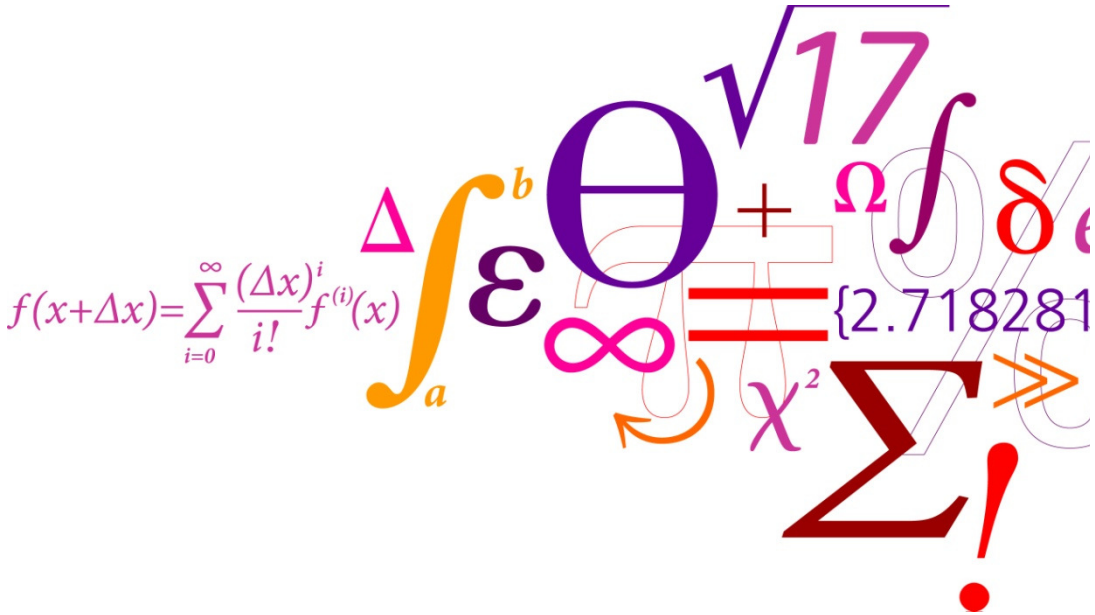
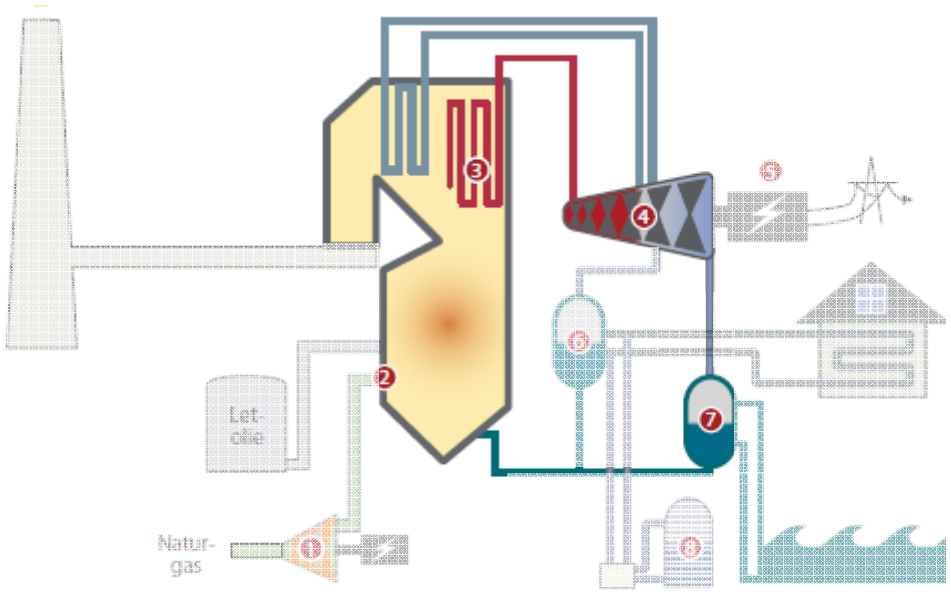
Measurement and Modelling of Electrical Conductivity in Aqueous Solutions

