Nanofiltration of concentrated amino acid solutions

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Outline

1. Introduction
   - Motive of the Study
   - Previous Works
   - Objectives
2. Experimental
   - Operation in Concentration Mode
   - Effect of pH and Concentration
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   - SK approach
   - Implementation

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Economic significance:

Estimated world market ($\gtrsim 1.6 \cdot 10^6$ t/a) doubles every decade *[1, 2]*

Use of amino acids:

- Human and animal nutrition
- Pharmaceuticals
- Cosmetics
- Agrochemicals
- Derivates for industrial uses

Production of amino acids:

- Hydrolysis
- Chemical
- Fermentation
- Enzymatic

Downstream processing of amino acids:

Potential alternative $\Rightarrow$ Nanofiltration

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Previous works

literature on higly diluted systems

- majority of studies
- pH = pI $\Rightarrow$ zwitterionic form, pH > pI $\Rightarrow$ anionic form
- $\mathcal{R}_{zwitterions} < \mathcal{R}_{anions}$

literature on concentrated systems

- few studies - limited experimental data
- greater rejection drop over concentration for charged components than for zwitterions
- charge shielding

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Objectives

Experimental study on amino acid permeation

- several NF and tight UF membranes
- concentration up to solubility limit
- wide pH range

Data evaluation

- identify major governing process parameters
- employ suitable model
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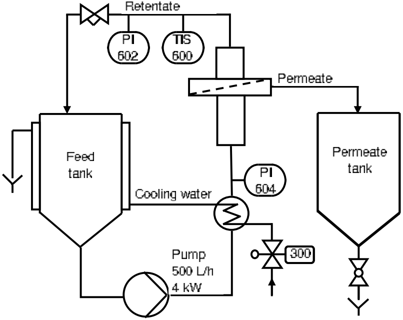
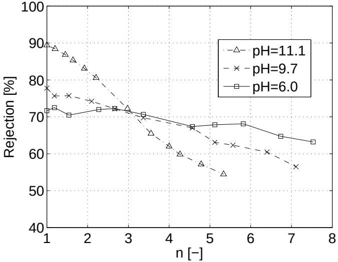
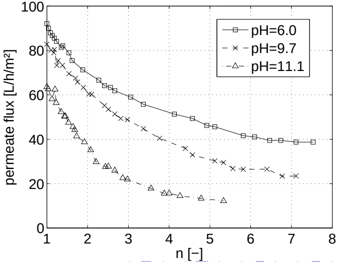
Concentration of L-alanine solution



(feed: 0.2 mol/L, concentrate: 0.9 mol/L, DK membrane, 30 bar, 25 $^{\circ}$C)

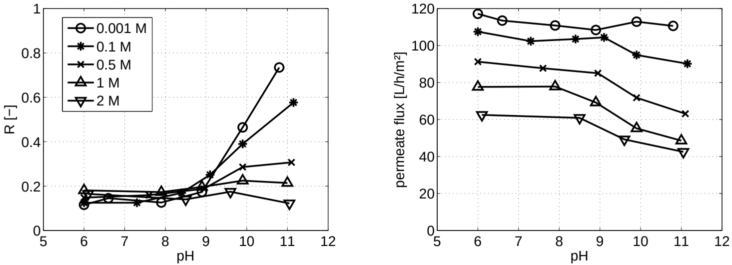




Experimental results

Rejection and flux in function of pH and concentration

(Glycine, GH, 30 bar, 25 $^\circ$C)



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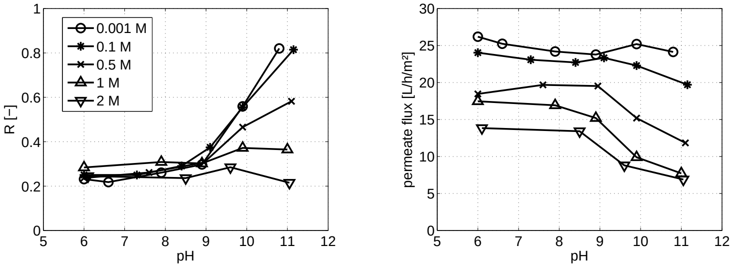
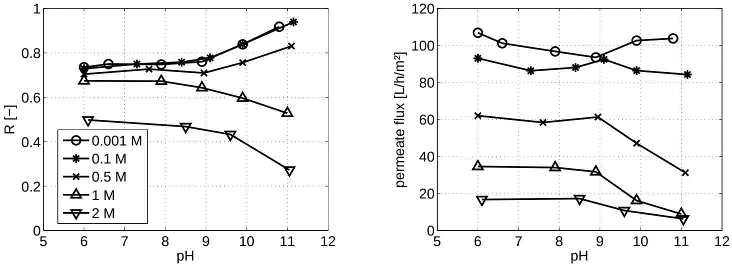


Experimental results

Rejection and flux in function of pH and concentration

(Glycine, DS5, 30 bar, 25 °C)



