Correlations between TDS and electrical conductivity for high-salinity formation brines characteristic of South Atlantic pre-salt basins

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Total dissolved solids (TDS) is an important property in the characterization of natural waters for diversified applications, such as in geochemistry and the petroleum industry. Under appropriate circumstances, the determination of this parameter through correlations with the electrical conductivity (EC) of aqueous systems yields considerable advantages over the gravimetric method. However, the development of empirical equations correlating TDS and EC is still required due to the physical-chemical complexity of charge transport in multicomponent natural waters. Most existing correlations were built considering systems in the lower or medium salinity range. In this context, this research aims to provide experimental correlations between TDS and EC in a broad concentration range for high salinity formation brines characteristic of the pre-salt reservoirs. It contributes to filling a gap in the literature for geochemical systems of this nature. Moreover, correlations were also obtained for a concentrated desulphated seawater and an aqueous sodium chloride solution in the same salinity range. For all aqueous solutions, the polynomial fittings of degree greater than one fit the experimental data better compared to both linear and exponential equations. In addition, the solutions with higher concentration of divalent ions had lower EC than the solutions dominated by monovalent ions with the same ionic strength. This evidences the effect of ion pairing on the EC, particularly in solutions of high ionic strength. Therefore, the use of a general correlation to represent solutions with dramatic variations in chemical composition carries substantial error, particularly in the high salinity range. Thus, a specific correlation must be developed to represent brines with similar composition.

INTRODUCTION

Total dissolved solids (TDS) is an important property in the characterization of natural waters. It is defined as the total concentration of inorganic and organic matter in aqueous solution, which can be in ionic form or not (Hubert and Wolkersdorfer, 2015; McNeil and Cox, 2000). The inorganic components of TDS are composed in their majority by the ions calcium, magnesium, sodium, bicarbonate, chloride and sulfate; whereas the organic components of TDS are estimated based on the biochemical oxygen demand (BOD) and the chemical oxygen demand (COD) (Balasubramanian et al., 1999).

The acquisition of TDS of natural waters encounters diversified applications in geochemistry (Jonker et al., 2013), desalination industry (Walton, 1989), hydrology (Leske and Buckley, 2004), soil and groundwater science (Douglas, 2001; Verwey and Vermeulen, 2011), and the petroleum industry (Sun et al., 2015; Lord and LeBas, 2013; Brown and Sheedy, 2002). In geochemistry, TDS is particularly relevant for interpreting electrical well logs, correlating stratigraphic units and investigating the movement of subsurface waters (Collins, 1975). In the petroleum industry, TDS is essential to evaluate the possibility of formation of inorganic scales throughout the entire oil production system (Gudmundsson, 2018). Furthermore, in the field of enhanced oil recovery (EOR), TDS is also critical to ensuring the chemical stability of the fluids injected into petroleum reservoirs with the aim of increasing the recovered volume of hydrocarbons (Sheng, 2010).

TDS characterization is also relevant for environmental reasons. Global concern has been raised regarding the effect of effluent TDS on the biotic integrity of the streams (Helms et al., 2009; Weber-Scannell and Duffy, 2007). Several studies discuss the importance of evaluating physicochemical alteration of aqueous environments considerably affected by human interventions (Moncayo-Estrada et al., 2014; Moreyra and Padovesi-Fonseca, 2015; Deksissa et al., 2003). Clear effects of water salinity alteration to the biotic integrity in different systems have been reported elsewhere (Daniels et al., 2016; Ivanova and Kazantseva, 2006; Timpano et al., 2015).

The gravimetric method is the standard procedure to determine TDS. It consists of weighing the dry residue resulting from evaporating a measured volume of a filtered water sample (Hubert and Wolkersdorfer, 2015). However, a number of disadvantages have been attributed to this method (Hem, 1985; Raju, 2007; Gustafson and Behrman, 1939; Walton, 1989; Hubert and Wolkersdorfer, 2015). Incorrect quantification of bicarbonate ions occurs as half of them volatilize as carbon dioxide at temperatures around 100°C (Walton, 1989). During evaporation, the crystalline structure of precipitated salts can confine some water into them. In this case, the crystallization water will be weighed jointly with the precipitated salts (Hem, 1985). Additionally, the volatilization of acids, mainly at low pH values, causes the loss of some anionic content, such as chloride and nitrite ions.

