

Measurement of pH in concentrated brines

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Accurate measurement of pH in concentrated brines is a critical aspect of materials testing in the oil and gas industry. Concentrated sodium chloride solutions, typically up to 4 M and saturated with carbon dioxide, are often used to simulate production water during testing programmes. The pH of the solution may be adjusted to the desired value by the addition of sodium bicarbonate (to raise pH) or sodium acetate and hydrochloric acid (to lower pH). Recently, concerns have been raised over reports of discrepancy between pH values of concentrated NaCl solutions measured in the laboratory and those predicted by thermodynamic models. Measurements carried out by Bodycote (UK) and IFE (Norway) are compared with predictions of the BP and Shell models in Figure 1. Here the concentration of NaCl is defined in terms of mass of solute per mass of *solution**.

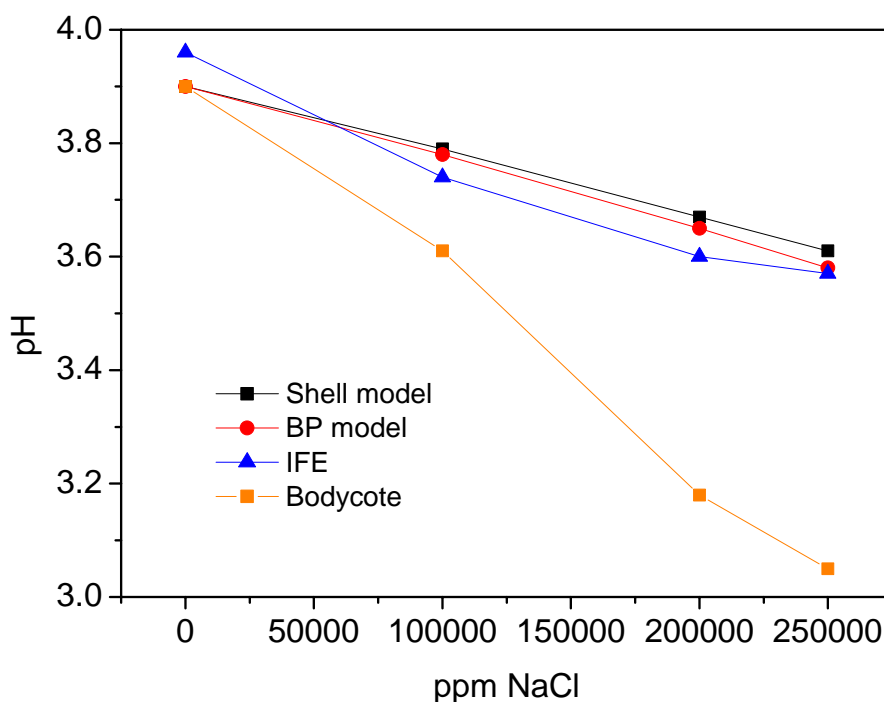


Figure 1 Comparison of pH measurement with model prediction as a function of NaCl concentration (1 atm CO₂, 25 °C).

The IFE measurements were carried out using a glass combination pH probe with a double junction reference electrode and were in fair agreement with both models (<

* It is recognised that many different units of concentration are employed in the oil and gas industry. It is not always clear whether molar or molal units are implied, particularly in the case of parts per million (ppm). This should always be defined explicitly to avoid confusion. Units with no physical basis such as % w/v should be discouraged.

0.1 pH units). The values measured by Bodycote using a glass combination pH probe with a single junction reference electrode were significantly lower than predicted (up to 0.5 pH units for the most concentrated solution). To establish the factors behind this variability, extensive measurements at NPL were carried out using glass combination pH electrodes with either single junction or double junction reference electrodes. Both conventional KCl-filled and gel-filled electrodes were used. The results are shown in Figure 2. The error bars describe the range of results from about 10 separate measurements at each concentration. Irrespective of the type of pH electrode used, the measured values lay between those reported by IFE and Bodycote and deviated significantly from the BP and Shell models.

