membranes

# Supplementary Materials: Diffusion Dialysis for Separation of Hydrochloric Acid, Iron and Zinc Ions from Highly Concentrated Pickling Solutions

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## 1 Membrane Properties

The properties of the Fumasep membranes (type FAD-PET-75, by Fumatech GmbH, https://www.fumatech.com/EN/Onlineshop/Products%2bof%2bHydrocarbon%2bpolymers/index.html) are presented in Table S1.

**Table S1.** Properties of Fumasep FAD type anion exchange membrane.

| Item | Unit | Specifications |
|---|---|---|
| thickness (dry) | µm | 70-80 |
| electric resistance [a)] | Ω $cm^2$ | <1 |
| selectivity [b)] | % | >90 |
| stability | pH | <9 |
| ion exchange capacity | meq/g | >1.5 |
| specific conductance [c)] | mS/cm | > 13 |
| weight per unit area | mg/$cm^2$ | 9-12 |
| proton ($H^+$) transfer rate [d)] | mmol/min/$cm^2$ | >1500 |
| Young's modulus [e)] | MPa | >1000 |
| tensile strength [e)] | MPa | >40 |
| elongation at break [e)] | % | >15 |
| bubble point test in water at T = 25 °C | bar | >3 |

[a)] in $Cl^-$ form in 0.5 M NaCl at T = 25°C, measured in standard measuring cell (through-plane)

[b)] determined from membrane potential measurement in a concentration cell 0.1/0.5 M KCl at T = 25°C

[c)] determined in $Cl^-$ form in 0.5 NaCl at T =30°C

[d)] determined from pH potential measurement in a concentration cell 0.5 M HCl/0.5 M KCl at T = 25°C

[e)] determined by stress-strain measurement at T = 25°C and 50 % r.h., according to DIN EN 527-1

## 2. Equilibrium Species Dissociation

Dissociation reactions equilibria for the HCl+ $ZnCl_2$ and HCl+ $FeCl_2$ systems are reported in Table S2 where also the equilibrium dissociation constants are shown (source: PHREEQC software, https://www.usgs.gov/software/phreeqc-version-3).

**Table S2.** Dissociation reactions for the HCl+ $ZnCl_2$ and HCl+ $FeCl_2$ systems and relative equilibrium constants (source: PHREEQC software).

| Dissociation reaction | $-\log K_{eq}$ | Equilibrium Constant $K_{eq}$ |
|---|---|---|
| $ZnCl^+ \leftrightarrow Zn^{2+} + Cl^-$ | 0.43 | $k_1 = 0.37$ |
| $ZnCl_2 \leftrightarrow Zn^{2+} + 2Cl^-$ | 0.45 | $k_2 = 0.35$ |
| $ZnCl_3^- \leftrightarrow Zn^{2+} + 3Cl^-$ | 0.5 | $k_3 = 0.32$ |
| $ZnCl_4^{2-} \leftrightarrow Zn^{2+} + 4Cl^-$ | 0.2 | $k_4 = 0.63$ |
| $FeCl^+ \leftrightarrow Fe^{2+} + Cl^-$ | 0.43 | $k_1 = 0.37$ |

Different species concentration for the HCl+ $ZnCl_2$ system were assessed from Equations (S1) to (S7):

$$[ZnCl^+] = \frac{[Zn^{2+}][Cl^-]}{k_1}\frac{\Upsilon_{Zn^{2+}}\Upsilon_{Cl^-}}{\Upsilon_{ZnCl^+}} \quad \text{(S1)}$$

$$[ZnCl_2] = \frac{[Zn^{2+}][Cl^-]^2}{k_2}\frac{\Upsilon_{Zn^{2+}}\Upsilon_{Cl^-}^2}{\Upsilon_{ZnCl_2}} \quad \text{(S2)}$$

$$[ZnCl_3^-] = \frac{[Zn^{2+}][Cl^-]^3}{k_3}\frac{\Upsilon_{Zn^{2+}}\Upsilon_{Cl^-}^3}{\Upsilon_{ZnCl_3^-}} \quad \text{(S3)}$$

$$[ZnCl_4^{2-}] = \frac{[Zn^{2+}][Cl^-]^4}{k_4}\frac{\Upsilon_{Zn^{2+}}\Upsilon_{Cl^-}^4}{\Upsilon_{ZnCl_4^{2-}}} \quad \text{(S4)}$$