On the other hand, extra mass can be considered due to oxidation or transformation into hydroxides during the heating process (Hubert and Wolkersdorfer, 2015).

Although the gravimetric method is laborious and time consuming, the accuracy of its results is not always acceptable as it mainly depends on selecting a drying temperature which allows the release of all crystallization water without provoking any chemical decomposition (Gustafson and Behrman, 1939). Another proposed method to estimate TDS relies on the conductivity of an electrolyte solution, which is its capability to conduct an electric current when a potential is applied between the electrodes immersed in it (Coury, 1999; Hem, 1985). In this context, the conductivity of a portion of an electrolyte solution, κ (in S/m or Ω^{-1}/m), with length l (in m) and area A (in m^2) is defined by Eq. 1 (Crow, 1994):

$$\kappa = \frac{1}{\rho} = \frac{l}{RA} = G\frac{l}{A} \tag{1}$$

where ρ is the reciprocal of κ, known as resistivity (in Ω·m), R is the resistance of the solution (in Ω) and G is the reciprocal of R, known as the conductance of the solution (in S or Ω^{-1}). In this work, the term electrical conductivity (EC) is used to refer to the conductivity measured at 25°C, which is also defined as specific conductance in other publications (Miller et al., 1988). The parameter l/A is called the cell constant and is utilized to convert the measured conductance of an aqueous solution to its conductivity using Eq. 1. This parameter is determined by calibrating the cell by measuring the conductance of a reference solution with known conductivity (Cazes, 2004; Hubert and Wolkersdorfer, 2015; Crow, 1994; Walton, 1989).

The relationship between TDS and conductivity is often described in the literature by the following correlation (Eq. 2) (Pawlowicz, 2008; Visconti et al., 2010; Visconti Reluy et al., 2004; Hem, 1985):

$$\text{TDS} = f \cdot \kappa_T \tag{2}$$

where f is a conversion factor and κ_T is the conductivity at a specified temperature T (usually 25°C). This conversion factor ranges between 0.5 and 0.9 for most water types (Walton, 1989). In particular, in South African mine waters this factor was found to vary from 0.25 to 1.34 (Hubert and Wolkersdorfer, 2015), and it can be as elevated as 1.4 in meromictic saline lakes (Pawlowicz, 2008). In particular, sulphate ions were shown to affect the relationship between EC and concentration due to incomplete dissociation (Tanji, 1969). As natural waters are complex aqueous systems with diversified ratios of ionic and undissociated species, in many cases a non-linear relationship between TDS and EC arises (Hubert and Wolkersdorfer, 2015). The reason for this is that the EC of an aqueous solution depends on the activity of each specific dissolved ionic component and the average activity of all in solution. These in turn are affected by temperature, concentration of each ionic component and TDS of the solution (Siosemarde et al., 2010). As a result, different electrolytes affect the EC in a different fashion. Hence, equal variations of EC at constant temperature can either result from alterations in the TDS of the solution or changes in the chemical composition (Marandi et al., 2013).

Under appropriate circumstances, the use of correlations with EC to determine the TDS of natural waters provides considerable advantages over the gravimetric method and the chemical analysis due to the simplicity, speed, low cost and accuracy of EC measurements (Hayashi, 2004; Raju, 2007). Conductivity of aqueous solutions increases with temperature. Usually, conductivity measurements are carried out at different temperatures in the field and adjusted to conductivity at a reference temperature (i.e. 25°C) using a temperature coefficient. Since the type and concentration of electrolytes alter this coefficient, it should be measured for each specific system (Smith, 1962).

Accurate EC data can be collected in the field for a broad range of geochemical applications (Shirokova et al., 2000; Marandi et al., 2013). As a result, correlations between TDS (or ion concentrations) and EC were reported in studies related to the quality of natural waters (Alhumoud et al., 2010; Daniels et al., 2016; Krishna Kumar et al., 2015; McNeil and Cox, 2000), soil salinity assessment (Zhang et al., 2009; Siosemarde et al., 2010; Daniels et al., 2016; Visconti Reluy et al., 2004), seawater intrusion analysis (El Moujabber et al., 2006; Sylus and Ramesh, 2015) and crustal fluids investigation (Sakuma and Ichiki, 2016; Guo et al., 2015; Shimojuku et al., 2014).

