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BINARY VLE of DEEA/H₂O, MAPA/H₂O and DEEA/MAPA SYSTEMS

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Introduction

A new breed of mixed amine systems which can form two liquid phases have recently received attention due to promising performance regarding low regeneration heat requirement. One reason is that only a highly concentrated rich solvent is sent to the stripper reducing both sensible heat loss and improving the equilibrium temperature sensitivity and thereby also reducing the need for stripping steam. On such process, DMX by IFPEN, is based on special solvents forming two immiscible phases and is now under testing in Italy [1]. This process is claimed to give a reboiler duty as low as 2.1 GJ/t CO₂ which is significantly lower than the 3.7 GJ/t CO₂ of the 30wt% MEA reference process. Another process with two liquid phases is based on a thermomorphic biphasic solvent type. It gives a single phase at lower temperature but two phases at higher temperature [2]. The advantage of this solvent was to adopt the concept of regenerating the solvent without steam.

A blend of DEEA and MAPA having characteristics of a biphasic/phase change solvent is now intensively studied at NTNU within the EU iCap project. At very low CO₂ loadings, this solvent behaves as a single phase but at higher CO₂ loadings it gives two phases. For design and modeling of this gas treating processes the knowledge of vapor–liquid equilibrium (VLE) of the mixed amine/CO₂/water system is required. At low CO₂ gas concentrations the phase equilibrium is governed by the binary/ternary DEEA/MAPA/water system. In this work, the data from ebulliometer measurements of DEEA/H₂O, MAPA/H₂O and DEEA/MAPA are reported and modeled with UNIQUAC [3].

Results and Discussion

Ebulliometric measurements of the DEEA/H₂O, MAPA/H₂O and DEEA/MAPA systems were conducted in a modified Swietoslowski ebulliometer [4]. The vapor pressure of pure DEEA and MAPA are reported together with literature data in Fig. 1. It is clear that pure MAPA is more volatile than DEEA due to the lack of any hydroxyl/alcohol group.

The binary VLE of DEEA/H₂O at different temperatures are reported in Fig. 2. As PT_{xy} data(a) and activity coefficients (b). It is seen that DEEA has a very high activity coefficient in water and increases with temperature.

The reported binary VLE of MAPA/H₂O at 40, 80 and 100C [4] were plotted together with the UNIQUAC model as PT_{xy} data (a) and activity coefficients (b). It is seen that there is a slight

inconsistency between the data and the model at higher concentrations ($x > 0.3$). The activity coefficients of MAPA in water are very low but increase with temperature. This is an advantage as it makes for low volatility in the process.

The binary VLE of DEEA/MAPA at different temperatures are reported in Fig. 4. as $P-T_{xy}$ data (a) and activity coefficients (b). It is seen that the activity coefficients of DEEA in MAPA are lower than those of DEEA in water and that they increase with temperature, while the activity coefficients of MAPA in DEEA are approximately similar to those of MAPA in water. Since the full matrix of the binary systems of DEEA, MAPA and H₂O have been measured, the binary interaction parameters for DEEA-H₂O, MAPA-H₂O and DEEA-MAPA can be determined and used to predict the ternary DEEA/MAPA/H₂O system. In the final results, the available literatures data for VLE, excess enthalpy and freezing point depression are included to give a full overview of the model capabilities.

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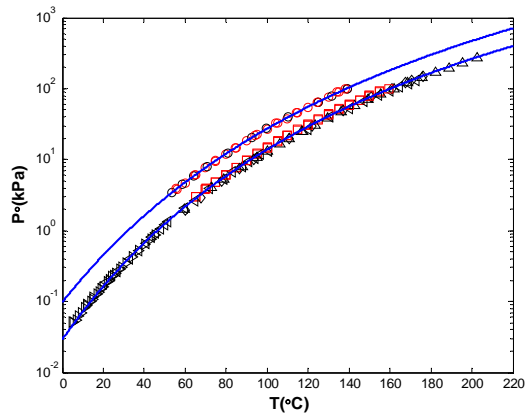


Figure 1. Saturation pressures of DEEA and MAPA at different temperatures (Red points, this work, Black points, literature and lines, Antoine Correlation [5])

