Acid-Base Reactions Enhancing Membrane Separation: Model Development and Implementation

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Reactive extraction of organic acids from an aqueous solution to an alkaline stripping fluid is based on a selective barrier allowing permeation of non-polar molecules, which subsequently react with the stripping agent. The shift from the organic acid to its base induced by the chemical equilibrium enhances mass transfer inside the membrane's porous substructure. A model of the porous layer of the membrane is implemented with the COMSOL Multiphysics Chemical Engineering Module, whose equation system is modified to account for instantaneous equilibrium reactions. The results are compared to an analytical solution.

Keywords: extraction, organic acids, chemical equilibrium, membrane-contactor

1. Introduction

Reactive extraction of organic acids from an aqueous solution to an alkaline stripping fluid is based on a polymeric membrane, which is preferably permeable for non-polar molecules and which keeps the two aqueous solutions separated. For instance phenol as a non-polar target molecule permeates through the membrane and reacts with the strong base (i.e. NaOH) present inside the porous membrane support. This results in larger concentration gradients for the permeating species, i.e. phenol, and thus increased mass transfer across the membrane (Figure 1).

To improve understanding of the non-linear behavior of the governing system parameters, the objective of this paper is to develop a model covering mass transport coupled to the acid-base equilibrium reaction inside a composite membrane with COMSOL, which may be extended to cover more complex effects.
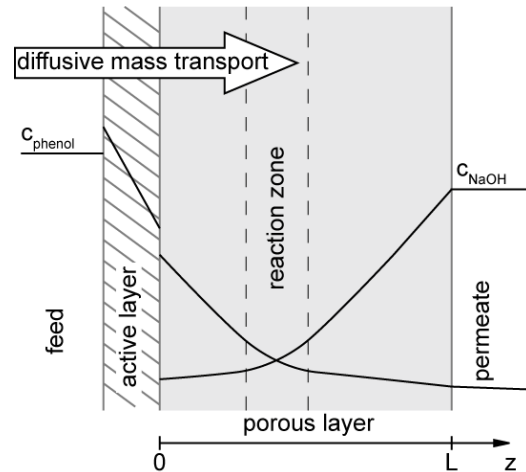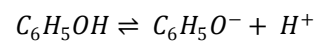

Figure 1. Schematic drawing of the separation principle

2. Chemical equilibrium of phenol and phenolate

Phenol consists of a hydroxyl group bonded to a phenyl ring. The chemical formula is C_6H_5OH. It tends to strip off the H^+-ion from the hydroxyl group at alkaline conditions forming the polar phenolate ion $C_6H_5O^-$.

$$C_6H_5OH \rightleftharpoons C_6H_5O^- + H^+$$

The distribution of the phenol-molecules among the different forms can be described by the equilibrium constant K:

$$K = \frac{c_{Phat}}{c_{Phol} \cdot c_{OH}} \qquad (1)$$

This separation process works most efficiently at neutral or acidic conditions in the feed and at highly alkaline conditions in the stripping fluid, thus ensuring the availability of permeating species in the feed and their reaction at the stripping side to a form that hinders reverse transport (Figure 2). The chemical reaction that occurs in the porous layer is orders of magnitudes faster than mass transport and thus assumed to be instantaneous.
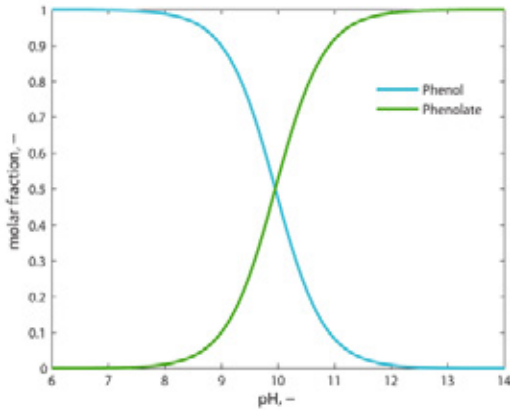
Figure 2. Distribution of phenolate and phenol as a function of pH

3. Use of COMSOL Multiphysics

COMSOL Multiphysics with its Chemical Engineering Module was chosen as modeling environment because of its coupling to Matlab and its ease of use regarding the modification of existing models to account for the differential-algebraic equation system outlined below.

