The pH of tap and deionized water at 13, 23, 33, and 43 ºC in the range of 0-140 g/L of NaCl salinity

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Abstract

The pH of water used to prepare liquid solutions and brines for various types of biochemical investigations may influence the experimental results and overall conclusions. The pH of four types of water such as tap, tap boiled, deionized and deionized boiled water were investigated at the temperatures of 13, 23, 33 and 43 ^{o}C in the salinity range of 0-140 g/L of NaCl. The pH of tap water decreased by 2 on average after deionization. The pH of tap water and brines varied from 7 to 9.5 while it varied from 5.1 to 6.5 for deionized water and brines at all salinities. The pH of tap water increased by 0.5-1.5 due to CO_2 release while the pH of deionized water did not change after boiling in 30 minutes. The addition of salt of more than 20 g/L of NaCl caused the pH decrease by 1-1.5. The pH of tap boiled and deionized boiled brines decreased with the temperature increase by 0.1 per 10 ^{o}C. The decreasing, increasing and neutral trends of pH change with the increase in salinity were observed. The brines of tap water, tap boiled water and deionized water were close to constant at 20-120 g/L. The increase in pH from 80 g/L for deionized boiled water could be addressed to a salting out effect because of the lower CO_2 solubility at highly concentrated brines.

1. Introduction

The understanding of the interaction of such parameters as pH, temperature and salinity of water is fundamental to many applications, environmental monitoring and health studies.

Solution pH is a key variable used to describe the equilibrium and kinetics of chemical processes in oceanic and fresh waters, and deep reservoirs (B. Yang *et al.*, 2014). The influence of acidity or alkalinity of the surrounding aqueous medium measured by pH on the aquatic life is significant because it controls the extent of ionization, enzyme function and oxidation potential. The average pH for sea water is. 8.2 but can range between 7.5 and 8.5. However, the determination of the pH of seawater has always been a rather difficult problem because it contains various ions (Gieskes, 1969).

Measurements of pH and salinity of formation water have a wide range of applications including determination of reservoir compartmentalization and contamination of water with drilling mud, characterization of transition zone and delineating of oil/water contact, prediction of corrosion and scaling, and for injection of polymers and gels. In Arabian Gulf region, salinity of aquifers reaches 20 g/L while brine salinity varies from 50 to 150 g/L (Alsharhan *et al.*, 2001). Salinity of formation water can be as high as 350 g/L. For example, salinity of Shuaiba and Natih formations in North Oman shows above 200 g/L (Al Lamki and Terken, 1996).

Water studies are usually performed using synthetic brines prepared using tap water in the distilled or deionised form. The distilled and deionised water are preferable to tap water because the latter contains ions and elements that can be corrosive or cause other complications and unpredictable results during investigations. The distilled water obtained by the steam condensing is free of impurities. High purity deionised water, that is believed generally similar to distilled water, is produced by deionization from tap water, and it is more available and cheap.

The optimum pH of tap water varies in different supplies according to the composition of the water and the nature of the construction materials used in the distribution system, but it is often in the range 6.5–9.5 (Eaton et al., 2017). The pH of most raw water sources lies within the range 6.5–8.5. The pH of distilled water is 4.5–6.5 (Youmans, 1972).

Temperature is one of the most important parameters for many chemical and microbiological processes controlling the quality of tap water due to its effects on copper solubility, the rate of corrosion, lead leaching from brass fixtures, bulk chlorine decay rate and formation of disinfection by-products (Zlatanovich *et al.*2017, Ong et al., 2007). In pure water, a decrease in pH of about 0.45 occurs as the temperature is raised by 25 ^{o}C .

Temperature decreases the pH due to the change of water dissociation constant. The pH measurements are sensitive to temperature and differ when measured by different devices or computed using different models (Marcus, 1989). The pH of water when heated in a closed environment changed from 7 at 25 ^{o}C to 5.8 at 150 ^{o}C. Higher temperature can increase biological activity twofold when temperature increases by 10°C (V. Kooij, 2003).

The solubility of the CO_2 and H_2S gases has a significant impact on the acidity of water. It generally decreases with increased water salinity and temperature and increases with pressure. An increased carbon dioxide concentration lowers pH, whereas a decrease causes it to rise.

