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Influence of liquid film composition on mass transfer in Taylor flow – the case of hydrogenation of nitrobenzene

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Objectives and approach

- Goal: Study influence of liquid composition on physical mass transfer in the liquid film of planar Taylor flow and the interaction with hydrodynamics to identify optimal operating conditions
- Two binary liquid mixtures relevant for nitrobenzene hydrogenation process are considered:
  - Nitrobenzene and aniline (NB+AN) as main reactant and product of the reaction
  - Nitrobenzene and ethanol (NB+ET) since ethanol is often used to dilute nitrobenzene[1]
- Composition-dependent physical properties for both liquid mixtures are determined by empirical relationship and theoretical models from literature
- Hydrogen concentration profiles in the liquid film are determined numerically to analyze mass transfer with physical properties depending on the liquid composition

Mixture physical properties and Taylor flow hydrodynamics

- Density and viscosity are estimated by empirical correlations for excess molar volume and excess viscosity of the NB+AN[2] and NB+ET[3] mixture. Fig. 2 (a) and (b) show deviations between estimated (ρ_m) and mixture-averaged (ρ_{MA}) properties
- Surface tension σ_m is estimated by two empirical correlations assuming the liquid as an ideal solution (Hildebrand and Scott, 1950)[4] and a regular solution (Hoar and Melford, 1957)[5]
- Hydrogen diffusivity D_{H2} is estimated by multicomponent and effective diffusivity models, the differences being small, see Fig. 2 (c)
- Henry number H_{H2} is obtained by empirical correlations[6,7] based on a regular solution theory
- Taylor flow hydrodynamics is governed by capillary number $Ca=\mu_m u_B/\sigma_m$ and Reynolds number $Re=\rho_m u_B h/\mu_m$ where u_B is bubble velocity and h the height of the planar channel. The Laplace number $La=Re/Ca$ is independent on u_B but varies with composition, see Fig. 2 (f)
- The film thickness d_F in a planar channel depends on Ca as[8] $d_F/h=0.21[1-\exp(-1.69Ca^{0.5025})]$

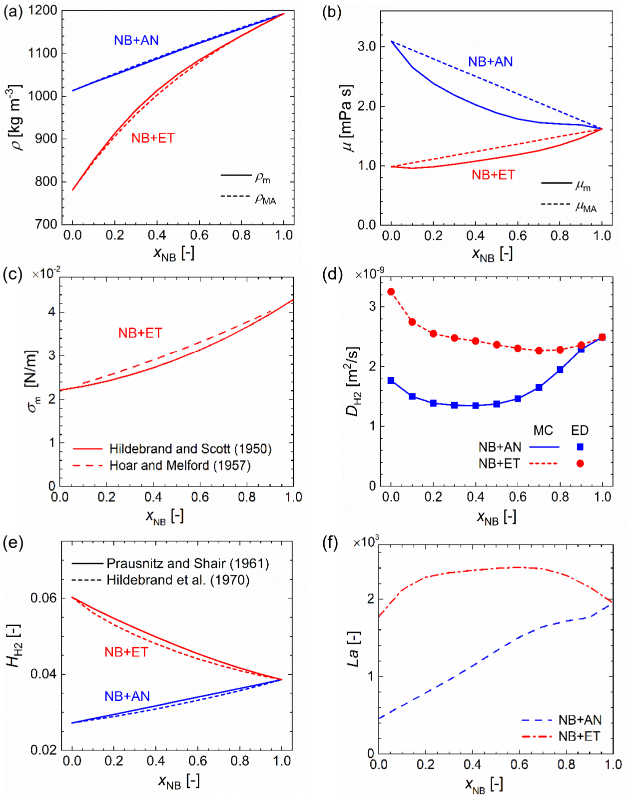

Fig. 2: Physical properties of NB+AN and NB+ET mixtures: liquid density (a), viscosity (b), surface tension (c), diffusivity of hydrogen in the mixture (d), Henry coefficient of hydrogen in the mixture (e). In subfigure (f), Laplace number of the mixture for channel height h=100 µm

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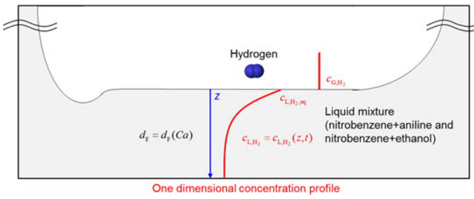

