Reactive Extraction: Stoichiometry and Equilibrium Experiments and Evaluation

PhD seminar on Extraction - DECHEMA - Aachen 28.09.2023

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PEPs CHEMICAL ENGINEERING

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about me

- Marc Philippart de Foy
  - chemical engineer from University of Liège
  - PhD student and teaching assistant
  - September 2020 – September 2026

agenda

- reactive extraction equations
- experiments and characterization
- experimental results
- equilibrium and stoichiometry evaluation

equilibrium constant and stoichiometric coefficient

- extraction reaction

$$M^{\beta+} + \alpha\overline{RH} \rightleftharpoons \overline{MR_\beta(RH)_{\alpha-\beta}} + \beta H^+$$

- equilibrium constant

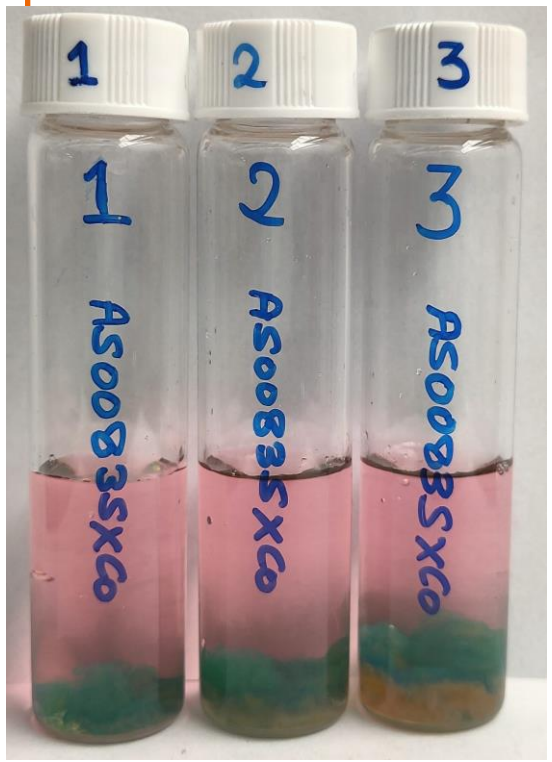
$$K_c = \frac{C_{MR_\beta(RH)_{\alpha-\beta}} C_{H^+}^{\beta}}{C_{M^{\beta+}} C_{RH}^{\alpha}}$$

$$K = K_c \frac{C_{RH}^{\alpha}}{C_{H^+}^{\beta}}$$

partition coefficient

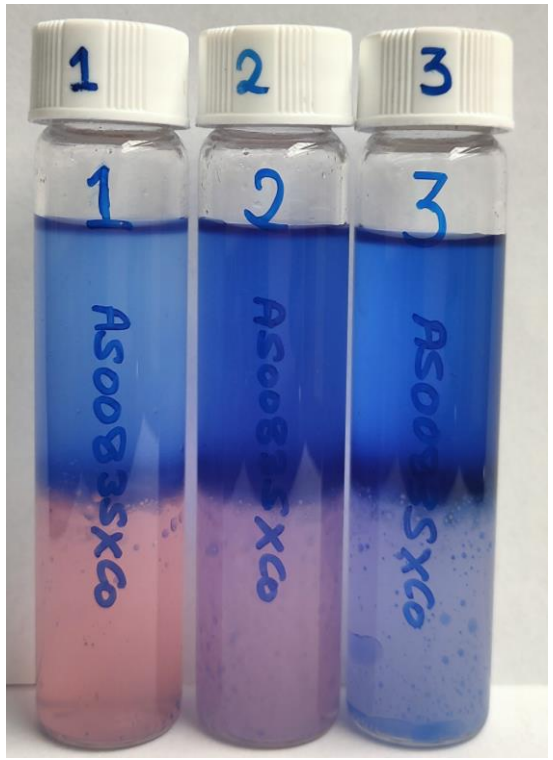
$$K = \frac{C_{MR_\beta(RH)_{\alpha-\beta}}}{C_{M^{\beta+}}}$$