$$[Zn]_{TOT} = [ZnCl^+] + [ZnCl_2] + [ZnCl_3^-] + [ZnCl_4^{2-}] + [Zn^{2+}] \quad \text{(S5)}$$

$$[Zn^{2+}] = \frac{[Zn]_{TOT}}{1 + [Cl^-]\Upsilon_{Zn^{2+}}\Upsilon_{Cl^-}\left(\frac{1}{k_1}\frac{1}{\Upsilon_{ZnCl^+}} + \frac{[Cl^-]}{k_2}\frac{\Upsilon_{Cl^-}}{\Upsilon_{ZnCl_2}} + \frac{[Cl^-]^2}{k_3}\frac{\Upsilon_{Cl^-}^2}{\Upsilon_{ZnCl_3^-}} + \frac{[Cl^-]^3}{k_4}\frac{\Upsilon_{Cl^-}^3}{\Upsilon_{ZnCl_4^{2-}}}\right)} \quad \text{(S6)}$$

$$[Cl^-] = [H^+] + 2[Zn^{2+}] + [ZnCl^+] - [ZnCl_3^-] - 2[ZnCl_4^-] \quad \text{(S7)}$$

For the HCl+$FeCl_2$ system, Eqs. from S8 to S11 were considered for the dissociation species concentrations evaluation:

$$[FeCl^+] = \frac{[Fe^{2+}][Cl^-]}{k_1}\frac{\Upsilon_{Fe^{2+}}\Upsilon_{Cl^-}}{\Upsilon_{FeCl^+}} \quad \text{(S8)}$$

$$[Fe]_{TOT} = [FeCl^+] + [Fe^{2+}] \quad \text{(S9)}$$

$$[Fe^{2+}] = \frac{[Fe]_{TOT}}{1 + \frac{[Cl^-]}{k_1}\frac{\Upsilon_{Fe^{2+}}\Upsilon_{Cl^-}}{\Upsilon_{FeCl^+}}} \quad \text{(S10)}$$

$$[Cl^-] = [H^+] + 2[Fe^{2+}] + [FeCl^+] \quad (S11)$$

The ions activity coefficients reported in Eqs. S1-S11 were evaluated from Davies equation[1] which gives the mean activity coefficient of an electrolyte that dissociates into ions having charges $z_1$ as a function of ionic strength I:

$$-\log \Upsilon_{\pm} = 0.5042 z_1^2 \left( \frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I \right) \quad (S12)$$

Specifically, for the HCl+$ZnCl_2$ system Eqs. S13 and S14 were considered, while for the HCl+$FeCl_2$ system Eqs. S15 and S16 are reported:

$$\Upsilon_{\pm} \simeq \Upsilon_{Cl^-} \simeq \Upsilon_{ZnCl^+} \simeq \Upsilon_{ZnCl_3^-} \quad (S13)$$

$$\Upsilon_{2\pm} \simeq \Upsilon_{Zn^{2+}} \simeq \Upsilon_{ZnCl_4^{2-}} \quad (S14)$$

$$\Upsilon_{\pm} \simeq \Upsilon_{Cl^-} \simeq \Upsilon_{FeCl^+} \quad (S15)$$

$$\Upsilon_{2\pm} \simeq \Upsilon_{Fe^{2+}} \quad (S16)$$

The dissociation % species is defined as the ratio between the concentration of the different species in solution and the total metal concentration.

$$dissociation\ \%_{species} = \frac{[species]}{[Metal]_{TOT}} \times 100 \quad (S17)$$

It is thus possible to evaluate the dissociation factor by multiply the different dissociation % species by the number of discrete ions obtained from the dissociation reactions of $ZnCl_2$ or $FeCl_2$ that produce the particular species:

$$ZnCl_{2\,dissociation\ factor} = \frac{3[Zn^{2+}] + 2[ZnCl^+] + [ZnCl_2] + [ZnCl_3^-] + [ZnCl_4^{2-}]}{[Zn]_{TOT}} \quad (S18)$$

$$FeCl_{2\,dissociation\ factor} = \frac{3[Fe^{2+}] + 2[FeCl^+]}{[Fe]_{TOT}} \quad (S19)$$

**References**

1. Davies, C. W. *Ion Association*; Butterworths: London, 1962.