

Supporting Information

Lactic acid extraction and mass transfer characteristics in slug flow capillary microreactors

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A. Extraction efficiency as a function of the residence time in physical extraction

With the refined mass transfer model (cf. Eq. 18), the fact that the extraction efficiency is only dependent on the residence time in the present physical extraction experiments as shown in Figure 2 can be well explained. From Eqs. 5 and 6, we can derive

$$C_{aq,0} - C_{aq,1} = \frac{(K_{ov}a)_{Phys} V_c \left(\left(C_{aq,1} - \frac{C_{org,1}}{m} \right) - \left(C_{aq,0} - \frac{C_{org,0}}{m} \right) \right)}{Q_{aq} \ln \left(\frac{C_{aq,1} - \frac{C_{org,1}}{m}}{C_{aq,0} - \frac{C_{org,0}}{m}} \right)} \quad (\text{A-1})$$

Under the investigated conditions, $C_{org,0} = 0$, $\tau = V_c / (Q_{aq} + Q_{org}) = V_c / (2Q_{aq})$. And according to the mass balance, $C_{org,1} = C_{aq,0} - C_{aq,1}$. Then, it is obtained that

$$C_{aq,0} - C_{aq,1} = \frac{2\tau (K_{ov}a)_{Phys} \left(\left(C_{aq,1} - \frac{C_{aq,0} - C_{aq,1}}{m} \right) - C_{aq,0} \right)}{\ln \left(\frac{C_{aq,1} - \frac{C_{aq,0} - C_{aq,1}}{m}}{C_{aq,0}} \right)} \quad (\text{A-2})$$

The concentration of the solute in the aqueous phase at equilibrium ($C_{aq,eq}$) can be found from

$$C_{aq,0} - C_{aq,eq} = C_{org,eq} - 0 \quad (\text{A-3})$$

Combining Eq. (A-3) with Eqs. 1 and 4, the extraction efficiency for physical extraction can be further written as

$$\eta = \frac{(m+1)(C_{aq,0} - C_{aq,1})}{mC_{aq,0}} \times 100\% \quad (\text{A-4})$$

Combining Eqs. (A-2) and (A-4) yields

$$\ln(1-\eta) = -2\tau \left(1 + \frac{1}{m}\right) (K_{ov}a)_{Phys} \quad (\text{A-5})$$

By substituting Eq. 18 to Eq. (A-5), it is obtained that

$$\ln(1-\eta) = -5.2\tau \left(1 + \frac{1}{m}\right) \left(\frac{1}{\frac{1}{2\sqrt{\frac{D_{aq}}{\pi\tau}}} + \frac{1}{2m\sqrt{\frac{D_{org}}{\pi\tau}}}} \right) \left(\frac{4L_{droplet}}{d_c (L_{droplet} + L_{slug})} \right) \quad (\text{A-6})$$

The above equation clearly corroborates that under the investigated conditions, η is independent of the concentration of acetanilide in the aqueous phase at the microreactor inlet and appears to be only a function of τ since the other physical properties of the system are fixed. The shorter the residence time, the lower the extraction efficiency. These analytical results are in good agreement with those shown in Figure 2.

B. Dissociation of lactic acid in the aqueous phase

According to the dissociation reaction of lactic acid in the aqueous phase (cf. Eq. 19), it is satisfied that

$$K_a = \frac{C_{H^+} C_{LA^-}}{C_{LA}} \quad (\text{B-1})$$

$$C_{LA} + C_{LA^-} = C_{aq} \quad (\text{B-2})$$

where C_{H^+} , C_{LA^-} , C_{LA} represent the concentrations of H^+ , dissociated lactic acid, free lactic acid at equilibrium in the aqueous phase, respectively. C_{aq} is the total lactic acid concentration of all forms in the aqueous phase. Under the investigated conditions, $\text{pH} \ll 7$. Thus, $C_{H^+} \approx C_{LA^-}$ (i.e., the influence of water dissociation is negligible) and it is obtained that

$$C_{LA^-} = \frac{-K_a + \sqrt{K_a^2 + 4K_a C_{aq}}}{2} \quad (\text{B-3})$$

The percentage of the dissociated form of the lactic acid is calculated as $(C_{LA^-}/C_{aq}) \times 100\%$. It was found that for 0.11 M lactic acid intake, the percentage of the dissociated form is 3.6% at the microreactor inlet and ranges from 5.5% to 13.4% at the microreactor outlet under the present experimental conditions (the longer the residence time, the higher the percentage of dissociation). For 0.055 M lactic acid intake, the percentage of the dissociated form is 4.9% at the microreactor inlet and ranges from 13.7% to 15.9% at the microreactor outlet. Thus, the average percentage of the dissociated form is below 11% throughout the microreactor. In view of the generally low extent of dissociation under our experimental conditions and to further simplify the model, we neglected the dissociation form of lactic acid in the aqueous phase (i.e., $C_{LA} \approx C_{aq}$), the refined effect of which on mass transfer will be further considered in our ongoing study.