Thus, the obtained results can in a great extent depend on the properties and quality of applied laboratory water.

Electrical conductivity is widely used for monitoring the mixing of fresh water and saline water, separating stream hydrographs, and geophysical mapping of contaminated ground water (Covington and Whitfield, 1988). Uncertainties, however, still exist regarding predictions of salinity using conductivity computed by various models. The generally used formulae for temperature correction give results that deviate considerably from the values determined by actual measurements.

(Jones et al., 2016) conducted measurements of pH, conductivity and dissolved CO_2 to asses carbon removal from drinking water, particularly from a carbon footprint/GHG perspective.

However, most of the publications available on the subject of pH dependency on salinity cover low salinity range, study each parameter differently, or did not study the relationships that existed between pH and temperature over the broad range of salinities. Sodium chloride solutions are mostly neutral solutions and might be expected to vary little in terms of their pH value. However, there is no clarity regarding whether the salt presence has increasing, decreasing or neutral effect on the pH.

The objective of this investigation is to study the relationship between pH, conductivity, temperature in aqueous high salinity solutions of sodium chloride (0-140 g/L) and different range of temperature (13–43 ^{o}C). The synthetic brines are prepared using distilled, deionised and tap water, boiled and unboiled, to investigate pH changes with the salinity and temperature and find out whether the pH differ for these types of water.

2. Materials And Methods

2.1 Sample preparation

Sodium chloride (99.9 0% NaCl) was used to make solutions of different salinity. Although the water from natural sources such as sea and deep reservoirs contains many various salts, only NaCl was used to avoid the effect of other salts. The tap and deionised water were used for preparing the salt solutions. For several sets of experiments, the water of all above mentioned types were boiled to exclude the effect of the dissolved CO_2. Potential influence of dissolved CO_2 in the water samples was reduced to minimal by boiling off the dissolved gas in the water used for the experiment before preparing the salty aqueous salt solutions for the experiment in glass flasks in 30 minutes where thus atmospheric CO_2 does not equilibrate with the solutions. The boiling point was achieved by placing the sample flask in water bath at temperature of 100 ^{o}C (to prevent aggressive boiling that can cause evaporation) until the boiling point was reached. Each of the sample flasks was covered with cap during the boiling process to prevent further evaporation.

The deionised water was obtained from the tap water by passing through the deionizer Silhorko – Eurowater A/S, Denmark (RO, 21 bar, and SILEX 2 B, 6 bar).

Totally four types of water are named in further description: tap, tap boiled, deionised, and deionised boiled. The composition of tap water is given in Table 1. The solutions of 0, 20, 40, 60, 80, 100, 120, 140 g/L of each type of water were prepared for measurements at four temperature points of 13, 23, 33 and 43 ^{o}C. The method adopted to prepare salty solutions was to accurately weigh a specific amount of sodium chloride using a mass balance and dissolve in 1000 mL of water (w/w% as molalities). Magnetic stirrer was employed to homogenize each aqueous salt solution of specific salinity.

The four temperature points selected were achieved by placing the flask containing the aqueous salt solutions in water bath until a constant value was reached for each point of temperature. For lower temperatures below room temperature, ice cubes were added to the water bath and regulated to $\pm$ 0.20 ^{o}C. Measurement for higher temperature was carried out with the aid of water bath with an in-built electric heater also regulated to $\pm$ 0.20 ^{o}C. The water bath employed in the experiment was Lauda-Brinkmann (Model E 200 W/Ecoline). The flasks were covered with caps to prevent evaporation. The cap used has capacity to insert a thermometer through a hole at its centre to measure the temperature of the sample inside the flask.

2.2 The pH measurement

Calibration of the pH meter (Model: PHM 210) was done by putting the electrode into pH 4.0 and pH 7.00 buffer solutions. The electrode was rinsed with distilled water from a wash bottle into an empty beaker before immersion into aqueous salt solutions. This was done every time electrode is moved from one solution to another in order to minimize contamination. The pH meter is automated for temperature correction and the electrode and solution was allowed to equilibrate thermally before measurements were taken. Every measurement as well as those, which deviated noticeably from the general trend was repeated several times and the average was found. The experimental measurements of all six types of water are plotted as pH versus salinity in Fig. 1 and versus temperature in Fig. 2. The corrections of the obtained results are not performed to avoid biases in the data interpretation.