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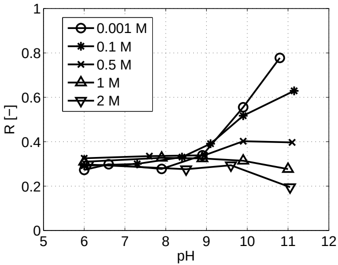

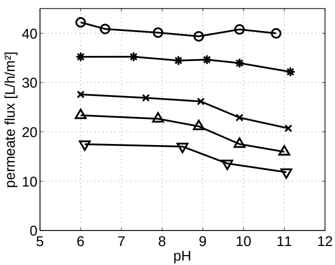

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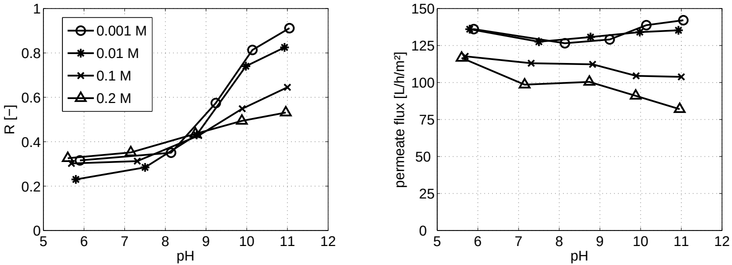
(L-glutamine, NP010, 30 bar, 25 °C)



Dissociation of diprotic amino acids

$$HOOC–R–NH_3^+ \rightleftharpoons {}^-OOC–R–NH_3^+ \rightleftharpoons {}^-OOC–R–NH_2$$

Ionic fractions at given feed pH

$$f_{A^+} = \frac{1}{1 + 10^{\mathrm{pH}-\mathrm{pK}_1} + 10^{2\mathrm{pH}-\mathrm{pK}_1-\mathrm{pK}_2}}, \qquad f_{A^-} = \frac{1}{1 + 10^{\mathrm{pK}_2-\mathrm{pH}} + 10^{\mathrm{pK}_1+\mathrm{pK}_2-2\mathrm{pH}}}$$

Osmotic pressure by van't Hoff law with altered dissociation factor

$$\pi = iRTc_A, \qquad \text{where} \quad i = \frac{f_{A^0} + 2f_{A^+} + 2f_{A^-}}{f_{A^0} + f_{A^+} + f_{A^+}}$$

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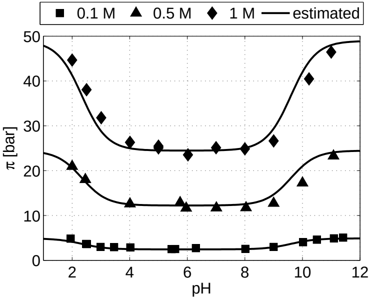
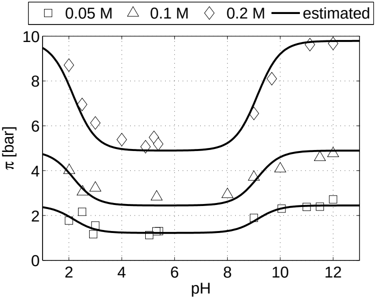
Vapor Pressure Osmometry

Predicted and measured osmotic pressure

(Knauer K-7000 vapor pressure osmometer, 25 °C)



glycine

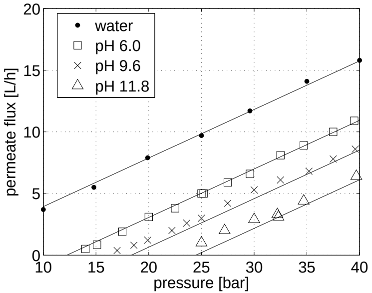


glutamine

RO investigations

Predicted and measured permeate flux

(SE type RO membrane (GE W&P Technologies), 0.5 mol/L glycine solution, $R \cong 100\%$, 25 °C)



Calculation method

1. hydraulic resistance from water measurements
2. osmotic pressure given by altered van't Hoff law
3. permeate flux:

$$J_w = \frac{\Delta P - \Delta \pi}{\mu_r R}$$

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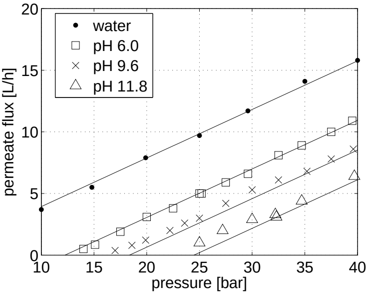

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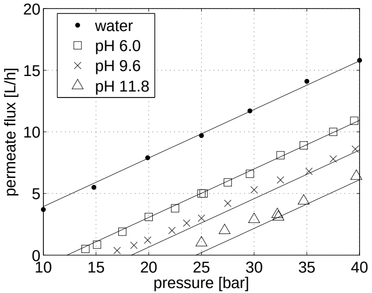