Fig. 1: Schematic diagram of the mass transfer in liquid film of Taylor flow assumed by one-dimensional diffusive mass transfer in wall-normal direction

Hydrogen concentration profiles and saturation time

- Unsteady 1D diffusion equation with composition-dependent physical properties is solved numerically to obtain time-dependent hydrogen concentration profiles in stagnant liquid film
- Two hypothetical scenarios: fixed capillary number (0.01) and fixed Reynolds number (100)
- Saturation times $t_{sat,L}$ and $t_{sat,G}$ defined below vary with nitrobenzene mole fraction, e.g. for Ca=0.01 the saturation time $t_{sat,L}$ is for x_{NB}<0.8 higher than the value for pure nitrobenzene

$$\frac{1}{d_F}\int_0^{d_F} c(t_{sat,L})\,dz = 0.9c_{H2,L,eq} \qquad \frac{1}{d_F}\int_0^{d_F} c(t_{sat,G})\,dz = 0.01c_{H2,G}$$

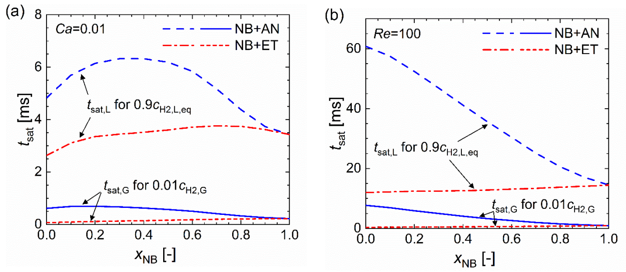

Fig. 3: Hydrogen saturation times for 90% of liquid equilibrium concentration and 1% of gas concentration. (a) Ca=0.01 (b) Re=100.

Necessary bubble length to achieve certain saturation

- Equating saturation time t_{sat} and film exposure time $t_{F,ex}=L_B/u_B$ yields a criterion for necessary bubble length $L_{B,sat}$ to achieve a certain saturation

$$\frac{L_{B,sat}}{h} = \underbrace{\frac{D_{H2}t_{sat}}{d_F^2}}_{=Fo}\frac{d_F}{h}\underbrace{\frac{d_F u_B}{D_{H2}}}_{=Pe_F}$$

$$= Fo\,Sc\,La\,Ca\frac{d_F^2}{h^2}$$

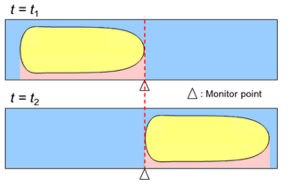

Fig. 4: Definition of film exposure time for a single Taylor bubble passing a monitor point

- The necessary bubble length shown in Fig. 5 (a) provides an idea to choose the proper Fourier and capillary numbers for an effective mass transfer in liquid mixture
- The necessary bubble length is also varying in terms of liquid composition and 1.76 times higher than the value for pure nitrobenzene

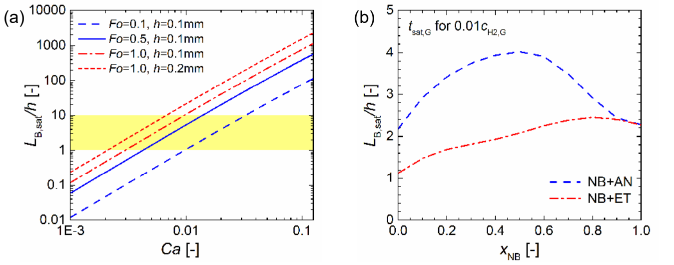

Fig. 5: Necessary bubble length $L_{B,sat}$. (a) Variation with respect to Fo, h and Ca for Sc = 545, (b) Saturation by 1% of H2 concentration in Taylor bubble with fixed capillary number Ca=0.01

Conclusions

- The change of liquid composition either during the reaction process or by adding a diluent has a notable influence on diffusive mass transfer of H2 in the liquid film of Taylor flow
  - In a wide composition range H2 diffuses slower in NB+AN mixture than in pure liquids
  - Dilution of nitrobenzene by ethanol increases diffusive mass transfer of hydrogen
- An estimation is provided for the bubble length required to achieve a certain degree of hydrogen saturation in the liquid film during the passage of a single Taylor bubble

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