Predicting Phase Equilibria for Sulfolane-Supported Selective Sour-Gas Absorption
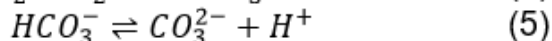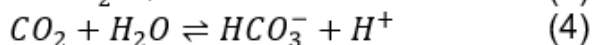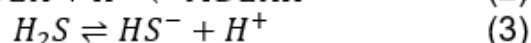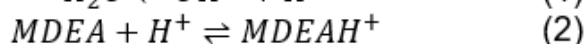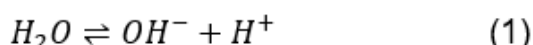
The model ePC-SAFT was used to predict the vapor-liquid equilibria in aqueous amine solutions

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In the chemical industry, aqueous amine solutions are widely used in sour-gas absorbers to reduce the emission of climate wrecking gases like CO_2. The effectivity of these amine solutions is enhanced by adding physical solvents. Predicting the absorption is challenging, involving multicomponent electrolyte systems, mutually affecting phase and reaction equilibria at wide temperature and pressure range. The thermodynamic model ePC-SAFT was used here to predict the selective absorption of CO_2 over H_2S (and vice versa) in an ultimately complex solution. The absorption depends on loadings of the sour gases and on the composition of the aqueous solution, which contains a chemical solvent (methyl diethanol amine (MDEA)) and a physical solvent (sulfolane).

Nowadays, industry aims at optimized absorption processes by reducing climate-wrecking gases in order to move towards a CO_2 neutral and environmentally benign chemistry. Aqueous amine solutions are typically applied to purify flue gas and natural gas in the oil&gas industry by absorption. This especially concerns the removal of sour gases like CO_2 and H_2S. To cover wider absorption ranges, including selective gas removal capabilities, the established aqueous solutions contain blends of different amines. On top, physical solvents are added to further expand the absorption range and the absorption kinetics to reduce the dimensions of the absorption columns. The design of efficient blends of amines and physical solvents is still based on very time consuming and costly experiments. Thus, robust predictive electrolyte thermodynamic models are required to drastically reduce the experimental effort.

In this work, ePC-SAFT was used to predict the phase equilibria for the absorption of the sour gases CO_2 and H_2S in an aqueous blend of MDEA and sulfolane. The following five reactions were taken into account:

$$H_2O \rightleftharpoons OH^- + H^+ \quad\quad (1)$$
$$MDEA + H^+ \rightleftharpoons MDEAH^+ \quad\quad (2)$$
$$H_2S \rightleftharpoons HS^- + H^+ \quad\quad (3)$$
$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+ \quad\quad (4)$$
$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \quad\quad (5)$$

Correctly predicting the experimental data requires simultaneously solving these reactions as well as vapour-liquid equilibria. Figure 1 shows the amount of absorbed CO_2 as function of its partial pressure in the aqueous blend for 313 K and 373 K, while in Figure 2 the amount of one sour gas in presence of the second one is illustrated. Sour gas concentration is depicted as moles gas absorbed per mole employed amine (loading α).

For all systems, ePC-SAFT predictions are in excellent agreement with the experimental data.
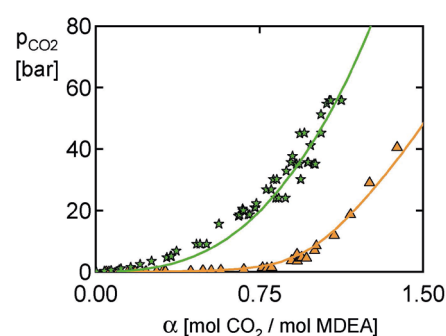

Figure 1: Amount of absorbed CO_2 in the aqueous solvent blend 20.9 wt % MDEA and 30.5 wt % sulfolane at 313 K (orange) and 373 K (green) for different CO_2 partial pressures. Symbols are experimental data, lines are ePC-SAFT predictions.
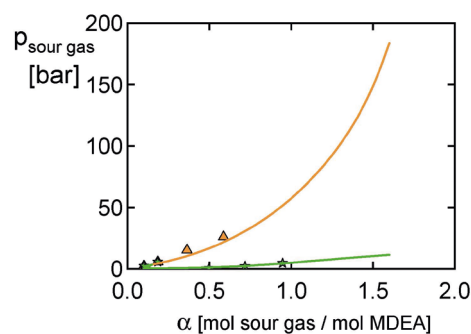

Figure 2: Amount of selectively absorbed sour gas in mixed aqueous solvent of 20.9 wt-% MDEA and 30.5 wt-% sulfolane. Symbols are experimental data, lines are ePC-SAFT predictions
Orange: CO_2 in presence of H_2S (α_{H_2S}=0.35, T=313 K)
Green: H_2S in presence of CO_2 (α_{CO_2}=0.35, T=373 K).

Thus, as a robust model, ePC-SAFT can be used to predict sour gas absorption even in highly complex systems containing electrolytes. This will help to reduce the experimental effort for discovering new solvent blends drastically.

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