2.3 Electrical conductivity measurement

The calibration for electrical conductivity meter (Model: CDM 210) was done with solution of known salinity. The measuring bottle was rinsed with deionised water. 100 mL of the calibration solution was put into the measuring bottle and the EC meter was put into the solution. Time was allowed for the solution to adjust to the temperature. The EC meter was adjusted until the display reads the same salinity as the calibration solution. For the electrical conductivity, linear temperature compensation for electrical conductivity is normally assumed. The linear temperature compensation assumed that the temperature coefficient of variation α has the same value for all measurements of temperature.

3. Results And Discussion

3.1 pH of tap and tap boiled water

The pH values at 0 g/L salinity of tap water were 8.5 at 13 ^{O}C and close to 8 at 23, 33 and 43 ^{O}C (Fig. 1a). According to the approved standards, the pH of the tap water in this region of Denmark may vary from pH 7 to 8.5.

The pH curves of brine prepared using tap water at various salinities split into two groups that have close pH: the curves of lower temperatures of 13 and 23 ^{O}C and the curves of higher temperatures of 33 and 43 ^{O}C. At 20 g/L, the pH decreased to 7.2 for 13 and 23 ^{O}C and very gently decreased to 7.1 at 140 g/L. The pH curves of 33 and 43 ^{O}C was 7.1 on average at the salinity of 20g/L and very gently decreased to 6.8 at 140 g/L.

The pH of boiled tap water varied from 8.6 to 9.5 at 0 g/L salinity which was by 0.5-1 higher than of tap water (Fig. 1b). The pH of brines remained close to constant in the range of 20–120 g/L and it increased at 140 g/L at all temperatures. The pH decreased by 0.1 with the increase in temperature from 13 to 43 ^{O}C. The pH value measured in the range of 20–100 g/L was 7.5 on average at 13 ^{O}C; 7.4 at 23 ^{O}C; 7.3 at

33 ^oC and 7.2 at 43 ^oC. The slight increase of pH at 13 ^oC in the entire range of 20–140 g/L and elevation at 80, 100 and 140 g/L at other temperatures were observed.

The brine of different salinity prepared using tap water and boiled tap water had pH value close to or higher than normal pH value of 7 at all investigated temperatures. The addition of NaCl decreased the pH of tap water by 1.1 on average and the pH of boiled tap water by 1.1-2. The pH of fresh boiled tap water was higher than of fresh tap water by 1 on average and by 0.2 on average for brines. The pH isotherms were more separated for tap boiled water reflecting higher sensitivity to temperature.

3.2 pH of deionised and deionised boiled water

At 0 g/L, the pH was close to 6 for all temperatures (Fig. 1c). In the salinity range of 20–100 g/L, the pH varied from minimum 5.2 to maximum 5.4 and increased to 5.5–5.6 at 140 g/L. The slight decrease in pH could be observed with the increase in temperature from 13 to 43 ^oC.

The pH values of deionised boiled water at 0 g/L have not increased compared to deionized water, as could be expected from the release of CO_2 (Fig. 1d). At 0 g/L, the pH values were lower than of deionised water by 0.1 on average.

The pH of deionised boiled water was by 0.6–0.7 lower at 20–60 g/L than at 0 g/L. The decrease of pH could be observed with the increase in temperature by 0.1 on average.

The pH graphs of deionised boiled brines had unusual shapes. The pH curves decreased from 0 g/L to 20 g/L and remained close to constant up to 60 g/L. Then, the pH increased to 5.5 on average for all temperatures at 100 g/L and fluctuated around this values 120–140 g/L.

To verify the obtained results, the deionised water was also boiled during 60 minutes in addition to 30 minutes used in the experiment. After boiling during 60 minutes, the pH increased not only beginning from 60 g/L but the start of pH increase shifted to the lower salinities. This showed very high impact of the CO_2 presence on the pH.

