5
<i>Kaolinite</i>	6.8
<i>Illite</i>	7.49
<i>Smectite</i>	22.4
<i>Mixed Layer</i>	34.18

Adsorption isotherm methodology was employed to determine the water activity of our native shale where cubical shale samples of dimensions (0.75'' x 0.75'' x 0.50'') were cut out of the native shale core and placed in several desiccators of different water activities. Complete explanation of procedures utilized to measure water activity, water content, cation exchange capacity (CEC), porosity and permeability of shale is given in [21]. Table 3 shows physical, chemical and petrophysical properties of shale.

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

2.2 Thermo-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 impact of temperature and dielectric constant of water on Debye Hückel length will be challenged and alternative approach will be presented. Moreover, 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 Fig. 3

Fig. 3 Water activities of NaCl and CaCl_2 solutions at different concentrations (%w/w).

- Cut shale samples of size (0.75 " x 0.75 " x 0.5 ") from our native core to run linear swelling tests.
- Insert a shale sample inside a high temperature plastic bag and place it between movable anvil and stationary anvil of a standard linear swelling device. The plastic bag can endure temperature up to 250C without being damaged.
- Pour 35 ml volume of 5% w/w NaCl solution in the plastic bag and firmly seal it after 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 (25C to 90C) and open the plastic bag allowing the applied heat to communicate with shale sample and 5% NaCl solution. Seal the oven door to prevent heat dissipation.
- 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 (1,440 minutes).
- Plot linear swelling (%) of shale sample versus time (minutes) on a semi-log plot.
- Repeat the above procedure using 12% & 20% NaCl solutions and 5%, 12% & 20% CaCl₂ solutions.
- Repeat the above procedure using saturated NaCl and CaCl₂ solutions.

3. Discussion & Analysis

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

Fig. 4 Shale's volumetric changes (swelling) when it was exposed to NaCl solution of 5% w/w concentration at 25 C, 50 C and 90 C.

It can be seen from Fig. 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 [22-25]. 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. Fig. 5 shows a schematic that explains the phenomenon of clay sites (platelets) activation by temperature.

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

More importantly, shale swelling increased slightly as temperature increased from 25 C 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 temperature where one would expect a more appreciable increase in (κ^{-1}) as temperatures increases. 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. I believe 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 dipoles interactions with the dissociated ions. I further think that thermal agitation of water molecules and consequent randomness in their alignment with the applied electric field may have increased due to temperature and this may have reduced water molecules polarization and dielectric constant. Fig. 6 shows dissociation of Na^+ and Cl^- ions in solution and resultant electric field in the presence of polarized water molecules.

Fig. 6 Dissociation of Na^+ and Cl^- ions in solution and resultant electric field in the presence of polarized water molecules.

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

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

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 which 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 Fig. 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 our shale.

Fig. 8 Shale's volumetric changes (swelling) when it was exposed to CaCl_2 solutions of 5% & 8% w/w concentrations at 25 C, 50 C and 90 C.

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:

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

where C is a constant and equals to:

$$C = \sqrt{\frac{\epsilon_0 K_B (T^* \epsilon_r)}{2 N_A e^2}} \quad (4)$$

where $(T^* \epsilon_r)$ represents the product of the temperature and dielectric constant of water at any given temperature. Results obtained from our 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 with 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.

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

The following analysis focuses on the % 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 behavior 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 quite 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. Figs. 9 and 10 show shale swelling/shrinkage response when exposed to NaCl and CaCl₂ solutions of different concentrations (ionic strength) for a wide range of temperatures (25 C up to 90C).

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

Fig. 10 Shale swelling/shrinkage when exposed to 5%, 12% & 20% w/w CaCl₂ solutions at different temperatures.

Every bar on the Figs. 9 and 10 represents the final swelling or shrinkage measurement of shale taken at 1500 minutes. I believe that changes in swelling or shrinkage response of shale after 1500 minutes will be minimal and can therefore be neglected for the purpose of our study as seen in Figs. 11 and 12. It is noticed from Figs. 11 and 12 that swelling or shrinkage of shale seems to equilibrate after 1000 minutes as it interacted with NaCl and CaCl₂ solutions. AL-Bazali [26] 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.