C. Extraction efficiency as a function of the residence time and inlet lactic acid concentration in reactive extraction

The concentration of lactic acid in the aqueous phase when the reactive extraction reaches equilibrium ($C_{aq,eq}$) was obtained from our additional experiments in batch reactors. Lactic acid at a range of concentrations (i.e., 0.1-0.2 M in water) was extracted using 15% (V/V) TOA in n-octanol as the organic phase. 5 mL of the aqueous phase and 5 mL of the organic phase were stirred in a batch reactor for 18 h at 500 rpm, afterwards the phases were allowed to settle and the aqueous phase was then analyzed to indicate the equilibrium concentration ($C_{aq,eq}$). The following linear relationship was found:

$$\frac{C_{aq,0} - C_{aq,eq}}{C_{aq,eq}} = 14.27 \quad (C-1)$$

Then, the extraction efficiency for reactive extraction under the investigated conditions can be further written as

$$\eta = \frac{C_{aq,0} - C_{aq,1}}{C_{aq,0} - \frac{C_{aq,0}}{15.27}} \times 100\% \quad (C-2)$$

From Eq. 24, we can derive

$$\ln \frac{C_{aq,0}}{C_{aq,1}} = \frac{(K_{ov} a)_{Chem} V_c}{Q_{aq}} \quad (C-3)$$

Under the current conditions, $\tau = V_c / (Q_{aq} + Q_{org}) = V_c / (2Q_{aq})$. Combining Eq. (C-2) and (C-3) yields

$$\ln \left(1 - \left(1 - \frac{1}{15.27} \right) \eta \right) = -2\tau (K_{ov} a)_{Chem} \quad (C-4)$$

Substitution of Eq. 25 into Eq. (C-4) leads to

$$\ln \left(1 - \left(1 - \frac{1}{15.27} \right) \eta \right) = -5.2\tau \left(\frac{1}{\frac{1}{2\sqrt{\frac{D_{aq}}{\pi\tau}}} + \frac{1}{2mE_i\sqrt{\frac{D_{org}}{\pi\tau}}}} \right) \left(\frac{4L_{droplet}}{d_c (L_{droplet} + L_{slug})} \right) \quad (C-5)$$

Since it is assumed that the TOA-lactic acid complexes were predominantly in the 1:1 form (cf. Ea. 20a), there is according to the mass balance

$$C_{TOA,0} - C_{TOA,1} = C_{aq,0} - C_{aq,1} \quad (C-6)$$

Combining Eq. 29 with Eqs. (C-2) and (C-6), E_i can be further approximated as

$$E_i \approx 1 + \frac{2 \frac{C_{TOA,0}}{C_{aq,0}} - \left(1 - \frac{1}{15.27}\right) \eta}{m \left(2 - \left(1 - \frac{1}{15.27}\right) \eta\right)} \quad (C-7)$$

From Eqs. (C-5) and (C-7), it can be seen that under the present reactive extraction experiments (i.e., constant inlet TOA concentration, practically constant interfacial area or droplet/slug lengths, fixed fluid properties), the extraction efficiency (η) only depends on the residence time and the inlet concentration of lactic acid in the aqueous phase (i.e., τ and $C_{aq,0}$). η increases with increasing τ . Moreover, the two equations indicate that E_i and η are both higher at lower $C_{aq,0}$. The influence of $C_{aq,0}$ on η should be more obvious at shorter τ . At sufficiently large τ , such influence is not discernable since η already approaches 100%. The above findings are in good agreement with the experimental results shown in Figure 7.

D. $(K_{ov}a)_{Chem}$ as a function of the residence time and inlet lactic acid concentration in reactive extraction

Eq. 25 predicts that $(K_{ov}a)_{Chem}$ is a function of τ and E_i : $(K_{ov}a)_{Chem}$ turns to be higher at lower τ or at higher E_i . The explanation in Supporting Information C makes it clear that E_i is higher at lower $C_{aq,0}$. Therefore, $(K_{ov}a)_{Chem}$ also depends on $C_{aq,0}$ and is higher at lower $C_{aq,0}$. According to Eq. (C-4), the influence of $C_{aq,0}$ on $(K_{ov}a)_{Chem}$ should be more obvious at shorter τ . In other words, $(K_{ov}a)_{Chem}$ does not differ much at sufficiently large τ for both inlet lactic acid concentrations (i.e., $C_{aq,0} = 0.11$ M and 0.055 M) since η already approaches 1 in both cases.

These discussion well explains the results of the experimentally measured $(K_{ov}a)_{Chem}$ as depicted in Figure 9.

However, according to Eq. 25, the predicted $(K_{ov}a)_{Chem}$ value should increase with increasing E_i and therefore should increase with decreasing $C_{aq,0}$ even at sufficient large τ values. Such difference in the behavior between the predicted and measured $(K_{ov}a)_{Chem}$ values is mainly because that the derivation of Eq. 25 has neglected the reversible nature of the complexation reaction between lactic acid and TOA. Even with this inadequacy, Eq. 25 in combination with Eq. 29 can describe the experimental measurements in $(K_{ov}a)_{Chem}$ with good approximation, which is reasonable since under the majority of our reactive extraction experiments, the reaction in all or at least a large portion of the microreactor is expected to be still far from equilibrium.