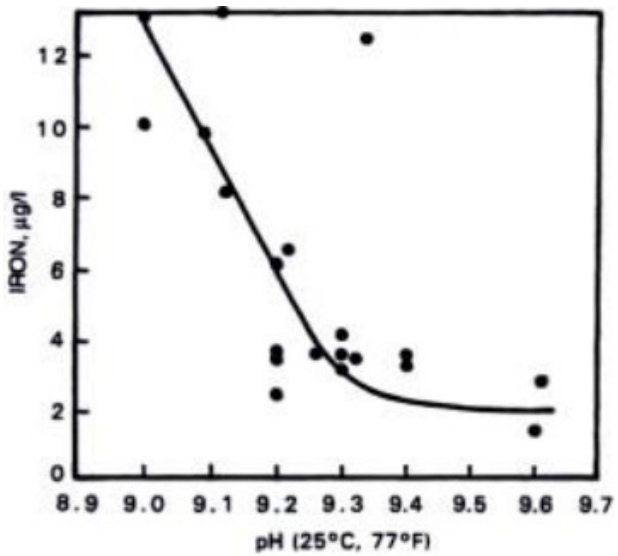
Thomas Krüger (s072181)
Supervisors: Kaj Thomsen and Philip Loldrup Fosbøl
Project carried out in spring semester 2012

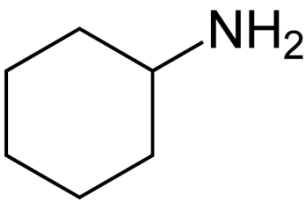


DTU Chemical Engineering
Department of Chemical and Biochemical Engineering

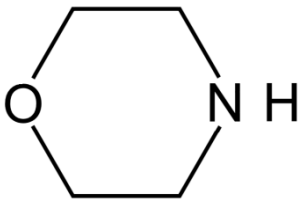
Conditioning of boiler water at Mongstad power plant







Cyclohexylamine



Morpholine

Theory

Weak electrolytes: $\Lambda = \alpha \Lambda^0$

Determination of α

Reactions:

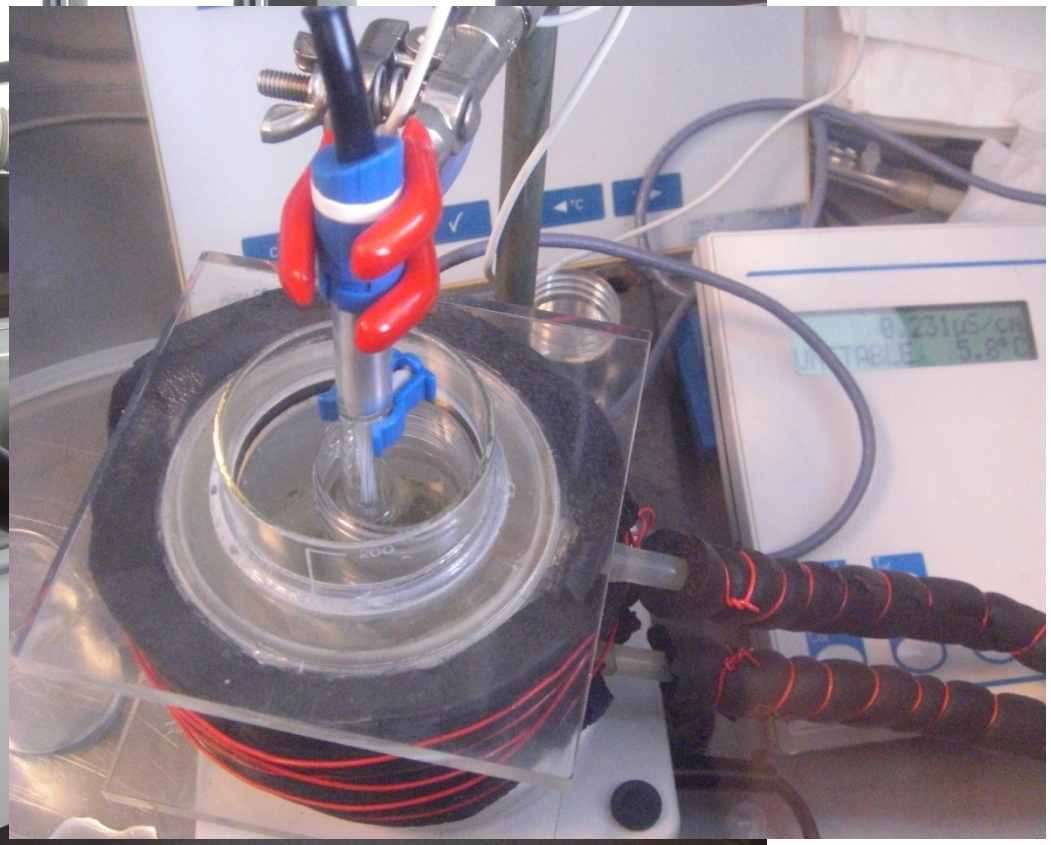
$$CHA + H_2O \leftrightarrows CHAH^+ + OH^-$$
$$MOR + H_2O \leftrightarrows MORH^+ + OH^-$$