3.3 The pH variation with salinity at various temperatures

The pH variations of four types of investigated water at 13, 23, 33 and 43 ^oC were compared in Fig. 2. At 13 ^oC and 0 g/L, the pH of the tap water and tap boiled water were 8.5 and 9.1, respectively, while the pH of deionised and deionised boiled water were 6 and 5.9, respectively (Fig. 2a). The pH of tap water and tap boiled water over salinity range of 20–140 g/L were 7.2 and 7.6 on average, respectively, while the pH of deionised and deionised boiled water were 5.1 and 5.5 on average, respectively.

The boiling of tap water generally increased the pH of brines by 0.3 on average. The boiling of deionised water has also increased the pH of brines by 0.3 on average at 13 ^oC but it did not have big impact at higher temperatures.

At 13 ^oC, the pH decreased in the following order: tab boiled, tap, deionised and deionised boiled water. At 23 ^oC, however, the pH of deionised boiled water was lower than of deionised water at all salinities (Fig. 2b). At higher temperatures, moreover, the pH of deionised boiled water was lower than of the deionised in the salinity range from 0 to 60 g/L and at 140 g/L and higher in the salinity range from 80 to 120 g/L (Fig. 2c,d). For the tap water, a very slight decreasing trend with the increase in salinity could be observed but the pH was close to constant for the tap boiled water at all temperatures.

From above, it could be deduced that pH of the tap boiled water followed by the tap water is by 1.5 as a minimum greater than the pH of deionised and deionised boiled water. The pH of brines prepared using deionised water was below 5.5 which could be inhibiting for many types of bacteria. The pH of brines prepared using tap water did not fall below 7, which makes it most suitable for the biochemical experiments.

3.4 Comparison of investigated types of water

The pH of fresh tap water was 8-8.5 and increased to 8.5–9.5 by 0.5-1 on average after boiling during 30 minutes due to gas release. The pH of fresh deionised water reduced by 1–2 from 8 to 6 due to deionisation of tap water but it did not increase after boiling.

The addition of NaCl into the tap and tap boiled water decreased the pH to 7-7.5 by 1.5-2 on average, as followed from the comparison of the pH at 0 and 20 g/L. The pH higher than 8 allowed to characterize tap and tap boiled water as slightly alkaline.

The addition of NaCl into the deionised and deionised boiled water decreased the pH to 5.3–5.5 by 0.8 on average, as followed from the comparison of the pH at 0 and 20 g/L. The pH lower than 6 allowed to characterize deionised and deionised boiled water as slightly acidic.

The increase in temperature from 13 to 43 ^oC caused the slight decrease in pH for all types of water; higher sensitivity to temperature was observed as bigger separation between the pH curves for tap boiled and deionised boiled water (Fig. 1).

The pH of brines prepared using tap water decreased insignificantly with the increase in salinity while it was close to constant for tap boiled water and deionised water in the range of 20–120 g/L; the substantial increase was only observed at 140 g/L.

At 13 ^oC only, the pH of deionised boiled water was substantially higher than of deionised water at all salinities but the pH did not change substantially with the increase in salinity (Fig. 2a).

For the brines prepared using deionised water at higher temperatures, the pH increased at 120–140 g/L only while for deionised boiled water the pH increased starting from 80 g/L at higher temperatures.

It could be assumed that the decrease of the pH from 0 g/L to 20 g/L and higher NaCl concentrations was caused by unavoidable introduction of carbon dioxide when NaCl was added into the tap boiled and deionised boiled water. For example, the pH at 0 and 20 g/L were similar at 23 ^{o}C for deionised water, which could indicate that the introduction of CO_2 was avoided. On the other hand, the high salt concentrations changed the ion activity.

The brines of tap and tap boiled water showed low sensitivity to the salinity effect probably because of the presence of many other ions. The brine of deionised water also showed low sensitivity to the salinity effect compared to the deionised boiled water. The increase in pH from 80 g/L for deionised boiled water could be addressed to a salting out effect because of the lower CO_2 solubility at highly concentrated brines. This conclusion was confirmed by the experiments carried out using deionised water boiled during 60 minutes which showed the pH increase starting from lower salinities.

