

Measurement of pH and Eh in saline solutions for a better knowledge of the chemical environment in nuclear repositories

(B. P. Vester, S. Hagemann)

> Introduction

The mobility of heavy metals and radionuclides in aqueous systems strongly depends on the two geochemical master variables Eh and pH. Their potentiometric measurement in highly concentrated solutions which are typical for salt formations is complicated by liquid junction potentials that alter the cell potentials in an unpredictable way. In order to maintain a relation between electrode potential and H⁺ concentration or rather Eh, a model for the calculation of the medium induced bias is developed experimentally.

> Materials and Methods

The dependence of the electrode potential from the solution composition was investigated by changing the salt concentration but keeping H⁺-concentrations (in case of Eh-measurements also Fe(II)/Fe(III)-concentrations) constant. An Orion Ross electrode and a combined Metrohm Pt ring electrode were used. All measurements were carried out at 25.0°C in a CO₂-free Argon atmosphere. For pH measurements the difference between apparent pH_{i=0} (i.e. at zero concentration) and the negative logarithm of hydrogen concentration p_{cH} was calculated and expressed as ΔpH.

> Results

The results are shown in Fig. 1 to 3; main findings are:

- ΔpH clearly increases with salt concentration in solutions of NaCl, KCl, MgCl₂ and CaCl₂, reaching up to 2.8 pH units for nearly saturated solutions of MgCl₂ and CaCl₂ (Fig. 1).

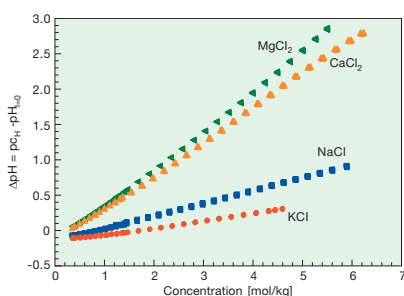


Fig. 1: ΔpH in relation to salt concentration by different binary chloride solutions at 0.001 m HCl

- In solutions of Na₂SO₄ and MgSO₄ ΔpH also increases with increasing salt concentrations, but it is negative for most of the concentration range. For the K₂SO₄ system the values for ΔpH even decrease slightly with increasing salt concentration.
- For ternary chloride systems a largely linear relation between the mole fraction of dissolved salts and ΔpH is observed (Fig. 2). The measured values for ΔpH can be readily explained by applying the functions for the corresponding binary systems.

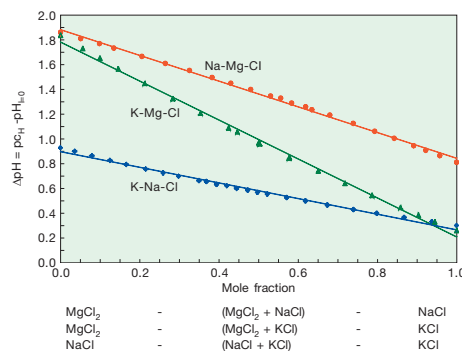


Fig. 2: ΔpH in relation to salt concentration by different ternary brine solutions at 0.001 m HCl

- In the five-component saturated solutions IP21 and IP9 ΔpH amounts to 1.6 respectively 2.7 pH units.
- The apparent Eh decreases in metal chloride solutions with increasing salt concentration (Fig. 3) reaching a maximum deviation of about 30 to 43 mV near saturation. One contribution may be the decreasing concentration of free Fe³⁺ due to the formation of Fe(III) chloro complexes.

Additional work is underway to provide more thermodynamic data which will help to further improve the interpretation of these results.

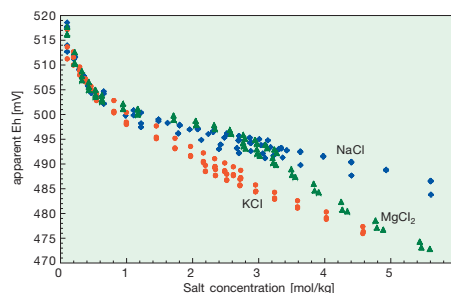


Fig. 3: Eh in relation to salt concentration of an redox defined system by concentration of Fe(II)/Fe(III) = 1 in 0.01m HCl; c(Fe_{tot}) = 10⁻⁴ M

> Conclusions

- The difference between apparent pH and the negative logarithm of H⁺ concentration (ΔpH) may amount to several pH units in highly saline solution. This distorts geochemical modeling results significantly.
- Solubility calculations for radionuclides or heavy metals made on the basis of measured Eh and pH without consideration of these effects may lead to wrong results by several orders of magnitude.
- For Eh measurements a rather small deviation is observed. For the calculation of the Fe²⁺/Fe³⁺ activities, further Pitzer ion interaction parameters valid in highly saline systems have to be developed.

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