Equilibria

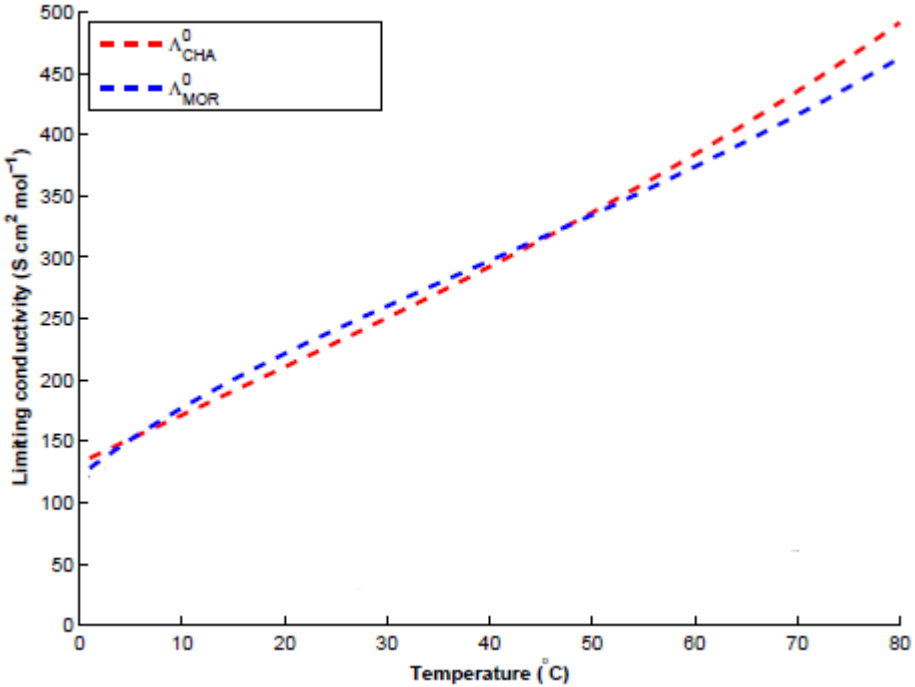
$$K_b = \frac{[\mathrm{WH^+}][\mathrm{OH^-}]}{[\mathrm{W}][\mathrm{H_2O}]} = \frac{\alpha c \cdot \alpha c}{c(1-\alpha)\cdot x_w} \times \frac{\gamma_{\mathrm{WH^+}}\gamma_{\mathrm{OH^-}}}{\gamma_{\mathrm{W}}\gamma_{\mathrm{H_2O}}} = \frac{\alpha^2 c}{(1-\alpha)x_w} \times \frac{\gamma_\pm^2}{\gamma_{\mathrm{W}}\gamma_{\mathrm{H_2O}}}$$