An alternative procedure for obtaining the TDS is through the full chemical analysis of the water sample. In addition, several methods to calculate the EC from the chemical composition are available in the literature. McCleskey et al. (2012a) published a comparison of 11 methods to calculate EC in natural waters. The authors identified the methods that performed best for waters with complex chemical compositions (Pawlowicz, 2008; McCleskey et al., 2012b). However, none of the methods were suitable for brines due to their lack of accuracy at high ionic strengths.

Moreover, geochemical computer programs, such as PHREEQCI (Charlton and Parkhurst, 2002), were developed to calculate EC of aqueous solutions from their chemical composition. A recent update (McCleskey, 2018) presents an alternative to extend the calculation over a large range of ionic strength, temperature and pH. Furthermore, industry application software that calculate the EC from chemical composition using different thermodynamic models are also available. A widely used tool is the Geochemist's Workbench (Aqueous Solutions LLC), which uses the USGS (McCleskey et al., 2012a) and APHA (American Public Health Association, 2017) models. Another product available is OLI Analyzer Studio (OLI Systems Inc.), which uses a mixed solvent electrolyte (MSE) model framework (Wang et al., 2002) combined with existing formulations (Bromley, 1972; Meissner and Kusik, 1978; Pitzer et al., 1978; Helgeson et al., 1981). Nevertheless, the accuracy of these tools for complex high salinity brines has yet to be assessed.

Charge transport in multicomponent aqueous systems is not yet entirely understood from the physical-chemical perspective. Hence, the development of empirical equations is still necessary to predict TDS from EC measurements (Visconti Reluy et al., 2004). To the best of our knowledge, published works in the literature mostly consider natural waters with a low salinity range, which does not exceed 40 000 mg/L (Rusydi, 2018; Marandi et al., 2013; McNeil and Cox, 2000; Raju, 2007; Alhumoud et al., 2010; Sylus and Ramesh, 2015). Hayashi (2004) studied brines of up to 133 000 mg/L; however, his work focused on the relation between temperature and conductivity. Although papers regarding the investigation of crustal fluids have analysed ionic solutions of higher salinities, their studies were limited to conditions of elevated pressures and temperatures (Sakuma and Ichiki, 2016; Guo et al., 2015; Shimojuku et al., 2014). Thus, data considering aqueous systems with salinities over 200 000 mg/L is scarce.

Brazilian pre-salt reservoirs have proven to be game-changers for the oil and gas industry (Filho et al., 2015; Pizarro and Branco, 2012). Additionally, basins in offshore Angola, Gabon, Cameroon, Democratic Republic of Congo, Equatorial Guinea and Namibia have been proposed as analogous prospects to the Brazilian Pre-Salt with outstanding potential for hydrocarbon reserves (Koch et al., 2013; Jameson et al., 2011). The formation brines in fields from South Atlantic pre-salt reservoirs can have TDS values over 150 000 mg/L (Drexler et al., 2019, 2020). Given the economic relevance of these reservoirs, it is important to study an adequate and efficient method for measuring the TDS of their brines, which are outside the range of the correlations present in the literature.

Table 1. Chemical composition, total dissolved solids (TDS, calculated as the sum of the concentrations of all ions) and electrical conductivity (EC) of the aqueous solutions

Ion	Ion concentrations (in mg/L)			
	Field B brine	Field D brine	Concentrated DSW	Sodium chloride solution
Na^+	57 584	65 745	69 698	114 950
K^+	1 202	1 735	2 906	0
Ca^{2+}	24 218	1 263	2 903	0
Mg^{2+}	2 121	303	9 884	0
Ba^{2+}	23	226	0	0
Sr^{2+}	1 259	716	51	0
SO_4^{2-}	54	0	0	0
Cl^-	139 904	106 511	143 790	177 250
CO_3^{2-}	0	0	181	0
HCO_3^-	0	0	587	0
Br^-	0	586	0	0
TDS (in mg/L)	226 365	177 085	230 000	292 200
EC (in µS/cm)	230 116	193 120	212 207	238 819

