

Prediction of pH in multiphase systems with ePC-SAFT advanced

The potential of a physical sound thermodynamic model

Moreno Ascani, Daniel Pabsch, Marcel Klinksiek, Nicolás Gajardo-Parra, Gabriele Sadowski and Christoph Held

The pH value expresses the proton activity, which is the crucial factor determining the species distribution in solution of weak electrolytes. Knowledge of the pH is mandatory, for instance, to assess enzyme activity in an Aqueous Two-Phase System (ATPS) or to estimate the CO₂ solubility in geological reservoirs. This work addresses the prediction of pH in multicomponent multiphase systems by solving the coupled reaction and phase equilibria, using the thermodynamic equation of state ePC-SAFT advanced to describe the nonideality in each phase. The predicted pH values were in excellent agreement with experimental data, using model parameters that were fitted exclusively to phase equilibrium properties.

pH is among the crucial properties that must be known for designing and operation of chemical and biochemical processes. However, pH measurements can be very challenging e.g. in deep geological aquifer systems or in the intracellular medium of living cells. According to the IUPAC definition, the pH value is defined as:

$$pH = -\log_{10}(a_{H_3O^+}) = -\log_{10}\left(\frac{\tilde{m}_{H_3O^+} \gamma_{H_3O^+}^{\tilde{m}}}{\tilde{m}^0}\right)$$

In Eq. 1, $\tilde{m}_{H_3O^+}$ is the proton molality in the system, \tilde{m}^0 is the standard molality (1 mol kg⁻¹) and $\gamma_{H_3O^+}^{\tilde{m}}$ is the molality-based activity coefficient of the proton, which at given temperature, pressure and composition is accessible by a thermodynamic model. This work considers two-phase systems with a distributed weak acid between an aqueous and an either organic or vapor phase. The equation of state ePC-SAFT advanced is used to calculate the pH in the aqueous phase, and to predict the chemical and phase equilibrium (CPE) composition of both phases at the experimental condition. Figure 1 provides a comparison between experimental and predicted pH-values in the pseudo-ternary system CO₂ + water + salt as function of the salt \tilde{m}_{salt} molality for the salts KCl, NaCl and NaHCO₃. The main difference between the three systems is that NaHCO₃ takes part to the reaction equilibrium of CO₂, whereas KCl and NaCl only influence the activity of all the components. The behavior of the three systems is quantitatively captured in our calculations. Figure 2 shows experimental and predicted pH values in the aqueous phase of three pseudo-ternary systems carboxylic acid + water + organic solvent. Systems with acetic and citric acid contain toluene, whereas the systems with oxalic acid contains MIBK as solvents. In all the three systems the predictions are in excellent agreement with the experimental data.

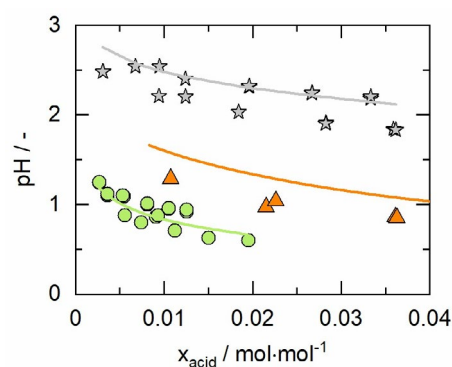


Figure 1: pH of the ternary system CO₂ + water + salt as function of salt molality. Predictions: solid lines. Experimental data: symbols (stars: NaHCO₃ at T = 308 K and p = 9.2 bar; hexagons: NaHCO₃ at T = 308 K and p = 43 bar; circles: NaCl at T = 343 K and p = 10 bar; triangles: KCl at T = 298 K and p = 9 bar). References: see publication.

In summary, ePC-SAFT advanced was able to quantitatively predict the influence of salts and organic solvents on the pH in multiphase systems. No parameter fitting to the experimental pH values was required.

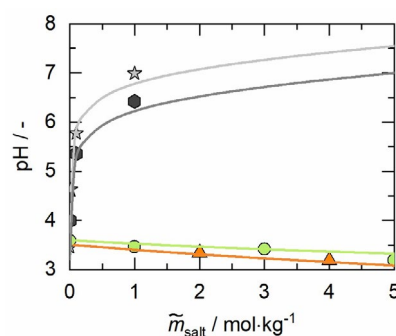


Figure 2: pH of the ternary system carboxylic acid + water + organic solvent as function of the water concentration in the aqueous phase. Predictions: solid lines. Experimental data: symbols (stars: acetic acid; triangles: citric acid; circles: oxalic acid). The experimental condition is for the three systems T = 298 K and p = 1 bar). References: see publication.

Contacts:

christoph.held@tu-dortmund.de
moreno.ascani@tu-dortmund.de

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