Debye-Hückel theory for c < 0.1 mol/kg

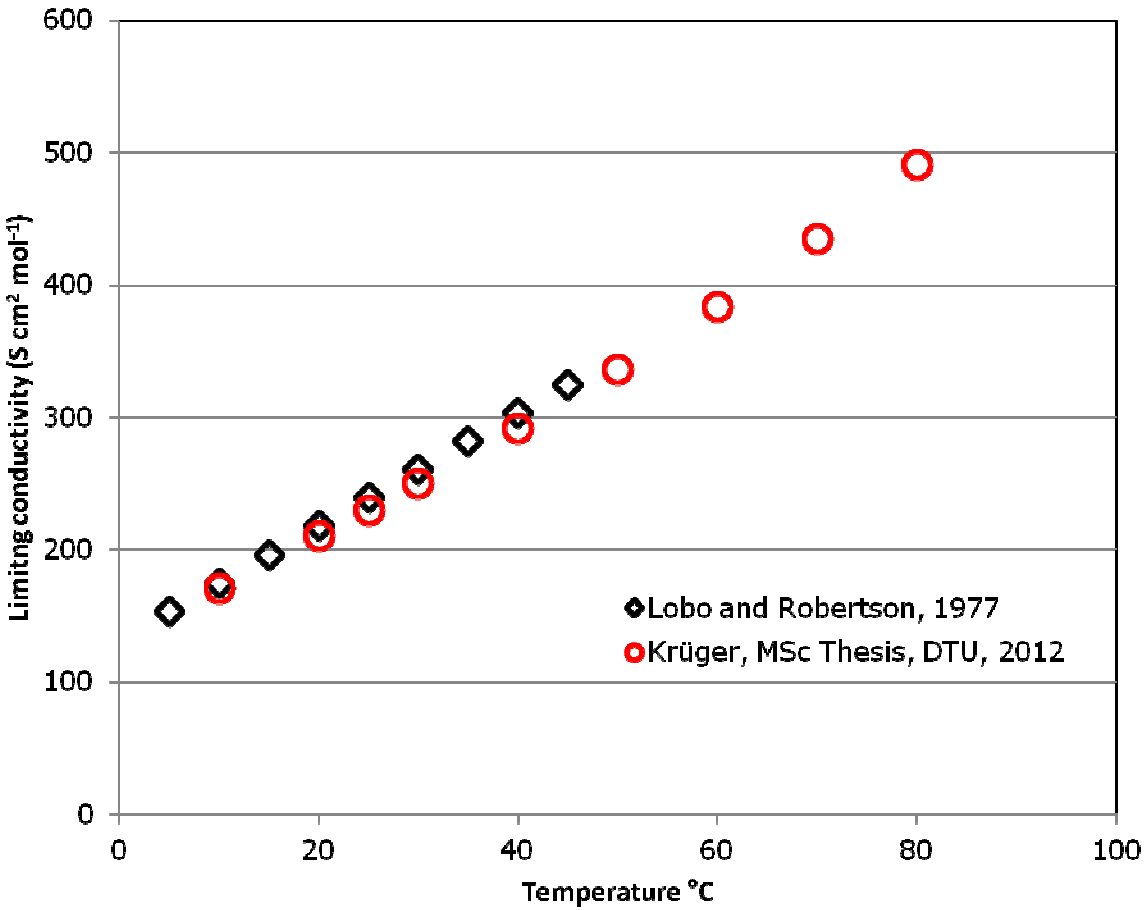
Eksperiments in glove box



Conductivity at infinite dilution Λ_0



Limiting conductivity of cyclohexylamine compared with data found in literature

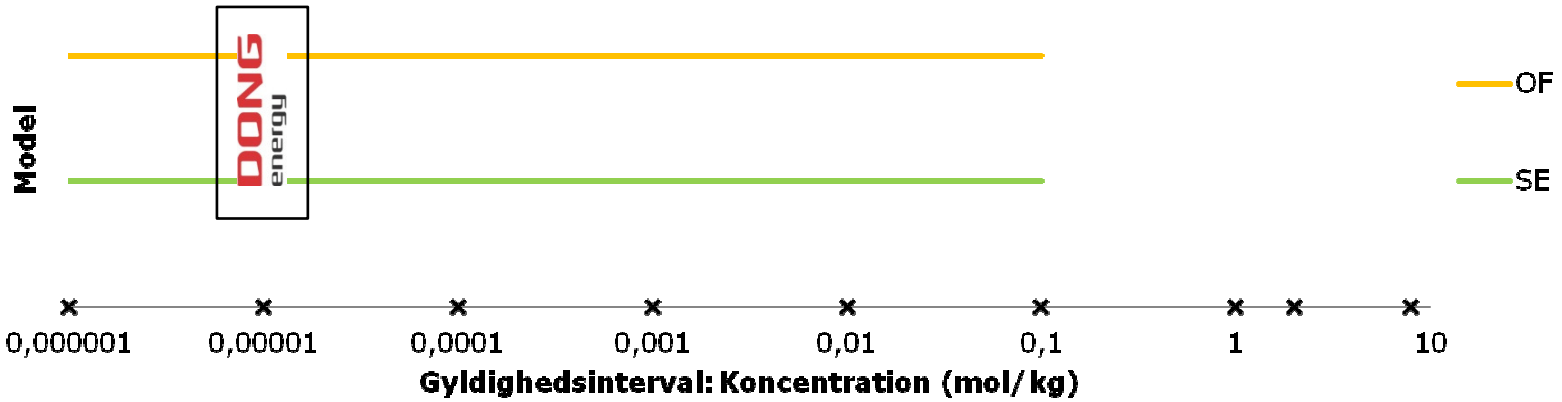


Modeling

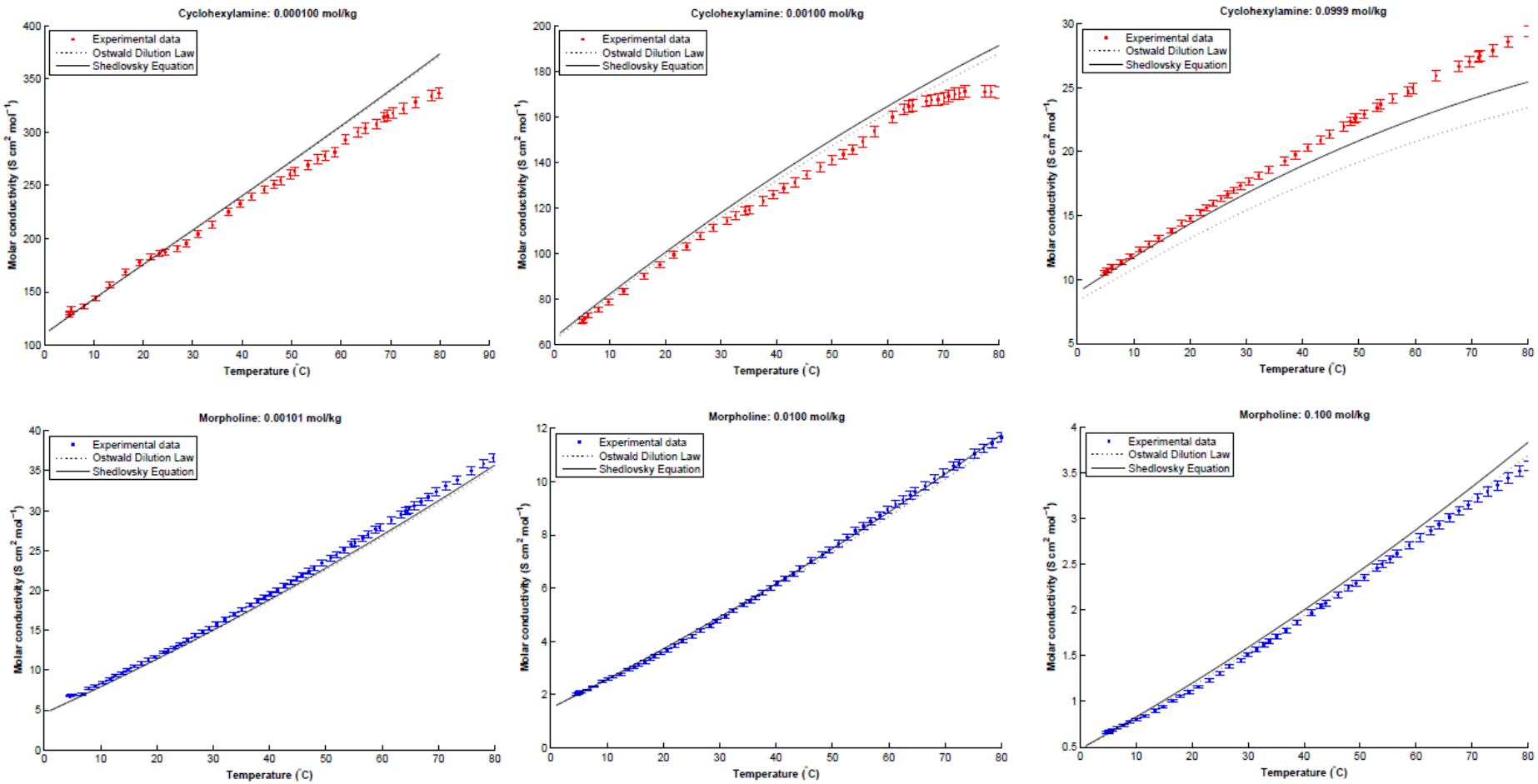