3.1 Governing equations and boundary conditions

With the equilibrium constraint as given in equ. (1) the equation system below describes mass transport coupled to an instantaneous equilibrium reaction of three species, i.e. phenol, phenolate and OH-ions, in a porous membrane support structure:

$$0 = \varepsilon D_{Phol} \frac{\delta^2 c_{Phol}}{\delta z^2} + \varepsilon D_{Phat} \frac{\delta^2 c_{Phat}}{\delta z^2} \qquad (2)$$

$$0 = \varepsilon D_{OH} \frac{\delta^2 c_{OH}}{\delta z^2} + \varepsilon D_{Phat} \frac{\delta^2 c_{Phat}}{\delta z^2} \qquad (3)$$

Since the membrane polymer is hydrophobic, it does not absorb polar molecules like phenolate- and OH-ions. Consequently, the dense layer is impermeable for these species and the flux of phenolate- and OH-ions at the left-hand boundary ($z = 0$) constrained to zero.

$$\dot{n}_{Phat}^{z=0} = 0 \qquad (4)$$
$$\dot{n}_{OH}^{z=0} = 0 \qquad (5)$$

The flux of the non-polar molecule phenol across the dense (active) layer can be described by a membrane-constant k_{mem} and the concentration-difference of phenol across the membrane:

$$\dot{n}_{Phol}^{act} = k_{mem} \cdot \left(c_{Phol}^{Feed} - c_{Phol}^{z=0} \right) \qquad (6)$$

Continuity requires a flux of identical magnitude at the interface of the porous support and the active layer inside the porous support:

$$\dot{n}_{Phol}^{act} = -\varepsilon D \frac{\delta c_{Phol}^{z=0}}{\delta z} \qquad (7)$$

which leads to

$$k_{mem} \cdot \left(c_{Phol}^{Feed} - c_{Phol}^{z=0} \right) = -\varepsilon D \frac{\delta c_{Phol}^{z=0}}{\delta z} \qquad (8)$$

The boundary conditions at $z = 0$ $z = 0$ are depicted in Figure 3.
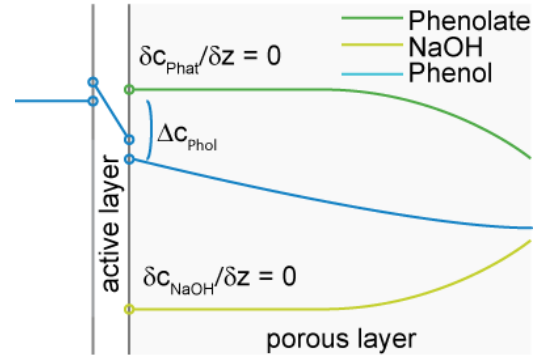

Figure 3. Boundary conditions at $z = 0$

The right-hand boundary ($z = L$) is constrained by the given concentration levels c_{Phol}^0 and c_{OH}^0 in the permeate bulk ($c_{Phol}^{z=L} = c_{Phol}^0$, $c_{OH}^{z=L} = c_{OH}^0$). Mixing effects in the permeate bulk are disregarded, since concentration gradients are insignificant at the observed rate of transmembrane mass flow.

The concentration of the third component follows from chemical equilibrium. The integral balance for the system yields the 6th boundary condition:

$$k_{mem} \, \Delta c_{Phol} \frac{c_{Phat}^{z=L}}{c_{Phol}^{z=L} + c_{Phat}^{z=L}} = D_{OH} \frac{\partial c_{OH}^{z=L}}{\partial z} \qquad (9)$$

with

$$\Delta c_{Phol} = c_{Phol}^{Feed} - c_{Phol}^{z=0} \qquad (10)$$

Equation 9 relates the conversion of phenol to phenolate with the caustic soda required to constantly enter the reaction zone (Figure 4).

3.2 Modification of the equation system

The DAE-system is implemented by modification of the equation system in coefficient mode and by exploiting COMSOL's extrusion coupling capabilities. The coupling with Matlab further offers the option to integrate the COMSOL Multiphysics model into a preexisting Matlab-routine for the evaluation of system-characteristics.
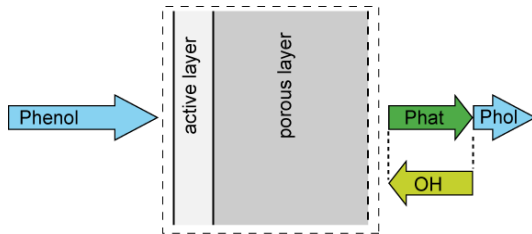
Figure 4. Boundary condition 6

An alternative implementation based on diffusion equations within the Chemical Engineering Module requires knowledge of reaction rates. However, the extremely high rate of reaction makes the choice of reaction rates non-trivial, because low reaction rates lead to an incomplete acid-base-equilibrium, thus reducing the calculated flow of phenol. In contrast, high reaction rates sufficiently approach chemical equilibrium conditions (Figure **5**), but tend to cause instabilities. As a consequence, the reaction rate parameter has to be newly determined for every set of operating conditions to ensure both chemical equilibrium and model stability.