extraction experiment – cobalt-D2EHPA system



aqueous
distilled water
Co^{2+}
NaOH

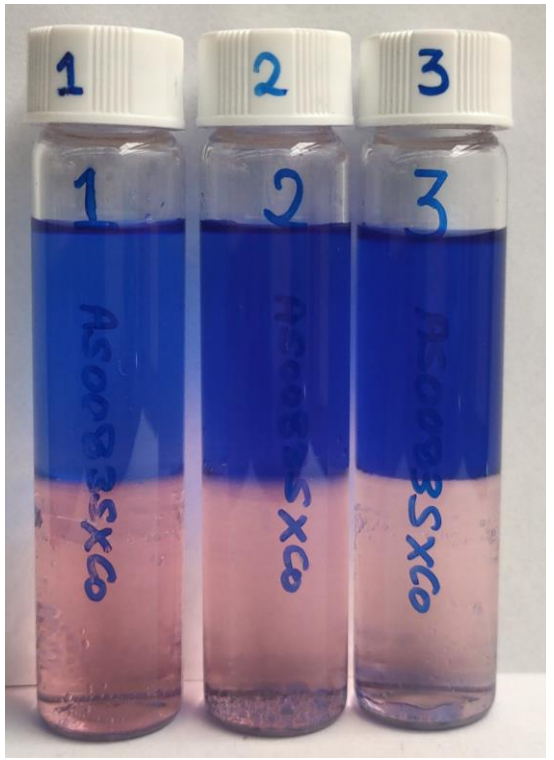
+



aqueous + organic
D2EHPA
kerosene

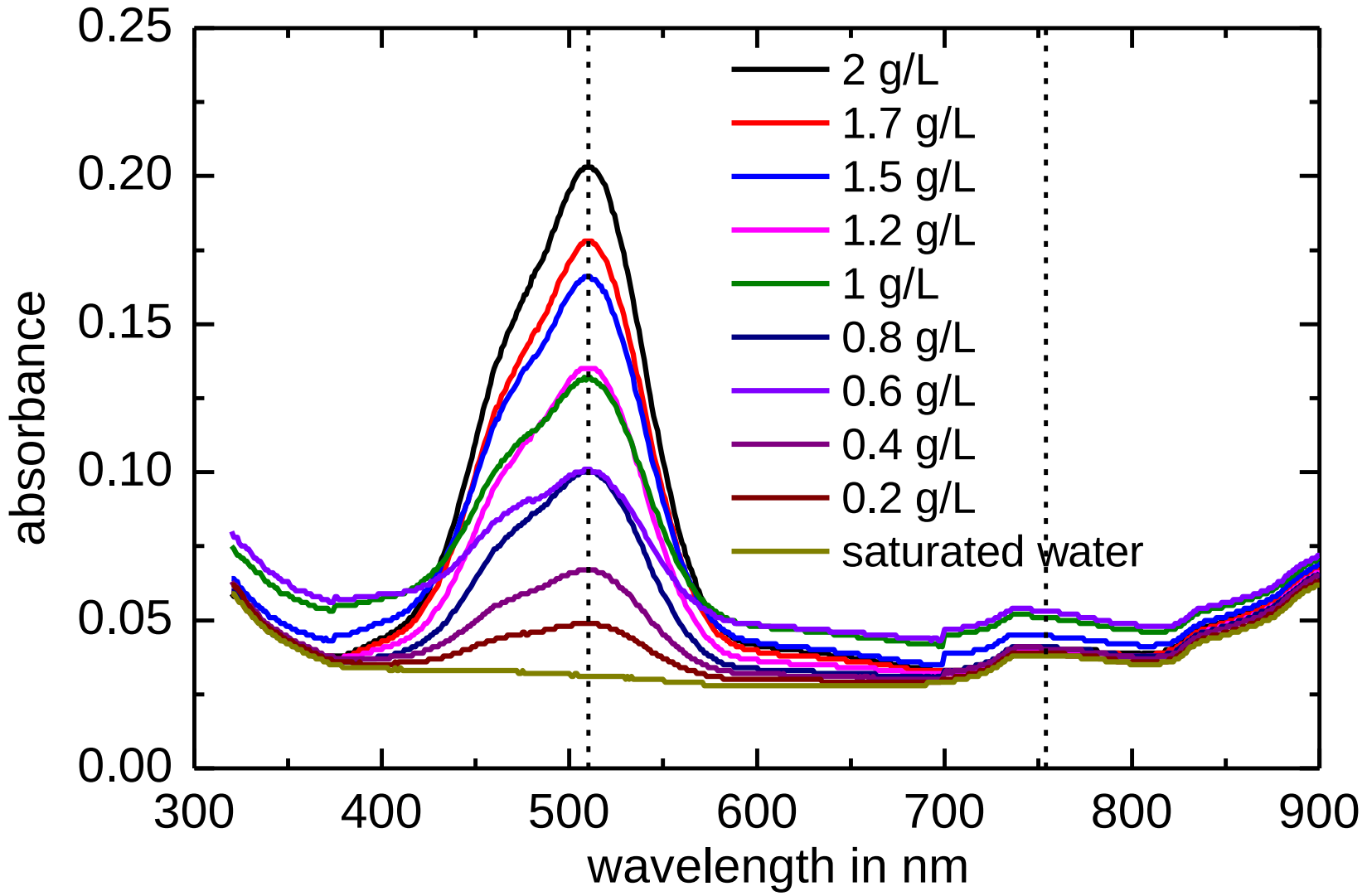
10 min mixing
1h settling

→

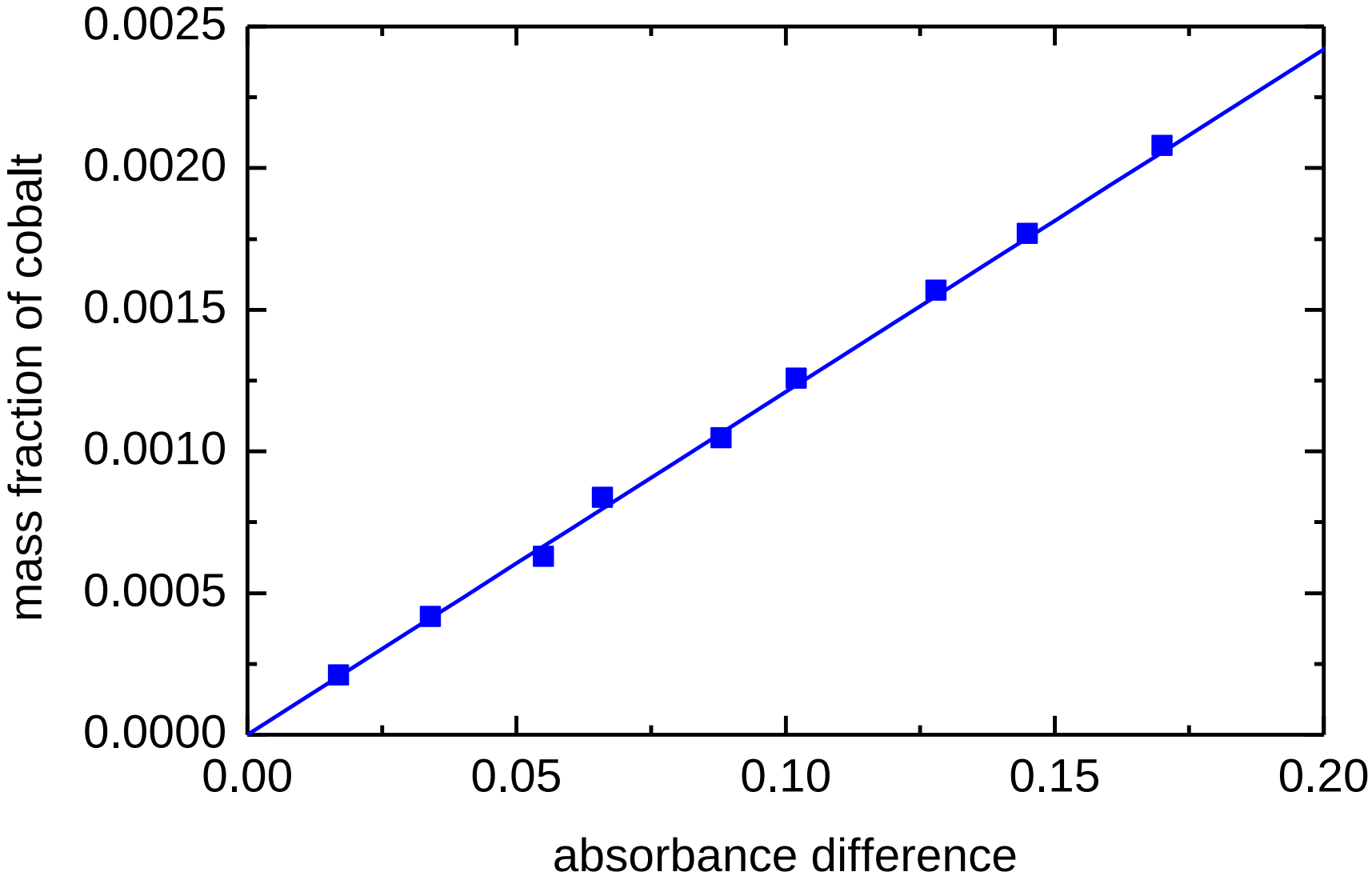


extraction equilibrium

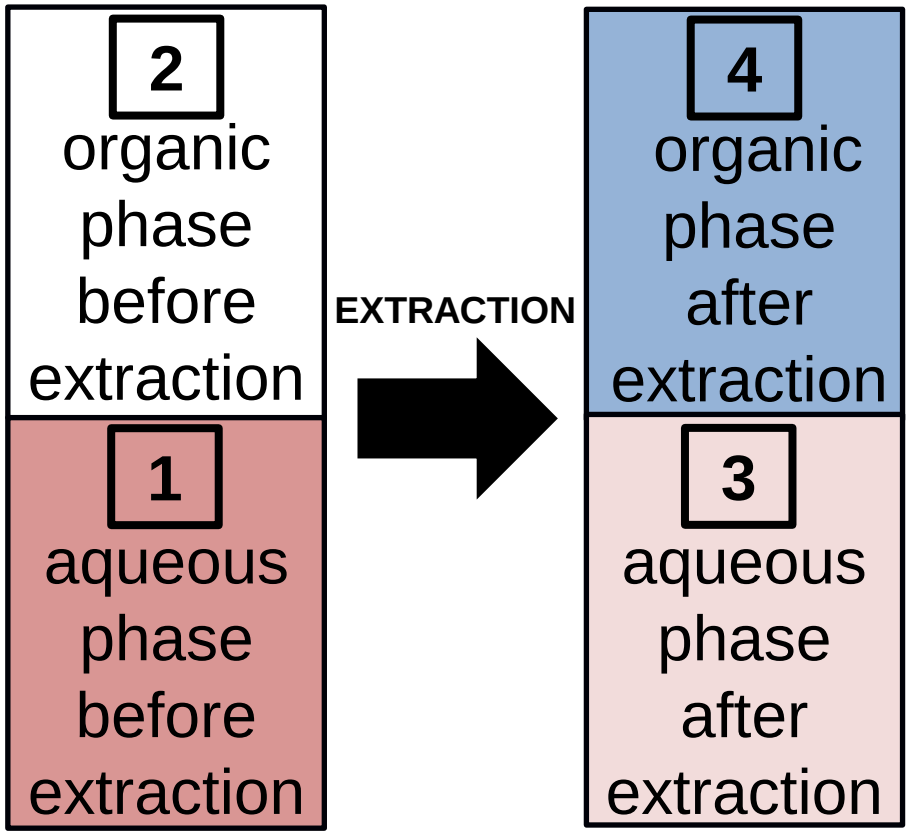
cobalt characterization – aqueous UV-vis spectroscopy