Debye-Hückel based models

Ostwald's dilution law (OF): $$\frac{1}{\Lambda_c} = \frac{1}{\Lambda_c^\circ} + \frac{\Lambda_c c}{K_b(\Lambda_c^\circ)^2}$$

Shedlovsky's equation (SE): $$\frac{1}{\Lambda S(Z)} = \frac{1}{\Lambda^0} + \frac{c\Lambda\gamma_\pm^2 S(Z)}{K_b(\Lambda^0)^2}$$



Models vs. data

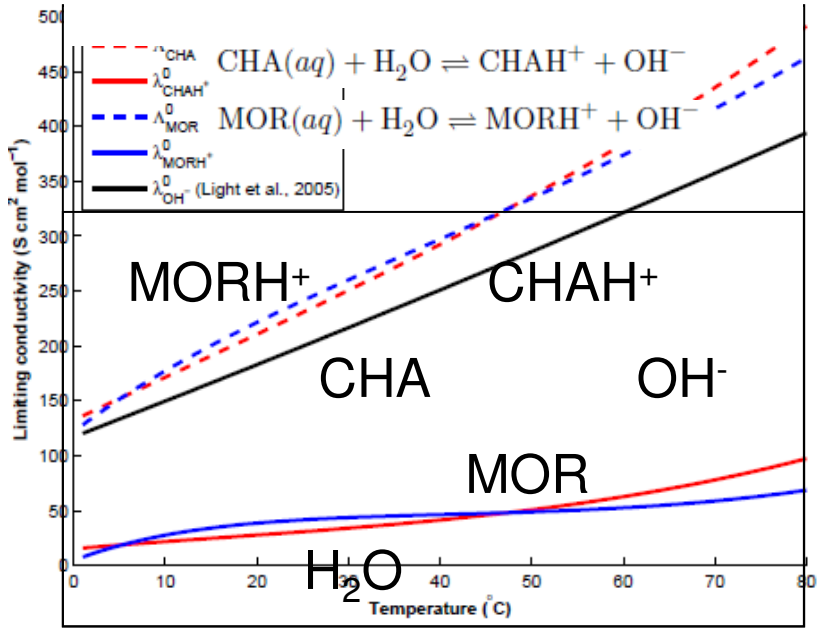


From conductivity to pH in morpholine – cyclohexylamine mixtures

$\Lambda^0 = \sum_i \nu_i \lambda^0_i$

$\Lambda = \alpha \Lambda^0$

$\Lambda = \sum_i \alpha_i \nu_i \lambda^0_i$



$$\Lambda = \alpha_1 \lambda^0_{\mathrm{CHAH^+}} + \alpha_2 \lambda^0_{\mathrm{MORH^+}} + (\alpha_1 + \alpha_2)\lambda^0_{\mathrm{OH^-}}$$