3.5 Conductivity measurements

The conductivity of tap, tap boiled and deionised water varied with the temperature but it increased with the salinity following a general trend, as shown in Fig. 3. The correlation between pH and conductivity was not found because the pH did not vary noticeably with the increase in salinity. However, the conductivity curves of deionised boiled water deviated from the general trend. The conductivity of 13 and 43 ^{o}C followed the upper curve (green) and of 23 and 33 ^{o}C followed a blue curve. Thus, the conductivity changes accompanied the deviations in pH.

4. Conclusions

1. The deionization of investigated tap water from Denmark caused the decrease of the pH by 2 on average and the boiling by 0.2-1.5. The fresh tap and tap boiled water were slightly alkaline with pH>8 while deionized and deionized boiled water were slightly acidic with pH<6. The brines prepared using tap or tap boiled water were close to normal pH=7 while the brines prepared using deionized and deionized boiled water were acidic with pH<5.5. This means that deionised water is not suitable for the experimental studies because its acidity can be inhibiting for biochemical processes. In addition, the pH of tap water brines was close to constant at all salinities showing its predictability.

2. The variations of pH with salinity showed a complex interplay between the ion activity and presence of CO_2 in the water. The decreasing, increasing and neutral trends of pH with the increase in salinity was observed. At higher temperatures of 23, 33 and 43 ^{o}C, the pH of brines prepared using deionised water increased starting from 80 g/L because of lower CO_2 solubility in highly concentrated brines and in the absence of other ions.

Declarations

The authors declare no competing interests.

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Table 1

Table 1. Composition of tap water.

Parameter	Composition
Turbidity [NTU]	<1
Dissolve Oxygen [mg/L]	7.0-8.0
Fe [mg/L]	<0.1
Fe(II) (as % of total Fe)	n.a.
Ca [mg/L]	40±4
Mg [mg/L]	4.3±0.3
Cl^- [mg/L]	34±2
SO_4^{2-} [mg/L]	17±1
P-PO_4 [mg/L]	<0.01
Organic carbon, NVOC [mg/L]	0.5*

*According to the Geological Survey of Denmark and Greenland database (GEUS).