cobalt characterization – calibration curve

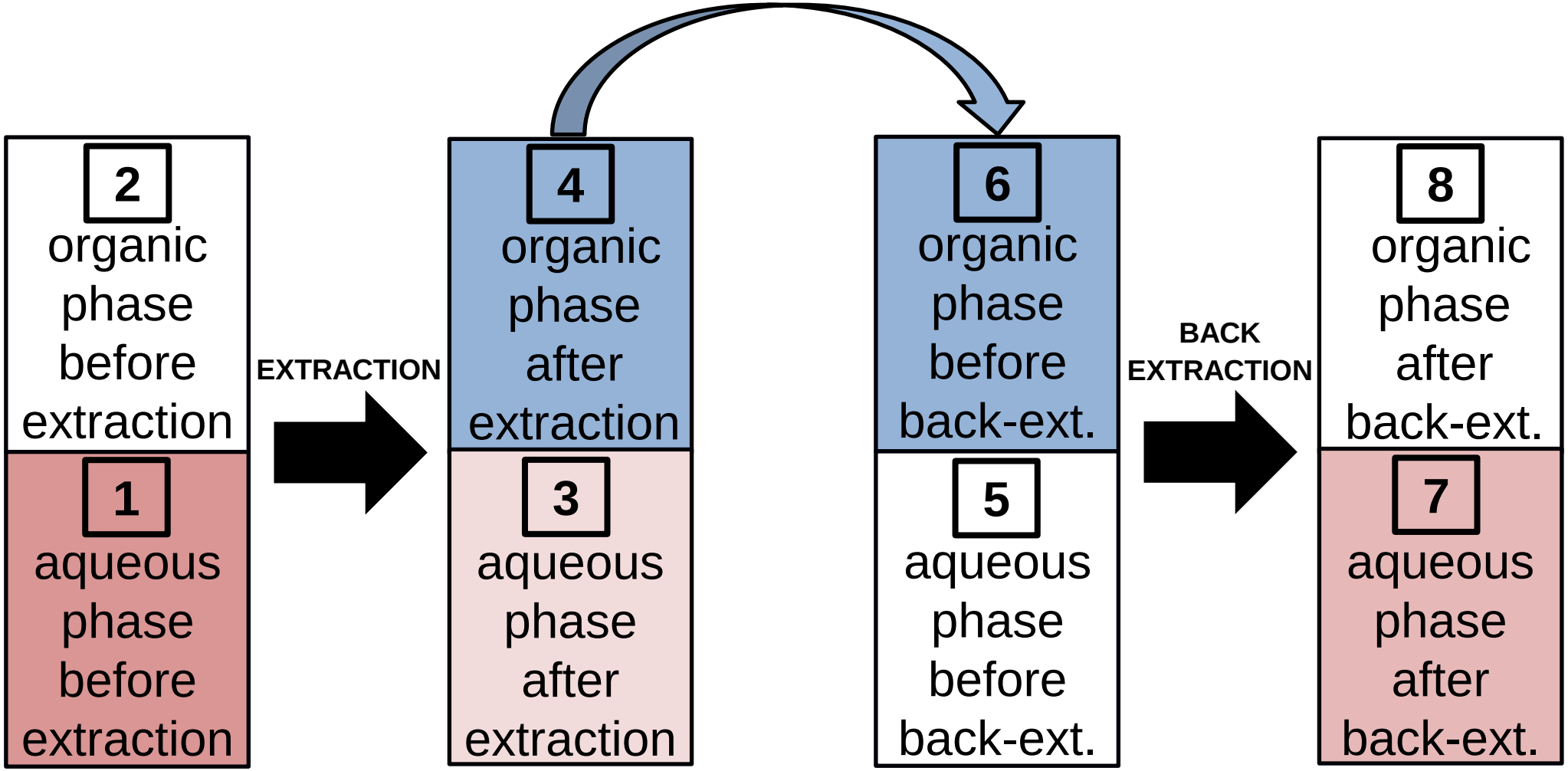


method 1: extraction

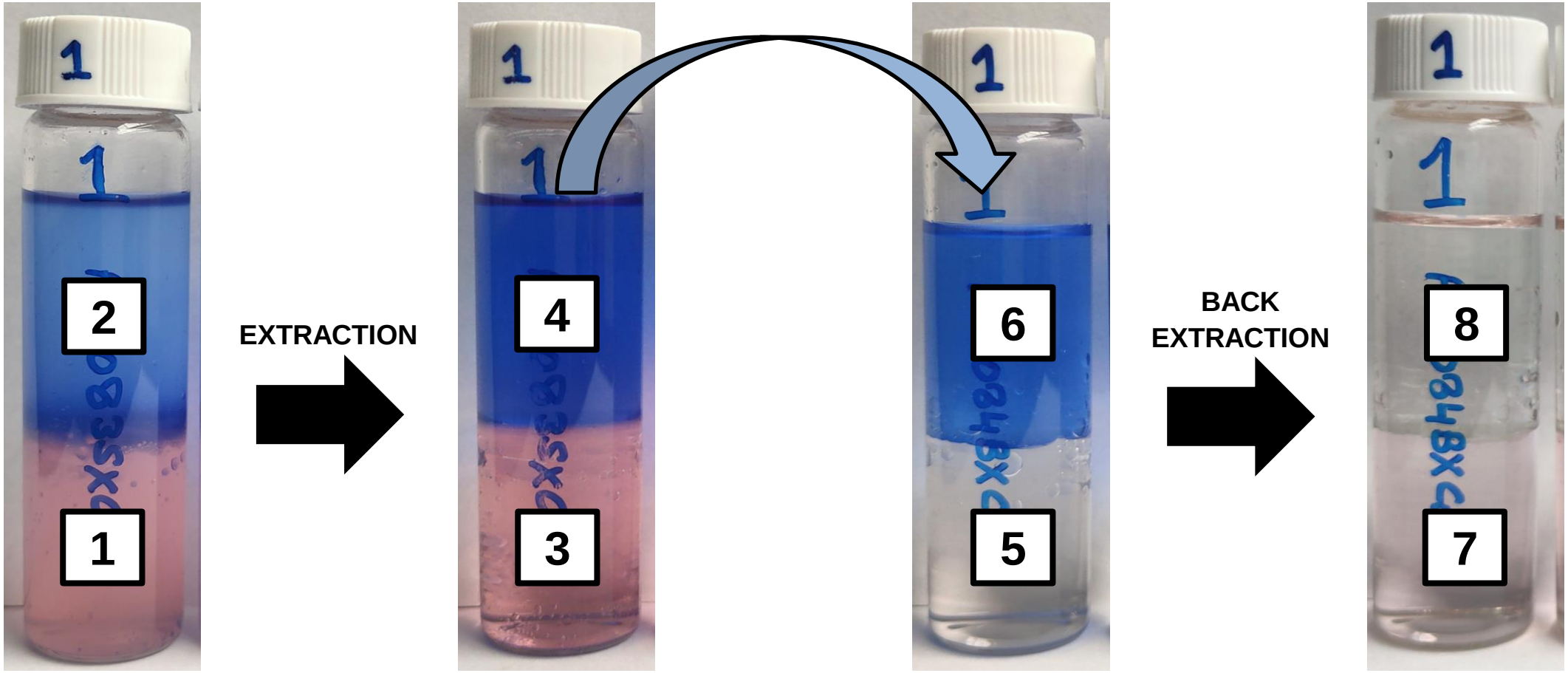


$$E = \frac{m_{M^{\beta+},1} - m_{M^{\beta+},3}}{m_{M^{\beta+},1}}$$

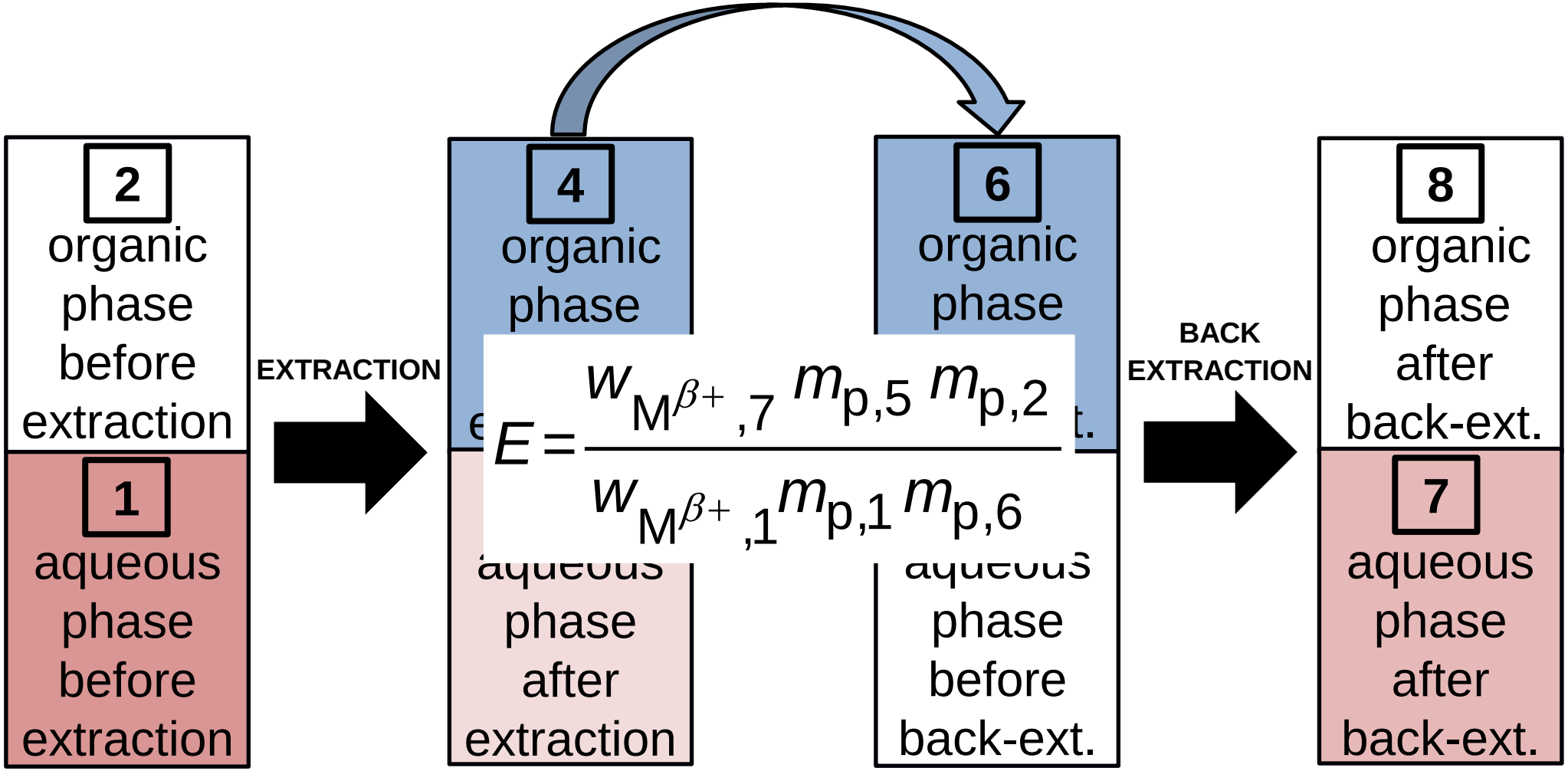
method 2: back-extraction



method 2: back-extraction