$$K_{b,CHA} = \frac{[\mathrm{CHAH^+}][\mathrm{OH^-}]}{[\mathrm{CHA}][\mathrm{H_2O}]} \approx \frac{\alpha_1 c_1(\alpha_1 c_1 + \alpha_2 c_2)}{c_1(1-\alpha_1)x_w} \times \frac{\gamma_\pm^2}{\gamma_{\mathrm{CHA}}\gamma_w}$$

$$K_{b,MOR} = \frac{[\mathrm{MORH^+}][\mathrm{OH^-}]}{[\mathrm{MOR}][\mathrm{H_2O}]} \approx \frac{\alpha_2 c_2(\alpha_1 c_1 + \alpha_2 c_2)}{c_2(1-\alpha_2)x_w} \times \frac{\gamma_\pm^2}{\gamma_{\mathrm{MOR}}\gamma_w}$$

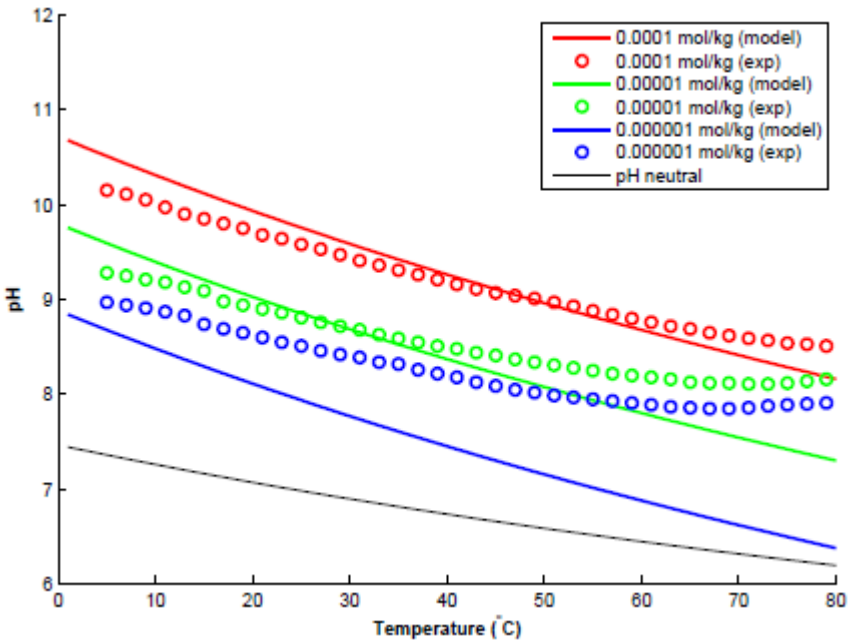
$$c_1 = 2.5 \times \frac{M_{\mathrm{MOR}}}{M_{\mathrm{CHA}}} \times c_2$$

From conductivity to pH

- 4 equations and 4 unknowns (c_1, c_2, α_1, α_2)