Figures

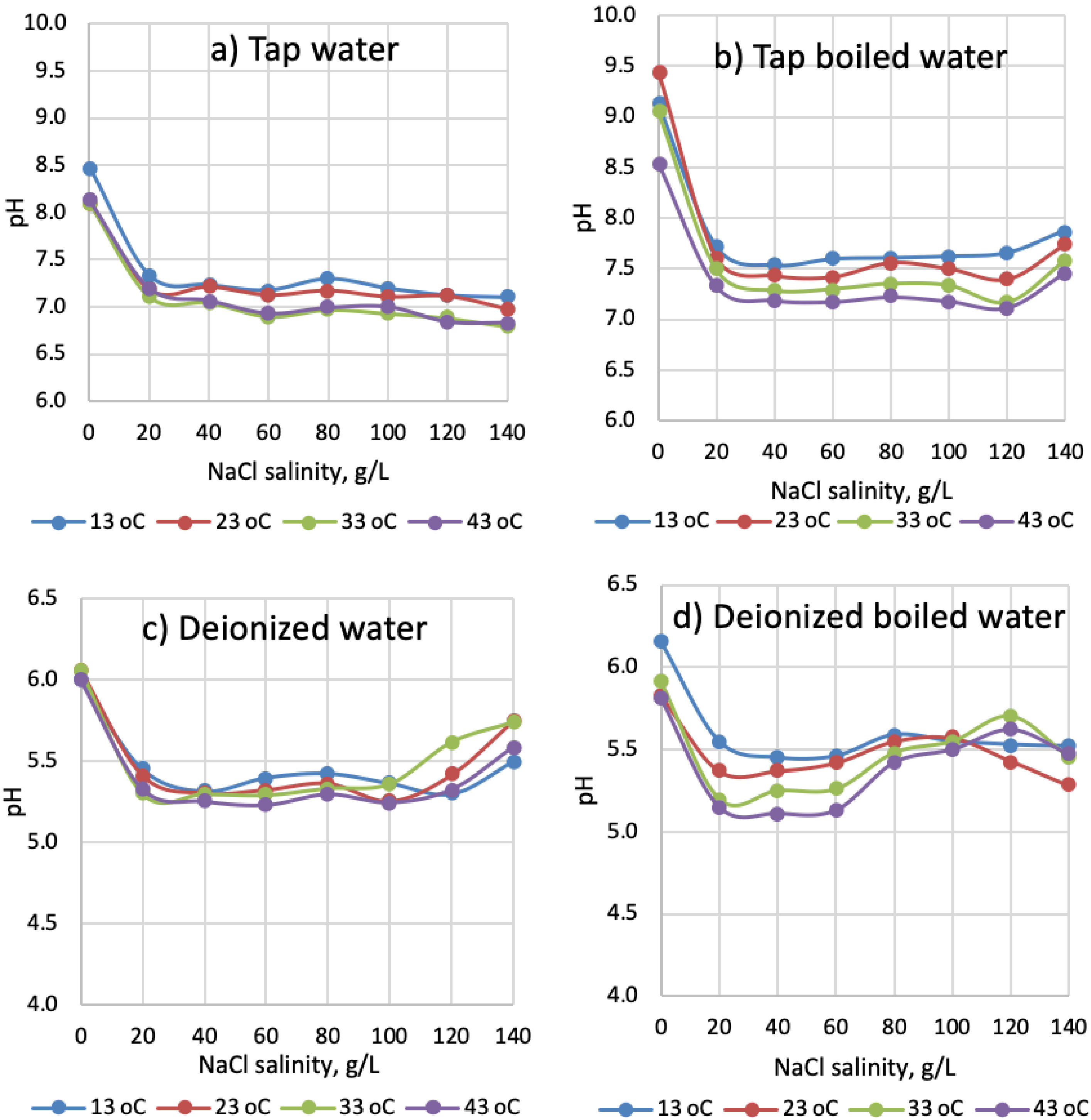

Figure 1

Experimental measurements of pH in the range of 0-140 g/L of NaCl at 13, 23, 33 and 43 ^{o}C: a) tap water; b) tap boiled water; c) deionized water; d) deionized boiled water.