method 2: back-extraction

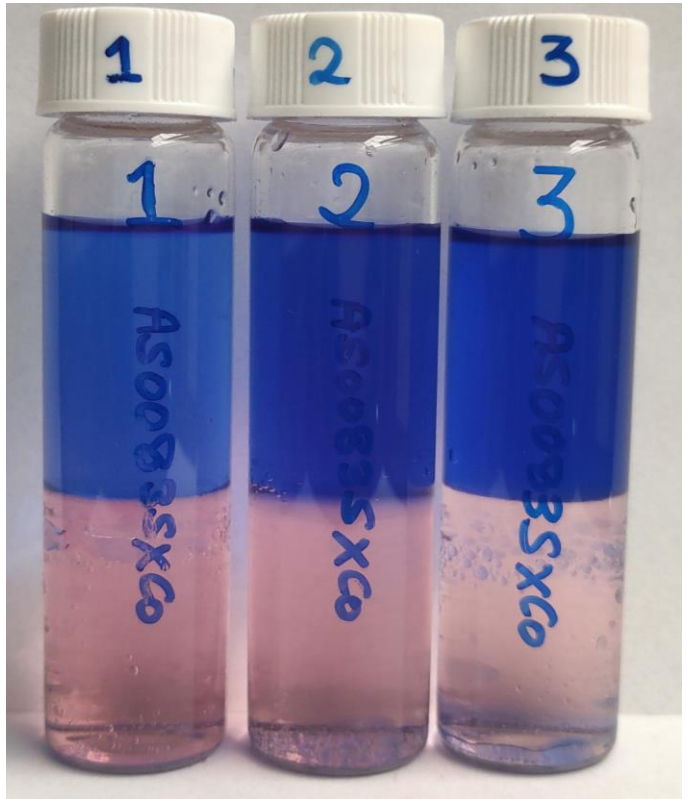


$$E = \frac{w_{M^{\beta+},7}\, m_{p,5}\, m_{p,2}}{w_{M^{\beta+},1}\, m_{p,1}\, m_{p,6}}$$

extraction experiments

- Co-D2EHPA system
- 2 g/L cobalt
- 10 vol-% D2EHPA
- kerosene diluent
- NaOH for *p*H shift
- 1 M HCl for back-extraction