In this regard, the aim of this research is to develop experimental correlations between TDS and EC in a broad concentration range for two highly concentrated formation brines characteristic of the pre-salt environment, to fill the existing gap in literature. Furthermore, two additional aqueous solutions were included in this study to evaluate the effect of the chemical composition. The data were fitted using polynomial and exponential regressions to produce a set of correlations with different fitting errors. In addition, the EC was calculated using OLI Studio Stream Analyzer for all brines. The results were compared with the experimental data to validate the use of both methods in high salinity environments. The equations generated in this work can be used to estimate TDS from EC measurements for similar aqueous systems under a wide range of concentrations when there is uncertainty in the concentration of any of the species obtained by standard methods (McCartney et al., 2005). They can also be used as an alternative calculation method for complex high salinity brines; this application is still undergoing validation for currently available software.

MATERIALS AND METHODS

Four high-salinity aqueous solutions were synthesized based on their natural compositions: two formation brines from Brazilian pre-salt fields, a concentrated desulphated seawater (DSW) used for injection at offshore operations and an aqueous sodium chloride solution. The typical TDS of the DSW injected in oil field operations is 39 548 mg/L; however, it was concentrated to 230 000 mg/L maintaining the ratio among the concentrations of all ions in order to compare the EC data from all of these aqueous solutions over a similar concentration range.

All brines were synthesized in the laboratory by weighting the corresponding masses of each inorganic salt on an analytical scale and dissolving them in deionized water (EC less than 1 µS/cm at 25°C, Gehaka OS10LXE reverse osmosis system), following their chemical compositions (Table 1). The salts used in this work, including their supplier and purity, are given in Table 2. After dissolution, brines were stirred for an hour before being connected to a vacuum pump for air removal. For each water type, triplicates were prepared to minimize experimental errors and to ensure the repeatability of the technique. Thereby, the presented results only consider the mean value of the triplicates of the EC measurements. The corresponding error bars on the plots indicate the standard error of the mean for each group of triplicates.

Table 2. Description of the inorganic salts used to synthesize the aqueous solutions

Inorganic salt	Supplier	Purity level
NaCl	Isofar	≥ 99.5%
$CaCl_2 \cdot 2H_2O$	Isofar	≥ 99.0%
$MgCl_2 \cdot 6H_2O$	Sigma-Aldrich	≥ 99.0%
KCl	Isofar	≥ 99.0%
$BaCl_2 \cdot 2H_2O$	Sigma-Aldrich	≥ 99.0%
$SrCl_2 \cdot 6H_2O$	Isofar	≥ 99.0%
Na_2SO_4	Sigma-Aldrich	≥ 99.0%
Na_2CO_3	Sigma-Aldrich	≥ 99.5%
$NaHCO_3$	Isofar	≥ 99.7%
NaBr	Sigma-Aldrich	≥ 99.0%

For all aqueous solutions, EC was measured using a Mettler Toledo InLab 731-ISM graphite, four-pole conductivity probe attached to a Mettler Toledo SevenExcellence S470 conductivity benchtop meter. This instrument has a 0.57 cm^{-1} cell constant and is able to measure EC values in the range of 0.01 to 1 000 mS/cm with a resolution of 0.01 µS/cm and an accuracy of ±0.5%. Using a four-pole conductivity cell makes the EC measurements more reliable by eliminating polarization effects, which become more relevant when measuring highly concentrated samples (Jespersen, 2006). Moreover, all measurements were carried out at 25°C using a thermostatic bath with temperature indication. Calculated data were obtained using OLI Studio Stream Analyzer 9.6.3.

RESULTS AND DISCUSSION

Validation of the procedures employed in this work

In order to validate the procedures employed in this work, the EC data obtained from this study, both experimental and calculated, were compared to those found in the literature (Robinson and Stokes, 2002) for aqueous sodium chloride solutions (Fig. 1).