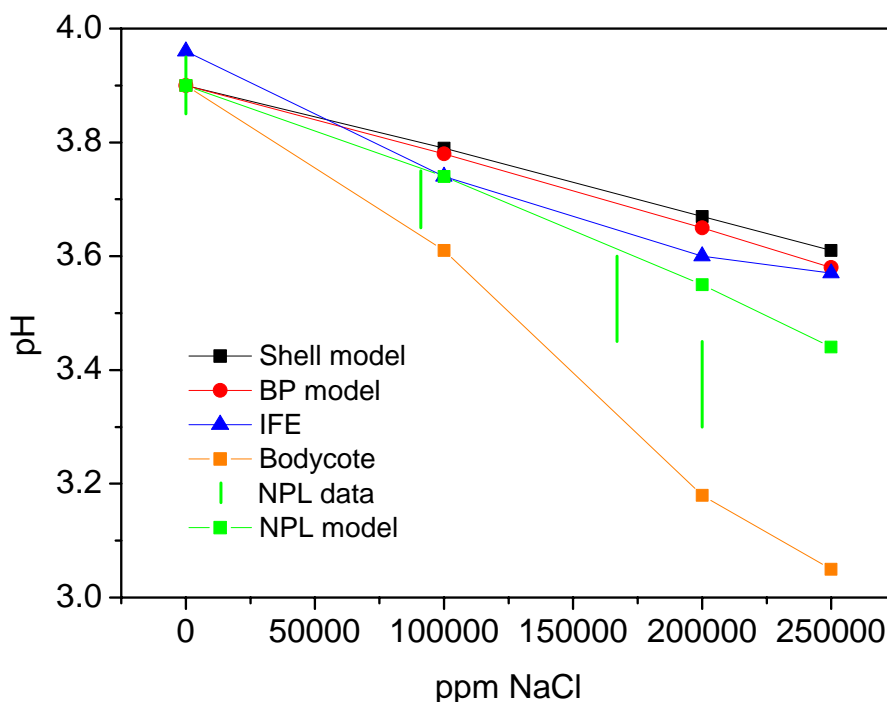


Figure 2 Comparison of pH measurement with model predictions as a function of NaCl concentration (1 atm CO₂, 25 °C). NPL data now included together with the NPL MTDATA predictions.

Contamination of the electrolyte in the reference electrode chamber is a possible explanation for these discrepancies in pH measurement. However, in the NPL measurements, no significant difference was observed between the pH values obtained with single junction and double junction reference electrodes, suggesting that contamination is not the dominant factor.

Another potential source of error is the liquid junction potential, which arises from differences in ionic diffusivity between the reference electrode solution and the sample solution. The liquid junction potential error occurs during calibration of the pH electrode when the reference electrode solution (typically 3 M KCl) is in contact with the dilute buffer solution. One way to minimise this error is to calibrate the pH electrode with buffers of the same ionic strength as the NaCl solution to be measured [1,2]. This requires formulation of specialist buffers which are not readily available and not traceable to the IUPAC definition of pH. The liquid junction potential itself is difficult to measure or calculate but is generally assumed to be of the order of a few

millivolts. Since 1 mV corresponds to 0.017 pH units, the liquid junction potential error is likely to be small in comparison to the observed discrepancies, but this requires further investigation.

Sodium error is a common problem for glass pH electrodes, arising from the fact that the selectivity of H^+ over Na^+ in the glass membrane breaks down at high sodium concentrations. However, sodium error usually only occurs at $pH > 10$ when $[Na^+]$ is 10 orders of magnitude greater than $[H^+]$. Sodium error is not expected in the pH range under investigation since here the ratio of $[Na^+]$ to $[H^+]$ is only 4 orders of magnitude or less.

It is notable that the predictions of MTDATA are somewhat lower than those of the models of BP and Shell, suggesting that the detailed relationships accounting for ionic strength effects are not wholly consistent.

Despite the extensive measurements, we are not much closer to resolving the source of variability. However, further measurements are planned to provide a more definitive measure of pH but have been delayed by more urgent work.

References

1. Y. Marcus, 'Determination of pH in highly saline waters', *Pure & Appl. Chem.*, **61**, 1133 (1989).
2. A.K. Covington, A. Whitfield, 'Recommendations for the determination of pH in sea water and estuarine waters', *Pure & Appl. Chem.*, **60**, 865 (1988).