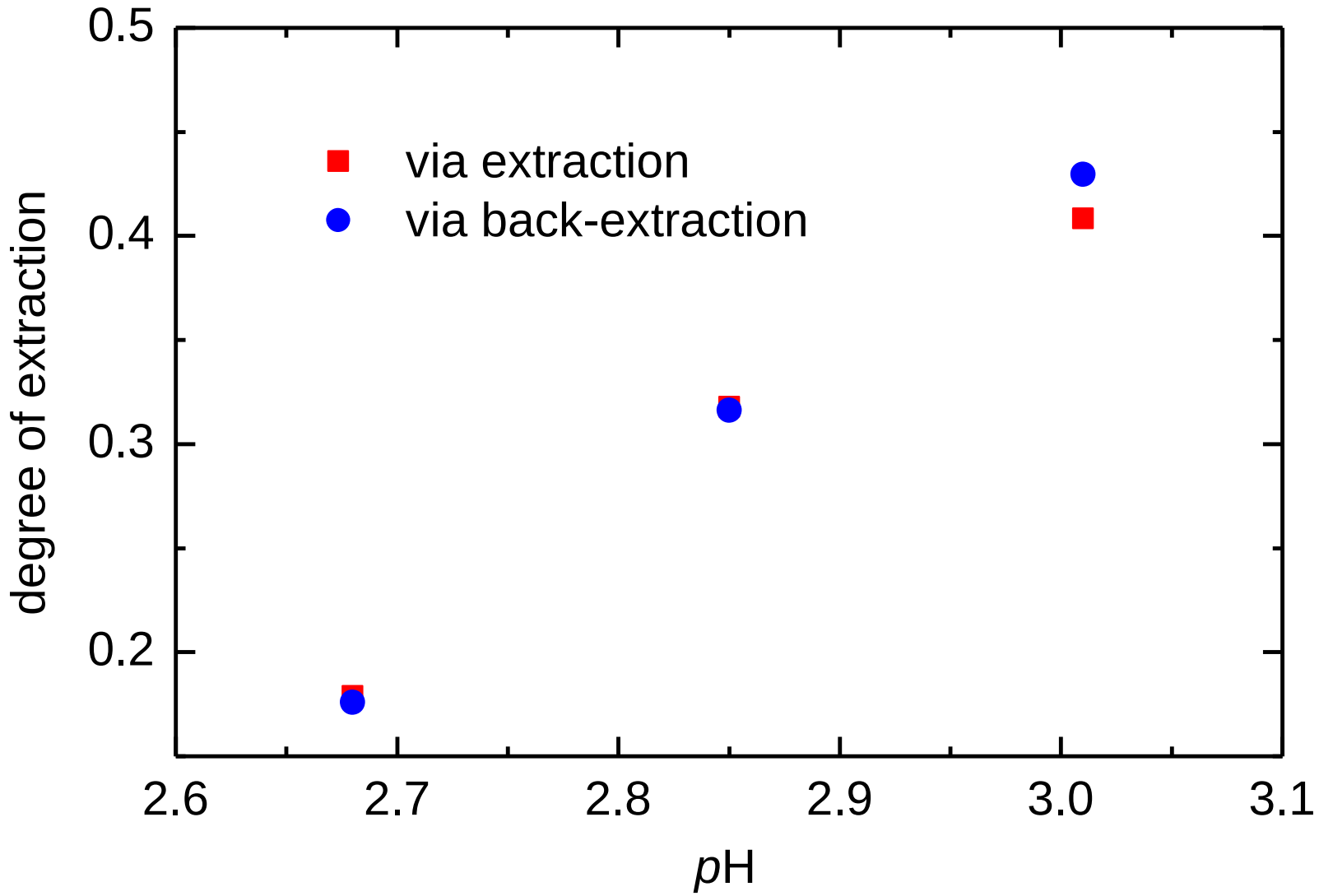
extraction



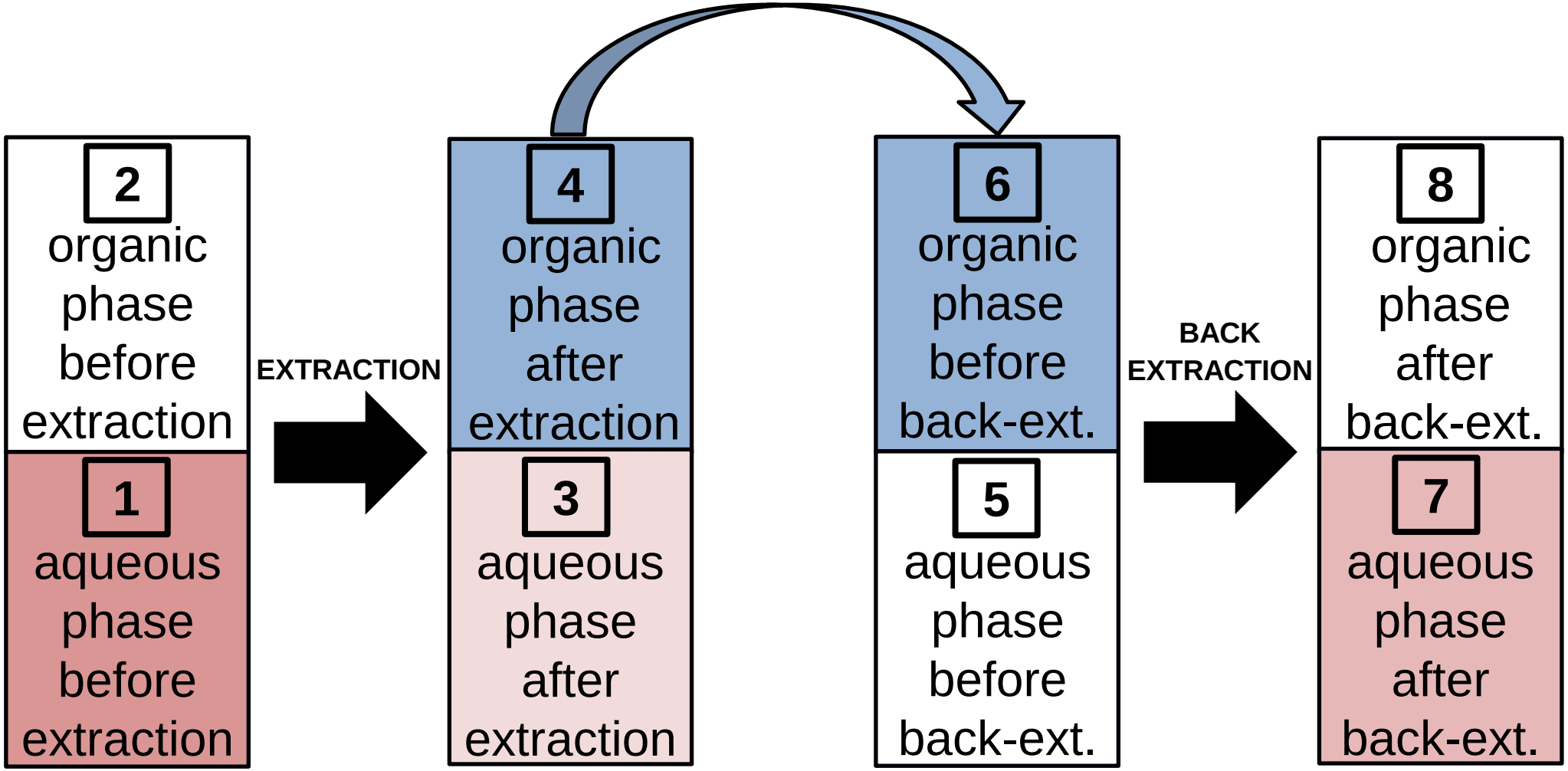
back-extraction

equilibrium *p*H: 2.68 2.85 3.01 1.44 1.52 1.58

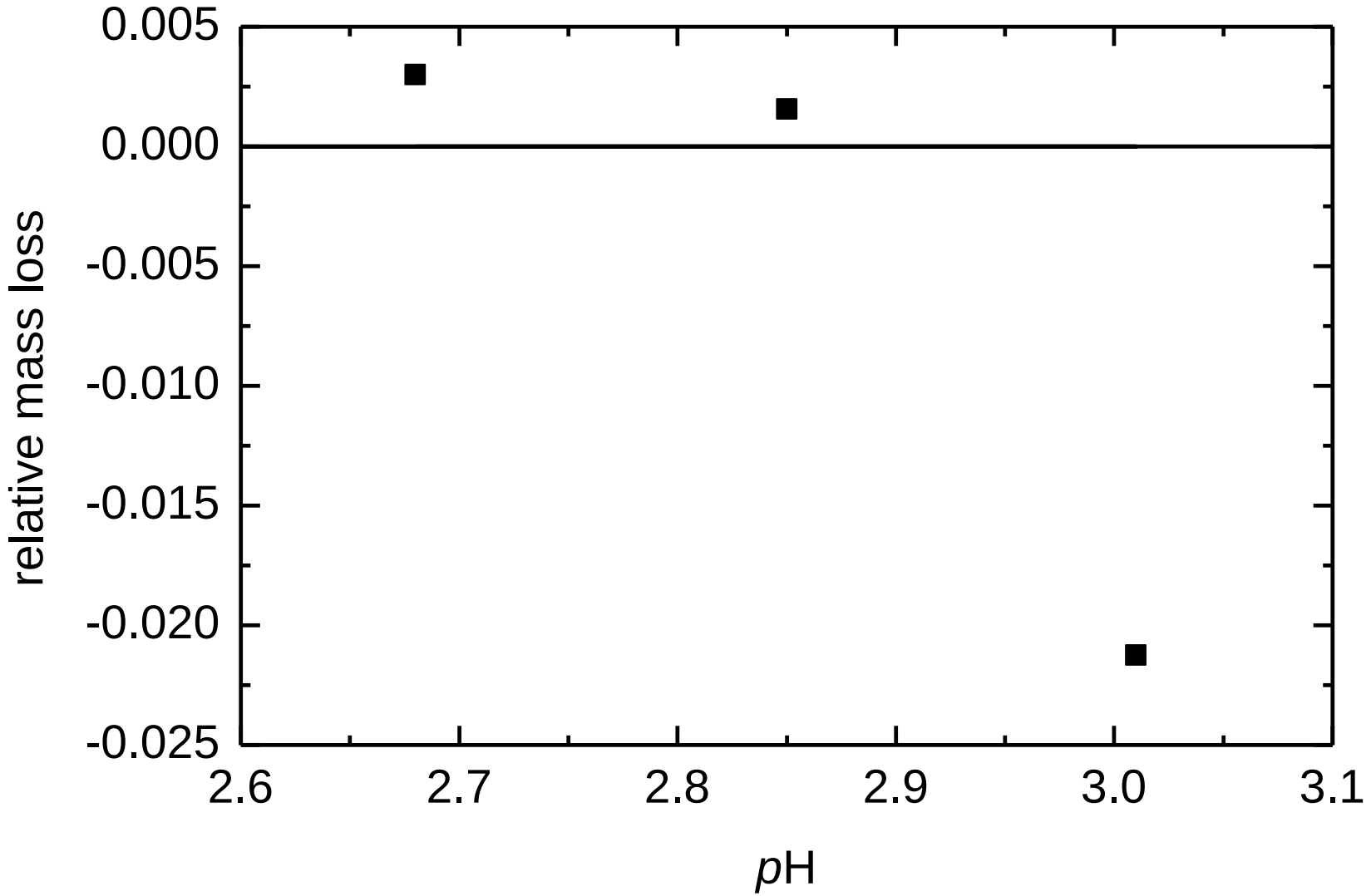
comparison of the two methods



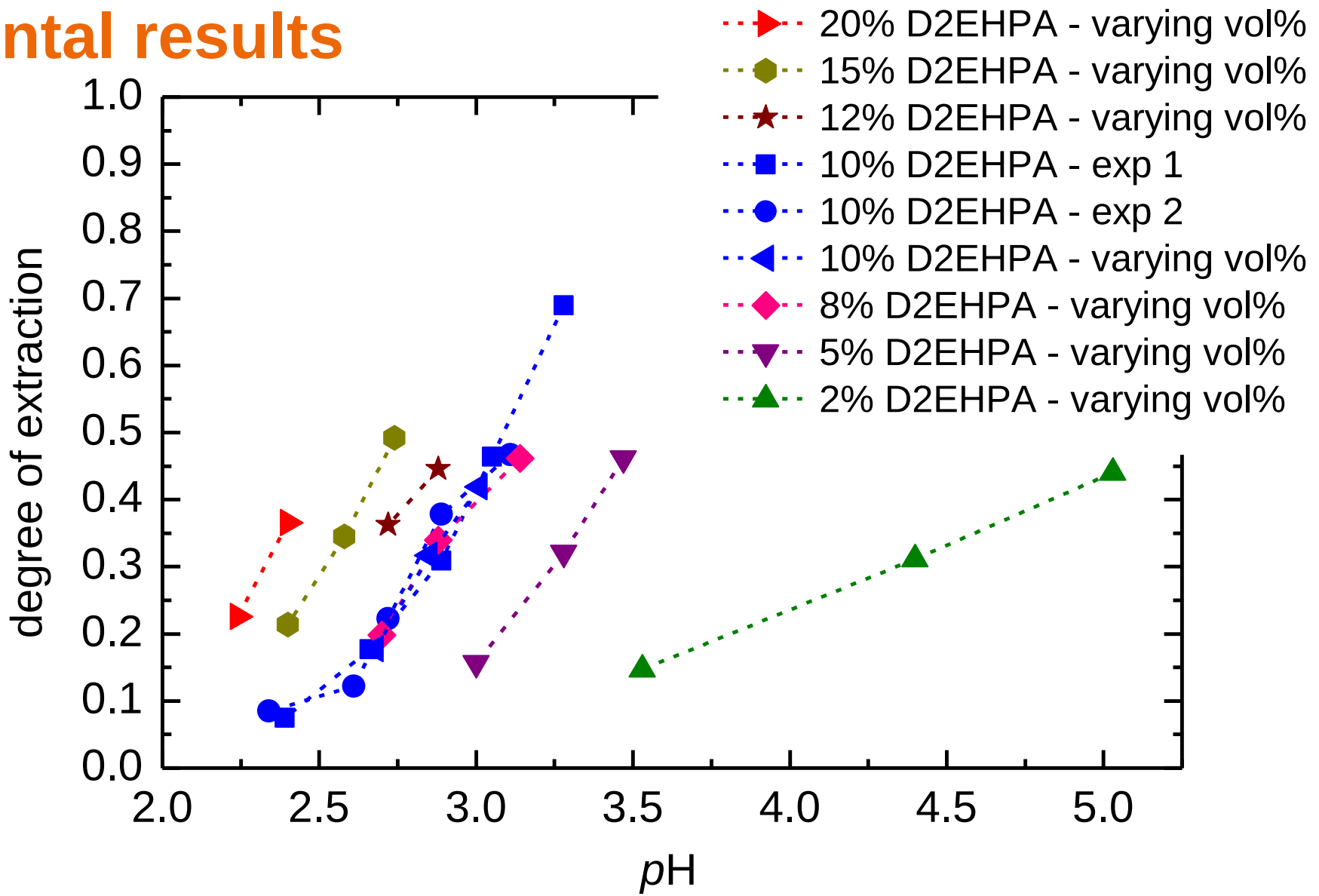
comparison of the two methods