- $[OH^-] = \alpha_1 c_1 + \alpha_2 c_2$

- $pH \approx -\log K_w + \log [OH^-]$



Limiting conductivity from Walden product $\lambda^0\eta$

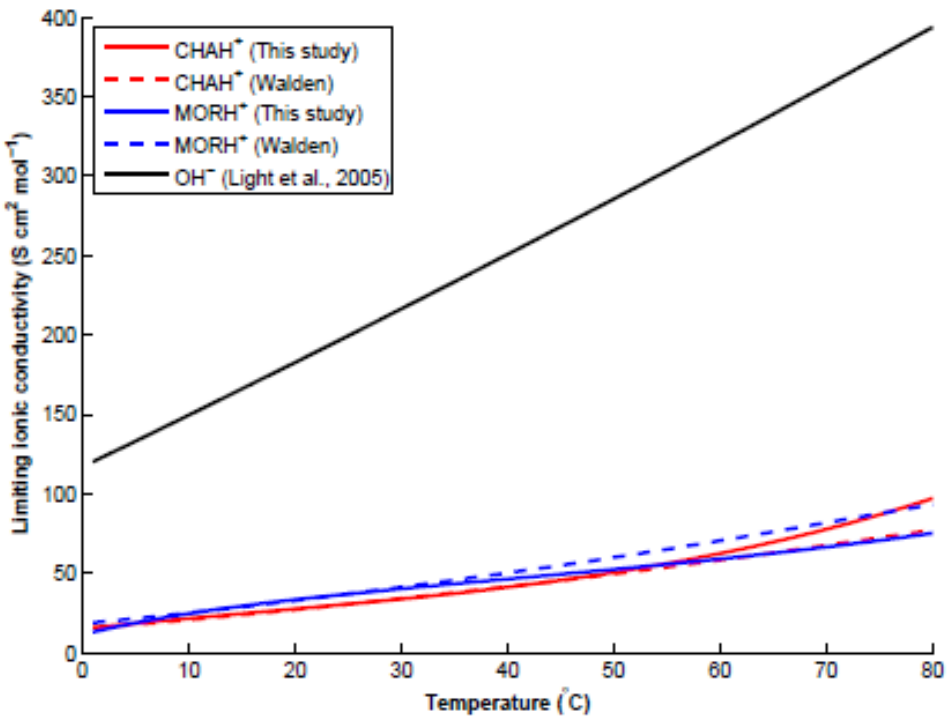


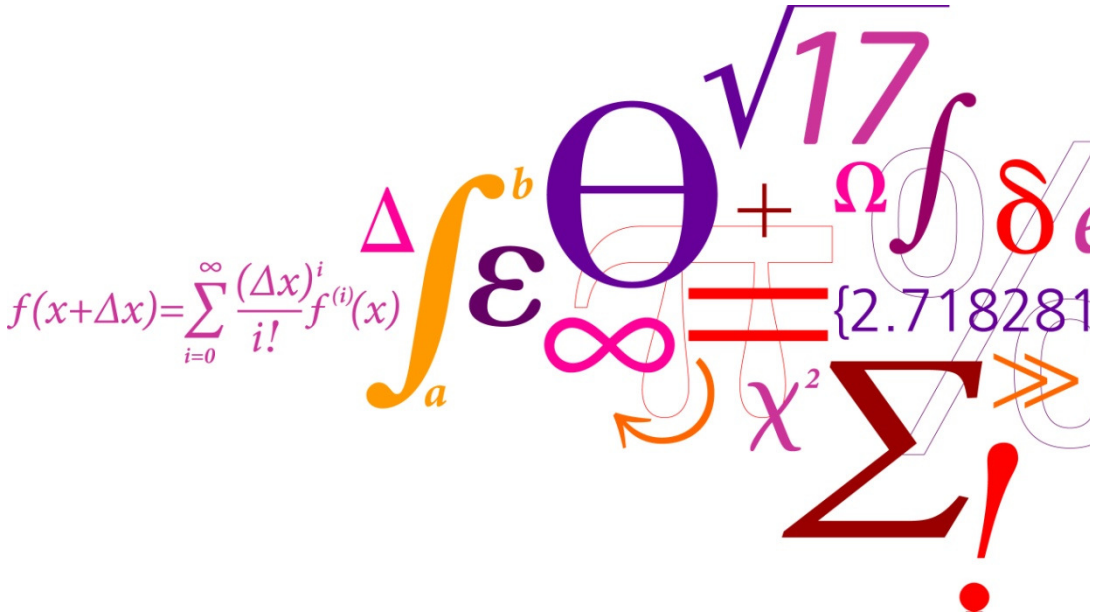
Figure 44: Limiting conductivities of $CHAH^+$ and $MORH^+$ determined from a) K_b at 25°C, experimental data and the Walden product and b) K_b at temperatures 5-80°C and experimental results (full line).

Conclusion

- Method for determination of conductivity at low ionic strength has been developed

- $\Lambda^0(T)$ for cyclohexylamine and morpholine has been determined at temperatures between 10 and 80℃

- Ostwald's and Shedlovsky's equations gives reasonable estimations of the concentration dependence of conductivity

- pH can be determined from the conductivity measurements. Measurement of pH in low conductivity solutions require special reference electrodes due to liquid junction potentials

Questions?