The chosen modification of the governing equations of the Chemical Reaction Module is based on the elimination of reaction rates while introducing the chemical equilibrium as algebraic constraint (equation (1)), rendering the simulation more convenient.

3.3 Enhancement factors

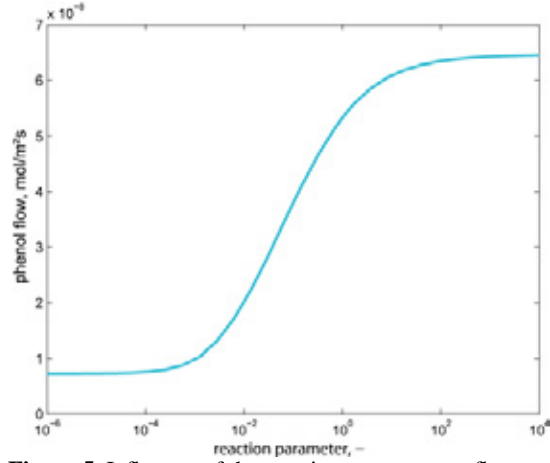Mass flow of phenol across a semi-permeable membrane can be described by

Figure 5. Influence of the reaction rate on mass flow

$$\dot{n}_{Phol} = \left(c_{Phol}^{Feed} - c_{Phol}^{Perm} \right) \cdot \cfrac{1}{\cfrac{1}{k_{act}} + \cfrac{1}{E\, k_{por}}} \qquad (11)$$

c_{Phol}^{Feed} and c_{Phol}^{Perm} describe the concentrations of phenol in the feed and permeate (stripping side) respectively. k_{act} and k_{por} stand for the transport resistances of the active (dense) and porous layers. The enhancement factor E relates the chemical reaction in the porous layer to the improvement in mass transfer and can range from 1 (no chemical reaction) to ∞ (chemical reaction reduces porous resistance to zero).

An analytical description for the transport of a species into a second phase, in which a reaction takes place, was formulated by Olander (1960). Olander's solution and the results of the COMSOL model are finally compared, thus validating the numerical model.

4. Results

As presented in Figure 6, the pH of the stripping solution strongly affects the concentration profile of phenol, the permeating substance of interest. With increasing pH the concentration level decreases due to the conversion of phenol to phenolate, which leads to larger concentration gradients and thus to

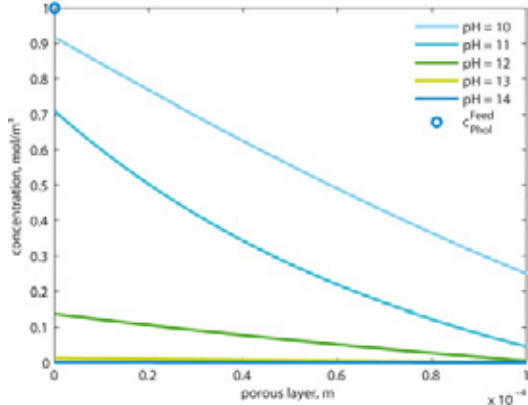improved mass transfer across the semi-permeable membrane (Figure 7).

Figure 6. pH dependence of the phenol concentration-profile in the membrane support structure
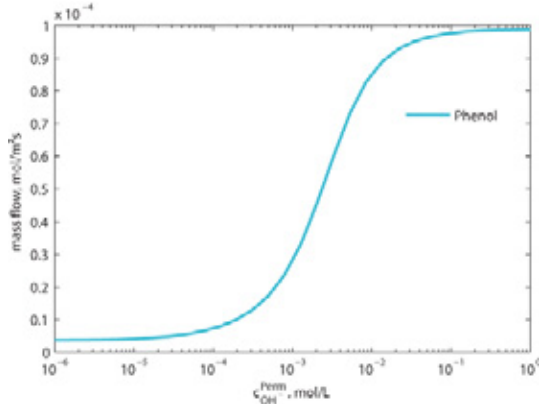

Figure 7. Phenol flow as a function of $c_{OH^-}^{Perm}$

This observation is consistent with the analytical solution derived by Olander. The analytical solution and the numerical model results match for moderate caustic soda concentrations. Based on enhancement factors (Figure 8), the COMSOL model and the analytical solution strongly deviate above a pH of 12. The COMSOL model significantly underestimates the enhancement factor E compared to the analytical solution.