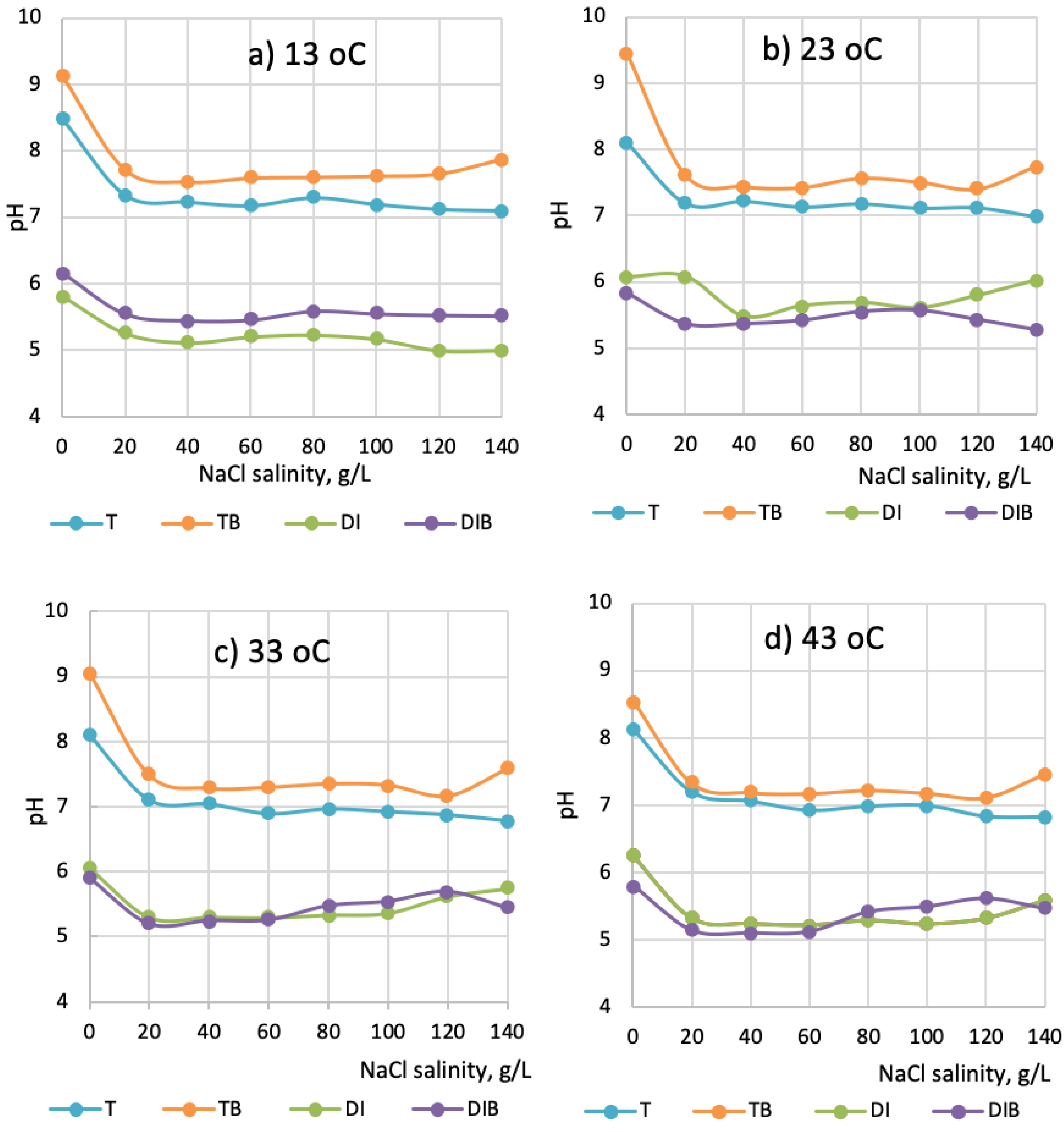

Figure 2

Experimental measurements of pH in the range of 0-140 g/L of NaCl: a) 13 ^{o}C; b) 23 ^{o}C; c) 33 ^{o}C; d) 43 ^{o}C.

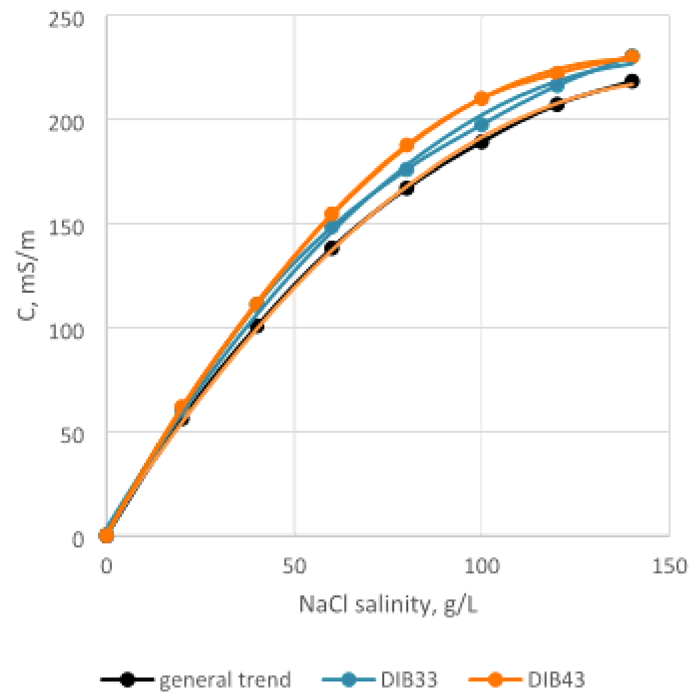

Figure 3

Conductivity measurements in the range of 0-140 g/L of NaCl at 13, 23, 33 and 43 ^{o}C. DIB33, DIB43 are deionized boiled water at 33 and 43 ^{o}C, respectively.