comparison of the two methods



experimental results



K_c and α computation – linear fit

- extraction reaction

$$M^{\beta+} + \alpha\overline{RH} \rightleftharpoons \overline{MR_\beta (RH)_{\alpha-\beta}} + \beta H^+$$

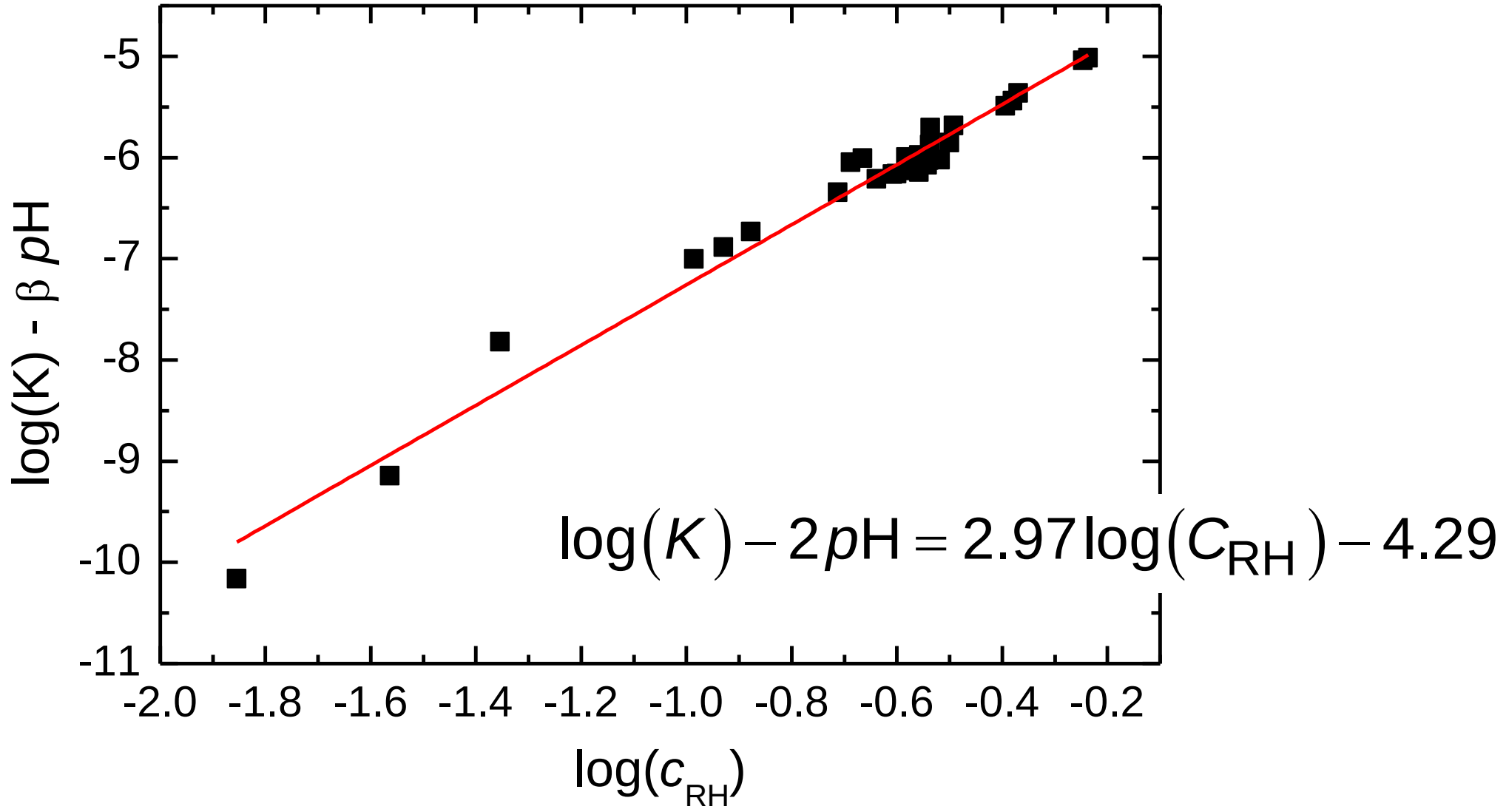
$$K = K_c \frac{C_{RH}^{\alpha}}{C_{H^+}^{\beta}}$$

- linear equation

$$\log(K) - \beta pH = \alpha \log(C_{RH}) + \log(K_c)$$

$$y = ax + b$$

K_c and α computation – linear fit



K_c and α computation – power fit

- extraction reaction

$$M^{\beta+} + \alpha\overline{RH} \rightleftharpoons \overline{MR_\beta (RH)_{\alpha-\beta}} + \beta H^+$$