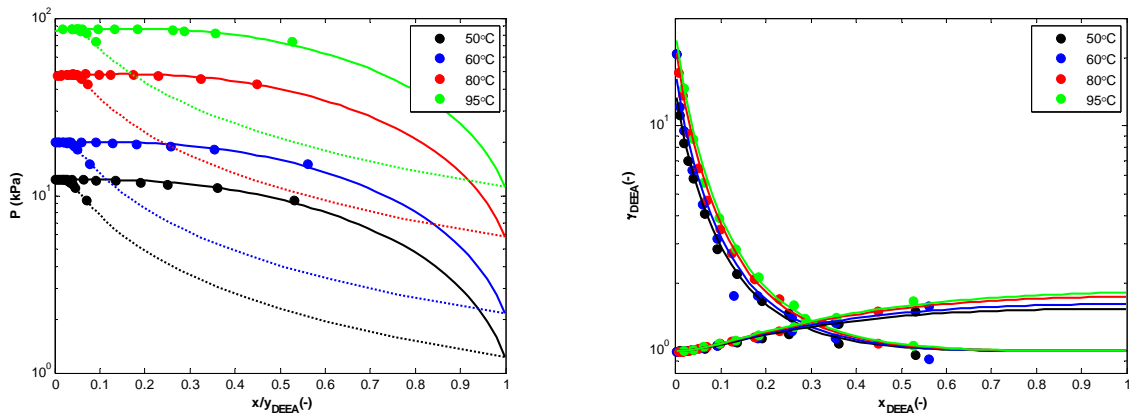


Figure 2. VLE of DEEA/H₂O system at different temperatures (a) PTxy (b) Activities coefficients (Points, this work and lines, UNIQUAC[3])

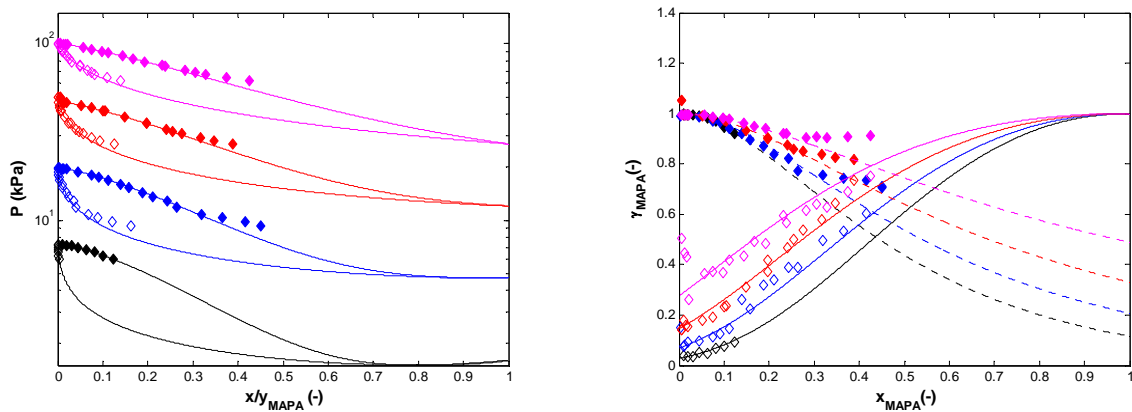


Figure 3. VLE of MAPA/H₂O system at different temperatures (a) PTxy (b) Activities coefficients [4] and lines, UNIQUAC[3])

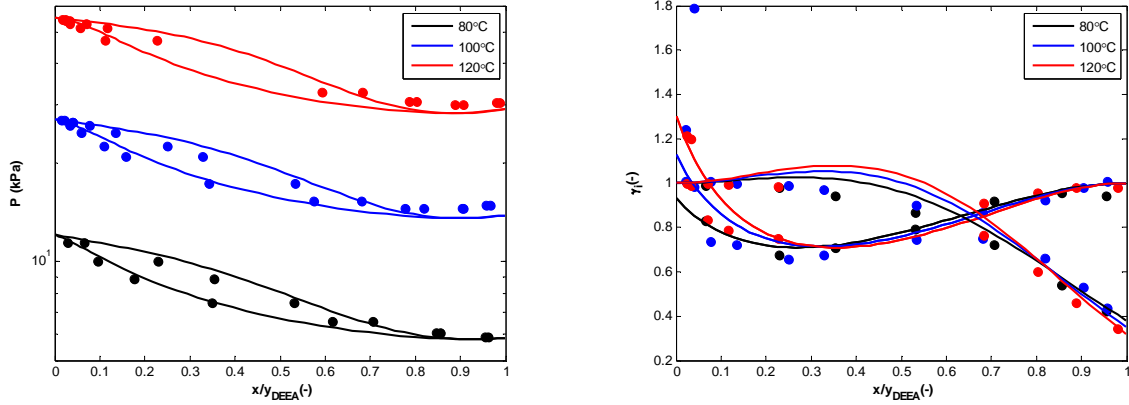


Figure 4. VLE of DEEA/MAPA system at different temperatures (a) P_Txy (b) Activities coefficients (Points, this work and lines, UNIQUAC[3])