Fig. 11 Swelling or shrinkage of shale seem to equilibrate after 1000 minutes as it interacted with NaCl solutions.

Fig.12 Swelling or shrinkage of shale seem to equilibrate after 1000 minutes as it interacted with CaCl₂ solutions.

It can be seen from Figs. 9 and 10 that when shale interacted with 12% and 20% w/w NaCl and CaCl₂ solutions, the % change in shale shrinkage as temperature incrementally increased from 25C to 90C is quite large and cannot be neglected. On the other hand, % change in shale swelling when shale interacted with 5%

w/w NaCl and CaCl₂ solutions is quite minimal. 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. 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 though, 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 diffuse double layer. Seal et al [27] argued 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 Figs. 9 and 10 where the % increase in shale shrinkage is much higher when shale interacted with 12% and 20% w/w NaCl and CaCl₂ solutions than when it interacted with 5% w/w NaCl and CaCl₂ 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 [28-30]. The following equation may be a better representation of Debye Hückel length in the presence of concentrated solutions:

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

where C is a constant and equals to:

$$C = \sqrt{\frac{\epsilon_0 K_B}{2 N_A e^2}} \quad (6)$$

and $\epsilon_r(T, I)$ 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 ion are expected to produce higher ionic strength solutions than monovalent ions such as sodium ion. Thus, multivalent ions should lower Debye Hückel length and produce less shale swelling than monovalent ions. This is confirmed by Figs. 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 solutions at 25C, 50C and 90C. AL-Bazali [31] 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.

Fig. 13 Shale swelling response when exposed to 12% w/w NaCl and CaCl₂ solutions at different temperatures.

Fig. 14 Shale swelling response when exposed to 20% w/w NaCl and CaCl₂ solutions at different temperatures.

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 CaCl₂ solutions were examined as shown in Fig. 15

Fig. 15 Shale swelling/shrinkage when exposed saturated NaCl and CaCl₂ solutions at different temperatures.

It can be seen from Fig. 15 that when shale interacted with saturated NaCl solutions, it experienced swelling for temperature range of 25 C to 50C and then it shrank thereafter for temperatures higher than 60C. As for saturated CaCl₂ solutions, shale swelling continued up 70C, after which it shrank. This is counter intuitive 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. I believe that increasing electrolytes concentration, especially at saturation levels, within diffuse double layer produced extreme electrostatic repulsion between identical ions which could have enlarged the diffuse double layer thickness. It is possible that the electrostatic repulsive forces developed between alike cations may have overcome their effect on shielding 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 CaCl₂ may be attributed to the divalent calcium ion which further reduces the ionic strength and resultant Debye Hückel length.

3.4 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 [32] 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 [33]. I believe, 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.

$$\pi = -\frac{RT}{V_m} \ln \left[\frac{a_{w1}}{a_{w2}} \right] \quad (7)$$

where:

π	Osmotic pressure [=] m/L-t ²
R	Gas law constant [=] 8.314x10 ³ kg.m ² / s ² . kg-mole. K
T	Absolute temperature [=] T
V_m	Molar volume of water, 0.018 m ³ /mol
a_{w1} & 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 thermo linear swelling test where shale interacted with dilute, concentrated and saturated NaCl and CaCl₂ 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 behavior of clay, was also investigated in the presence of dilute, concentrated and saturated NaCl and CaCl₂ 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 our thermo-swelling experiments where shale swelling increased slightly as temperature increased from 25 C to 90 C in the presence of dilute NaCl and CaCl₂ 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 CaCl₂ solutions, the % change in shale shrinkage as temperature incrementally increased from 25C to 90C is quite 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 CaCl₂ solutions, shale exhibited swelling behavior at moderate temperatures (up to 50C for NaCl and up to 70C for CaCl₂) followed by shale shrinkage thereafter. This could be attributed to the development of repulsive forces between alike ions with 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 soften the repulsion action produced by ions.

Lastly, 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 25C, 50C and 90C.

STATEMENTS AND DECLARATIONS

Funding: Not applicable.

Conflicts of Interest/Competing interests: The authors declare that there was no funding, grants, or other support was received for conducting this study. Moreover, the authors have no relevant financial or non-financial interests to disclose.

Availability of data and material: Not applicable.

Code availability: Not applicable.

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