Both experimental and calculated EC data presented relative errors lower than 5% when compared to the EC data provided by Robinson and Stokes (2002) for all the concentrations considered. This result shows that the EC data produced through the experimental measurements and the calculations with OLI Studio in this study are in agreement with Robinson and Stokes (2002), which supports their validity.
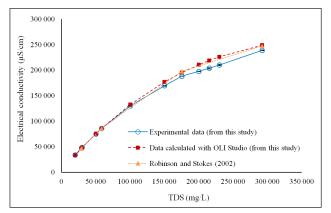
Figure 1. Curves of electrical conductivity as a function of total dissolved solids experimentally obtained and calculated with OLI Studio (both from this study) and that provided by Robinson and Stokes (2002) for aqueous sodium chloride solutions. The error bars on the experimental data indicate the standard error of the mean for the triplicate experiments
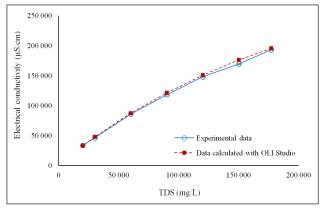

Figure 2. Curves of electrical conductivity as a function of total dissolved solids experimentally obtained and calculated with OLI Studio for Field B brine (TDS range: from 20 000 to 226 365 mg/L). The error bars on the experimental data indicate the standard error of the mean for the triplicate experiments

Figure 3. Curves of electrical conductivity as a function of total dissolved solids experimentally obtained and calculated with OLI Studio for Field D brine (TDS range: from 20 000 to 177 085 mg/L). The error bars on the experimental data indicate the standard error of the mean for the triplicate experiments

Figure 4. Curves of electrical conductivity as a function of total dissolved solids experimentally obtained and calculated with OLI Studio for concentrated DSW (TDS range: from 20 000 to 230 000 mg/L). The error bars on the experimental data indicate the standard error of the mean for the triplicate experiments

Development of correlations

As can be seen, both experimental and calculated data for all water types (Figs 2 to 5) generate curves with a decreasing slope, particularly at the higher concentration range. This behaviour agrees with well-known effects that retard the movement of ions in systems subject to an electrical field (Wright, 2007). First, the relaxation effect is caused by the attractive force exerted by oppositely charged ions in the surrounding atmosphere, which reduce the activity coefficient (Atkins and De Paula, 2006; Glueckauf, 1949). In addition, the electrophoretic effect is the consequence of ion interactions with the solvation molecules around the other ions (Simón and García, 1999). As concentration increases, ion–ion and ion–solvent interactions become more substantial. As a result, the EC of the aqueous solutions rises at progressively lower rates with increasing TDS (Hem, 1985; McNeil and Cox, 2000; Walton, 1989). This explains the non-linearity observed in EC with increasing TDS (Walton, 1989).

Moreover, Figs 2 to 5 illustrate good agreement between experimental and calculated data. For concentrations below 100 000 mg/L in all aqueous solutions, the maximum relative difference between calculated and experimental EC values was 3.14%. Furthermore, the maximum difference for the higher TDS range in all aqueous solutions was 9.29%.

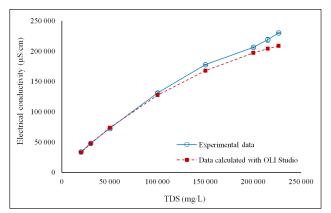The previously discussed phenomena are linked to ion concentration. In contrast, ion pairing is related to both

Figure 5. Curves of electrical conductivity as a function of total dissolved solids experimentally obtained and calculated with OLI Studio for sodium chloride solution (TDS range: from 20 000 to 292 200 mg/L). The error bars on the experimental data indicate the standard error of the mean for the triplicate experiments
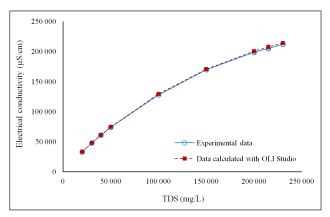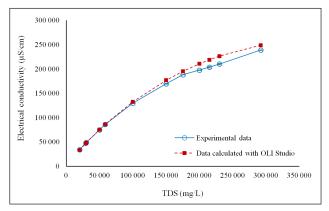
concentration and type of ions in solution (Smedley, 1980). Divalent ions (such as Ca^{2+}, Mg^{2+} and SO_4^{2-}) are more likely to form ion pairs than monovalent ions like Na^+, K^+ and Cl^- (Alzubaidi and Webster, 1983). These pairs may have reduced (or even neutral) charge, having lower contribution to the conductivity. As a result, ion pairing decreases the EC of the solution (Chang et al., 1983; Simon et al., 1994; Simón and García, 1999).