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Irreversible thermodynamics model

Kedem and Katchalsky equations *[3]*

$$
\begin{aligned}
J_v &= L_p(\Delta P - \sigma \Delta \pi), \\
j_s &= \omega \Delta \pi + (1-\sigma) J_v \overline{c},
\end{aligned}
$$

Symbol	*Name*	*Unity (S.I.)*
J_v	*total volume flux*	m/s
j_s	*molar solute flux*	$mol/(m^2\ s)$
$\triangle P$	*transmembrane pressure*	Pa
$\triangle \pi$	*osmotic pressure difference*	Pa
$\overline{c}$	*mean concentration across the membrane*	mol/m^3
L_p	***hydraulic permeability***	m/Pa
σ	***reflection coefficient***	–
ω	***solute permeability coefficient***	$mol/(m^2\ s\ Pa)$

Manipulation of KK equations

$$c_r(1-\mathcal{R}) - \frac{P_s c_r \mathcal{R}}{L_p \triangle P - L_p \sigma i R T c_r \mathcal{R}} + (1-\sigma)\overline{c} = 0$$

Theoretical study of pressure dependency by A. Kargol *[5]*.

$$\overline{c} = \frac{c_r - c_p}{2} \qquad \rightarrow \text{algebraic solution}$$

Case of logaritmic mean

$$\overline{c} = \frac{c_r - c_p}{\ln c_r - \ln c_p} \qquad \rightarrow \text{numerical solution}$$

Numerical computation:

$$\mathcal{R} = f(c_r, \mathrm{pH}, \triangle P)|_{L_p, P_s, \sigma}$$

Estimate rejection by solving the nonlinear equation:

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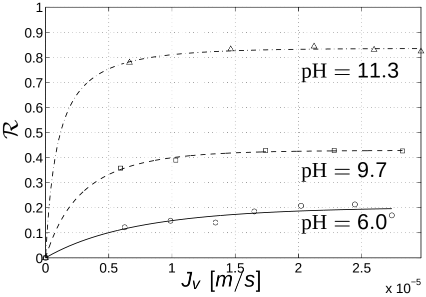


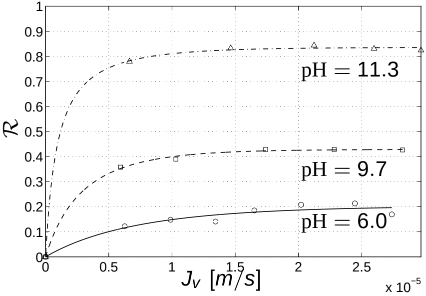
Figure: Experimental values and computed fitting models for $10^{-3} mol/L$ glycine solution at different pH

Spiegler-Kedem model *[4]*

$$\mathcal{R} = \frac{\sigma\left(1 - \exp\left(\frac{\sigma - 1}{P_s} J_v\right)\right)}{1 - \sigma \exp\left(\frac{\sigma - 1}{P_s} J_v\right)}$$

pH	σ	P_s
7.0	*0.2032*	$6.92 \times 10^{-6}\ m/s$
9.7	*0.4284*	$2.62 \times 10^{-6}\ m/s$
11.3	*0.8355*	$8.90 \times 10^{-7}\ m/s$

Table: Estimated values of σ and P_s for glycine at different pH



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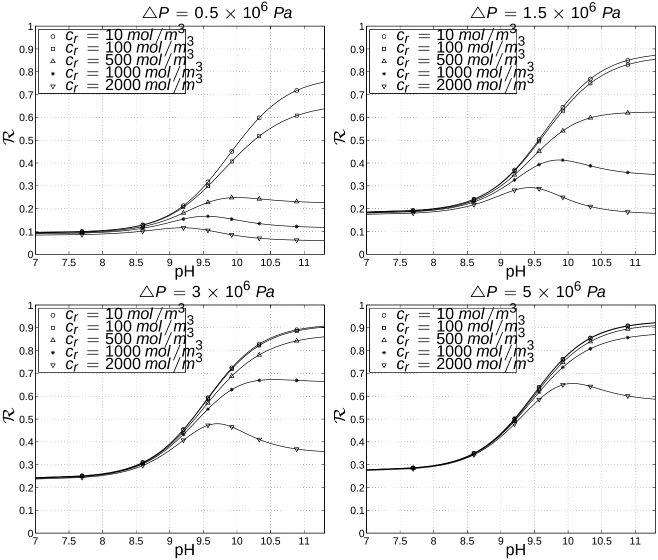
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0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
7
7.5
8
8.5
9
9.5
10
10.5
11

Summary

- The pH dependency of osmotic pressure has major role influencing separation.
- Altered form of van't Hoff law was delivered and experimentally confirmed.
- Special form of Kedem-Katchalsky equations was derived and numerical method applied to simulate rejection and flux behavior.

- Outlook
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