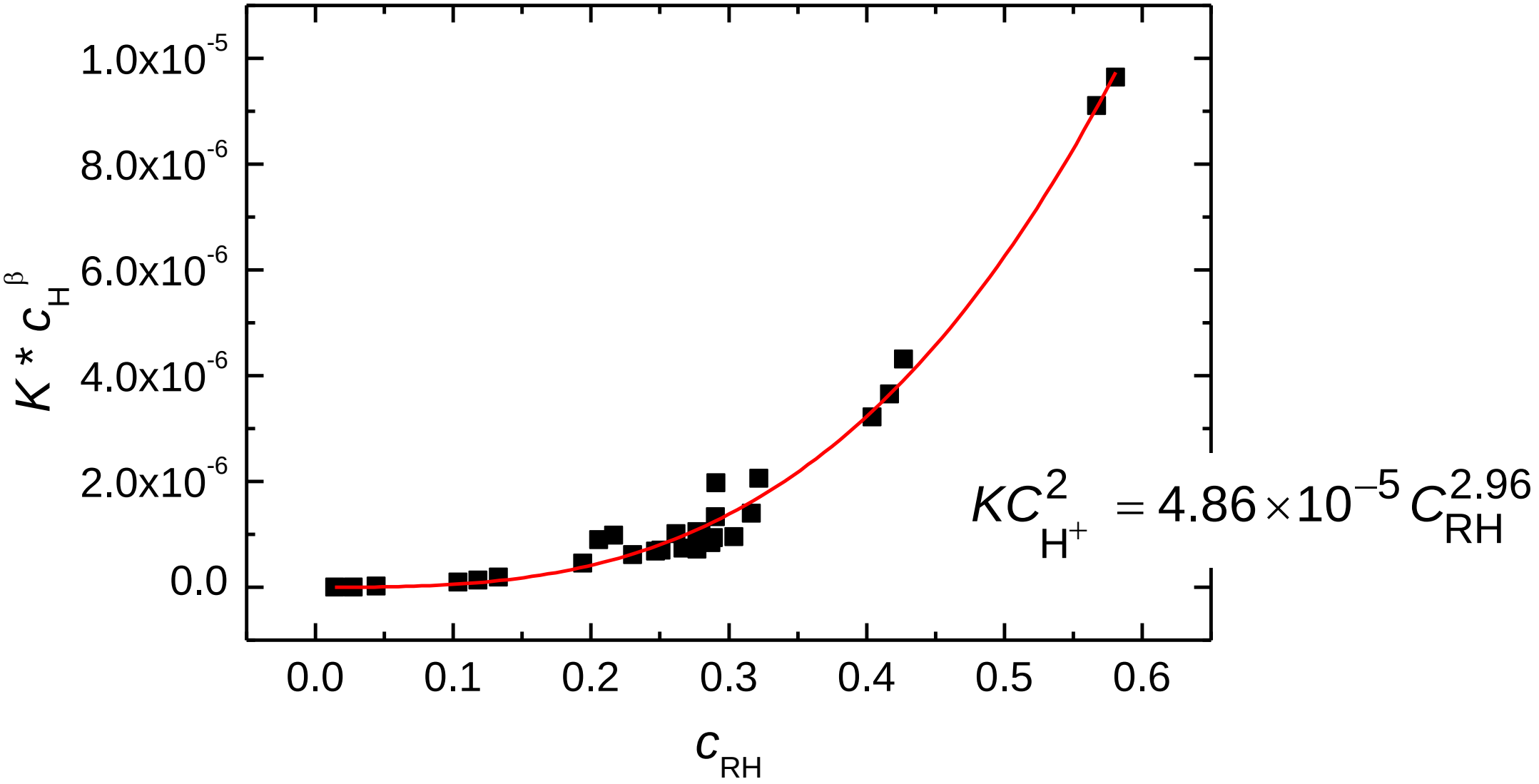
$$K = K_c \frac{C_{RH}^{\alpha}}{C_{H^+}^{\beta}}$$

- power equation

$$KC_{H^+}^{\beta} = K_c C_{RH}^{\alpha}$$

$$y = bx^a$$

K_c and α computation – power fit



K_c and α computation – comparison with literature

- obtained values

$K_c = 4.86 \times 10^{-5}$ $\alpha = 2.96$

[1]: $K_c = 1.15 \times 10^{-4}$ $\alpha = 2.87$

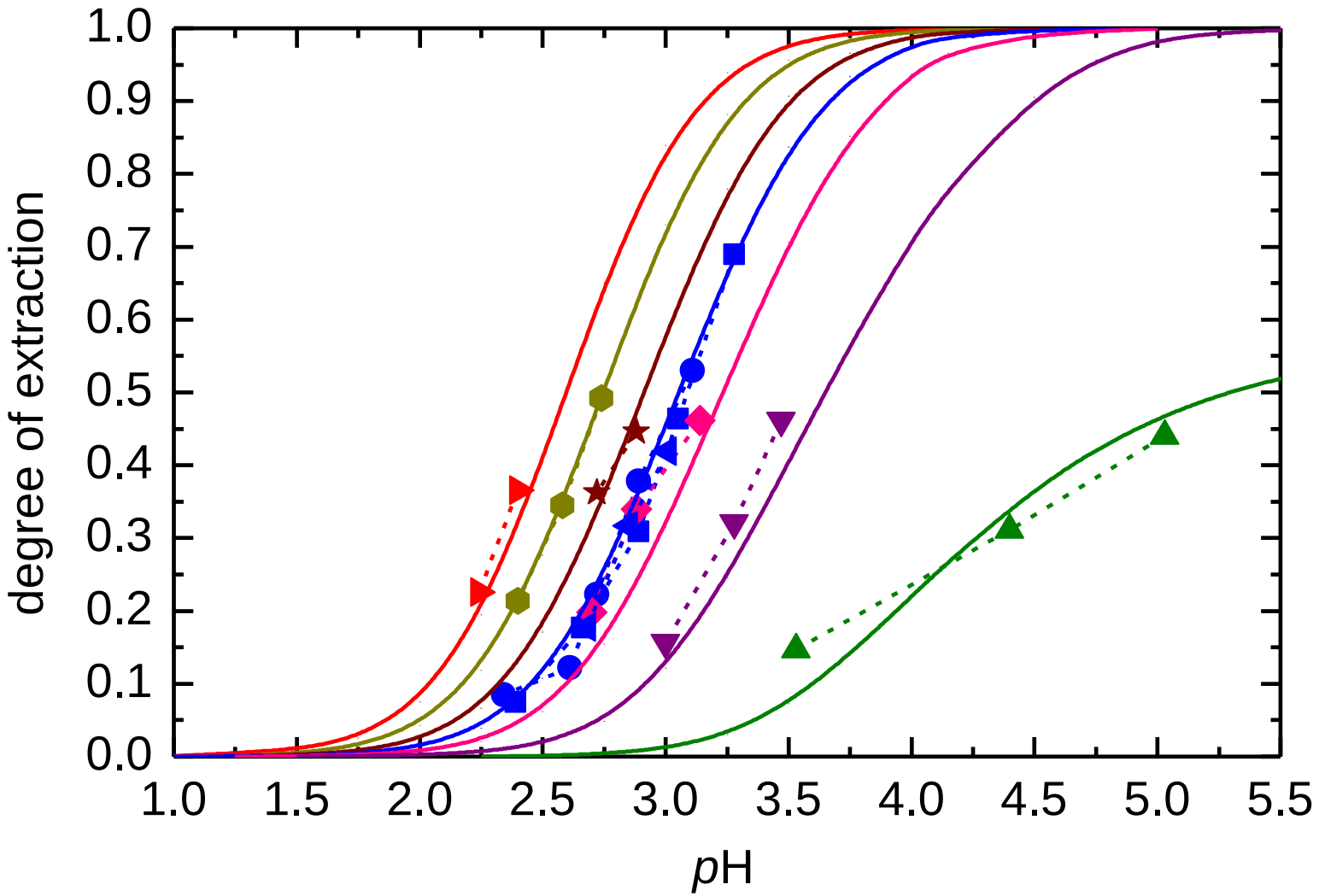
- stoichiometry
  monomer RH → dimer $(RH)_2$

~ 3 ~ 1.5

$$Co^{2+} + 1.5\overline{(RH)_2} \rightleftharpoons \overline{CoR_2(RH)} + 2H^+$$

[1] Keller, A., Sterner, P. L., Hlawitschka, M. W., & Bart, H. J. (2022). Extraction kinetics of cobalt and manganese with D2EHPA from lithium-ion battery recyclate. Chemical Engineering Research and Design, 179, 16-26.

experimental results and models



20% D2EHPA - varying vol%
15% D2EHPA - vary vol%
12% D2EHPA - vary vol%
10% D2EHPA - exp 1
10% D2EHPA - exp 2
10% D2EHPA - vary vol%
8% D2EHPA - vary vol%
5% D2EHPA - vary vol%
2% D2EHPA - vary vol%
model 20%
model 15%
model 12%
model 10%
model 8%
model 5%
model 2%

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