Table 3. Coefficients and R^2 values of the polynomial correlations between total dissolved solids and electrical conductivity obtained from the experimental data for each aqueous solution

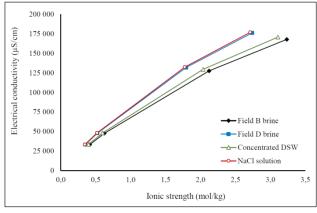| Aqueous solutions		Linear	Second degree	Third degree	Fourth degree
				Polynomial fittings	
Field B brine	a	0	0	0	-2×10^{-16}
	b	0	0	3×10^{-12}	1×10^{-10}
	c	0	3×10^{-6}	1×10^{-6}	-2×10^{-5}
	d	1.0631	0.3989	0.5489	1.9209
	e	−24,761	4,982.6	591.89	−29,028
	R^2	0.9875	0.9982	0.9982	0.9988
Field D brine	a	0	0	0	-2×10^{-16}
	b	0	0	6×10^{-13}	1×10^{-10}
	c	0	2×10^{-6}	2×10^{-6}	-1×10^{-5}
	d	0.9755	0.481	0.5025	1.5452
	e	−18 380	1,956.5	1,393.5	−19,524
	R^2	0.9899	0.9994	0.9994	0.9996
Concentrated DSW	a	0	0	0	1×10^{-16}
	b	0	0	2×10^{-11}	-5×10^{-11}
	c	0	4×10^{-6}	-3×10^{-6}	8×10^{-6}
	d	1.1589	0.1501	0.9445	0.2187
	e	−30,537	13,592	−9,187.9	5,415.5
	R^2	0.9817	0.9988	0.9998	0.9999
Sodium chloride solution	a	0	0	0	-8×10^{-17}
	b	0	0	2×10^{-11}	6×10^{-11}
	c	0	5×10^{-6}	-2×10^{-6}	-1×10^{-5}
	d	1.2366	−0.04	0.8056	1.3738
	e	−38,632	20,818	−5,617.4	−18,467
	R^2	0.9669	0.9975	0.9991	0.9991

Figure 6. Curves of electrical conductivity as a function of ionic strength for all aqueous solutions using data calculated with OLI Studio

Table 4. Coefficients and R^2 values of the exponential correlations between total dissolved solids and electrical conductivity obtained from the experimental data of each aqueous solution

Aqueous solutions		Exponential fittings
Field B brine	a	17,410
	b	1×10^{-5}
	R^2	0.9717
Field D brine	a	15,900
	b	1×10^{-5}
	R^2	0.9670
Concentrated DSW	a	16,747
	b	1×10^{-5}
	R^2	0.9817
Sodium chloride solution	a	16,905
	b	1×10^{-5}
	R^2	0.9826

To evaluate the effect of the concentration of divalent ions, Fig. 6 shows the EC as a function of the ionic strength using data calculated with OLI Studio, whose model considers ion–ion interactions (Wang et al., 2002). As can be seen, both solutions with the lowest concentration of divalent cations (sodium chloride solution and Field D brine) have higher EC values at the same ionic strengths. In addition, Field B brine, which contains the greatest concentration of divalent ions, has the lowest EC. Furthermore, the difference in EC between the solutions dominated by monovalent ions (sodium chloride solution and Field D brine) and the brines with greater concentration of divalent ions (Field B brine and concentrated DSW) broadens as the ionic strength increases. This is in agreement with previous investigations studying ion-pairing in solutions with lower ionic strengths than those considered in this work (Timpson and Richardson, 1986; Marion and Babcock, 1976; Simón and García, 1999).