Inspection of the behavior of the enhancement-factor shows very large gradients $\partial E/\partial n$ at high enhancement factors (Figure 9). Infinitesimal changes in the phenol flux n lead to significant changes in $E_{Olander}$, limiting the robustness of the enhancement-factor and rendering it inappropriate as a validation criterion.

In contrast, validation based upon absolute mass flow yields good agreement of the analytical solution and the numerical model (Figure 10).
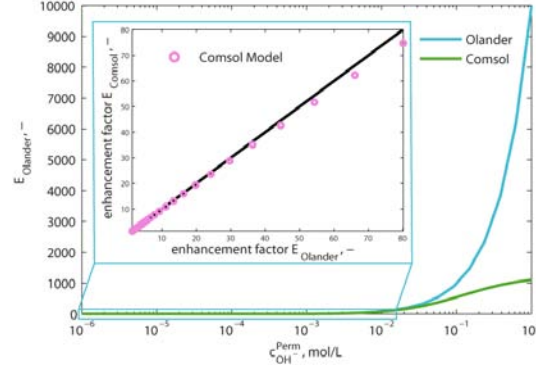

Figure 8. Comparison of the enhancement factors of the numerical model with Olander's solution (8 < pH < 14)
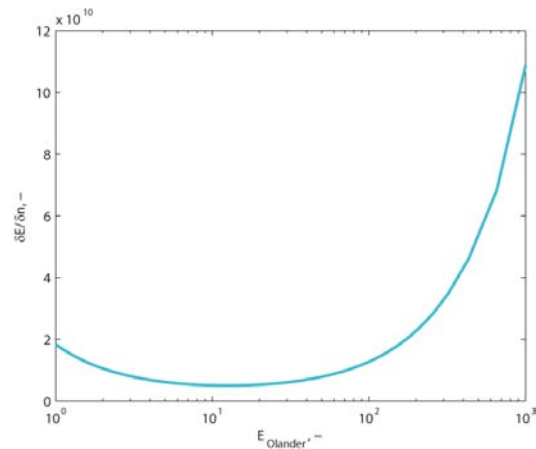

Figure 9. Gradient of the enhancement factor as a function of $E_{Olander}$

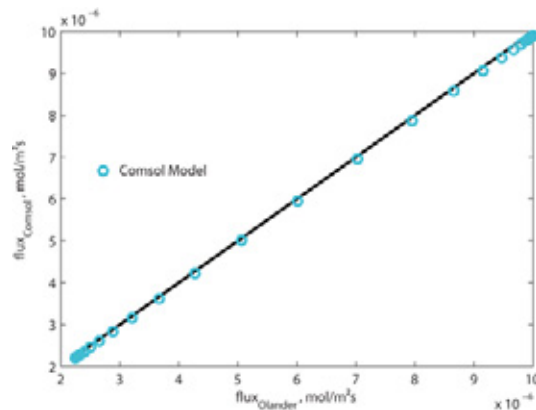**Figure 10.** Comparison of the phenol flow of the numerical model with Olander's solution (8 < pH < 14)

5. Summary and Conclusion

A model describing membrane-based reactive-extraction of organic acids into water as well as the implementation of the resulting DAE system in COMSOL was presented. A comparison of numerically and analytically calculated enhancement factors yields significant deviations at very high caustic soda concentrations. However, at operating conditions resembling large enhancement factors the mass flux of phenol is virtually insensitive to changes in the enhancement factor. This renders the enhancement factor a poor criterion for validation. A comparison in terms of mass fluxes shows good agreement of the COMSOL model with the analytical solution for the concentrations of caustic soda under investigation.

The model will be further applied to investigate the relative importance of system parameters like thickness and porosity of the membrane support structure. The model will also be extended to cover aspects like concentration polarization, which limits most high-flux and/or high-selectivity membrane applications and is therefore of particular interest.

6. References

1. D.R. Olander, Simultaneous mass transfer and equilibrium chemical reaction, *A.I.Ch.E.*, **6**, 233-239 (1960)