To provide accurate correlations for TDS as a function of EC measurements, several curve fittings were executed on the experimental data of each aqueous solution. The curve fittings consisted of 1-to-4-degree polynomial fittings and exponential fittings. The resulting correlations of the polynomial fittings can be expressed in the form of the following general equation:

$$\text{TDS} = a\kappa^4 + b\kappa^3 + c\kappa^2 + d\kappa + e \qquad (3)$$

where TDS is total dissolved solids in mg/L, κ is EC in μS/cm and a, b, c, d and e are coefficients whose values are presented in Table 3 for each type of polynomial fitting and aqueous solution. Table 3 also gives the coefficients of determination (R^2) obtained for all polynomial fittings.

For the exponential fittings, a generic equation was used to obtain the correlations (Eq. 4), where TDS is total dissolved solids in mg/L and κ is EC in μS/cm. The values of coefficients a and b for each aqueous solution along with the coefficients of determination (R^2) of all of the exponential fittings are presented in Table 4.

$$TDS = ae^{b\kappa} \tag{4}$$

Considering the R^2 values (Tables 3 and 4), the exponential correlations did not result in a better fit than the polynomial ones. For only the sodium chloride solution did the exponential fitting presented a higher R^2 than the linear one. Moreover, the polynomial correlations of second and higher degrees fit the experimental data better than both linear and exponential correlations. The fact that the experimental data are better described by polynomial correlations of higher degrees is in agreement with the non-linear relationship between TDS and EC, especially at a higher concentration range. For instance, if the linear equation were used to calculate the TDS of a sodium chloride solution from a measured EC of 238 819 µS/cm (last experimental point in Fig. 5), the relative error compared to the experimental value would be 12.15%. On the other hand, if the quadratic equation were used for the same purpose, the relative error would be 1.45%. However, increasing the degree of the polynomial correlations above the second degree did not yield a substantial increase in R^2 in any of the aqueous solutions. In the aforementioned example, if the fourth-degree correlation were used to calculate the TDS of the same sodium chloride solution, the relative error would be 1.40%, only 0.05% lower than the one obtained from the second-degree correlation.

As this study shows, the determination of the TDS based on the EC needs brine-specific correlations. The relevance of the chemical composition of aqueous systems for their EC has been reported elsewhere (Marandi et al., 2013; Siosemarde et al., 2010; Walton, 1989). The equations generated in this work (Tables 3 and 4) also support this relevance. For instance, if the quadratic equation obtained for Field D brine was used to calculate the TDS of the sodium chloride solution of the example in the previous paragraph, the relative error would be 20.98%, as opposed to the 1.45% obtained when the correct second-degree correlation was used. This corroborates the relevance of developing specific correlations for complex brines containing high concentrations of divalent cations (Van Niekerk et al., 2014). The use of correlations generated with model brines regardless of proper chemical composition characterization is not recommended as it may result in erroneous TDS determinations (Pawlowicz, 2008; Raju, 2007; Hubert and Wolkersdorfer, 2015).

CONCLUSIONS

The determination of total dissolved solids (TDS) has application in a variety of fields, such as geochemistry, hydrology and environmental science. The characterization of waters in the petroleum industry requires estimating the TDS in high salinity brines, for which ion–ion and ion–solvent interactions have a substantial effect. This study presents experimental correlations of the TDS as a function of electrical conductivity (EC) for brines typical of pre-salt formations, with salinities between 20 000 and 292 200 mg/L.

For all brines, the higher degree polynomials presented a better fitting of the experimental data, showing that there is no linear correlation between TDS and EC for higher brine concentrations. In contrast, the use of exponential correlations did not improve the R^2 of the fitting.

Chemical composition is of remarkable relevance for the calculation of TDS. The correlations between TDS and EC depend on the type of ions and their concentrations in the aqueous solution. Therefore, a specific correlation should be generated for each type of brine. The use of equations developed for model brines may carry substantial error, particularly when analysing high salinity brines.

This study may serve as reference for the EC of high-salinity pre-salt brines. Moreover, the correlations generated in this work can be used to estimate the TDS from EC measurements when the chemical composition is analogous to the pre-salt waters used by our group. As previously discussed, given the tendency of divalent cations to form ion pairs, having a similar concentration and type of divalent cations is particularly important when using these correlations in analogous solutions.

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