

# **How to model the sorption affinity of cationic organic compounds to natural organic matter?**

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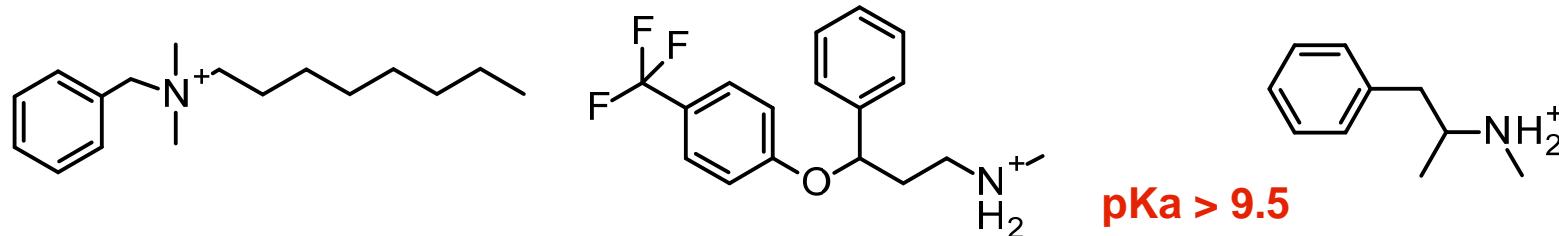
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# Cationic organics



$\text{pK}_a > 9.5$

## Fate models optimized for neutral organic chemicals

Natural organic matter (NOM) + clay + membranes:

**Negatively charged** sorbents

**Positively charged** organic chemicals:

- very hydrophilic + *high sorption affinity* ( e.g. soil )
- models needed: availability, transport, tox, etc.

# Outline

- examples sorption organic cations

**sorption process = ion-exchange**

**I-E sorption model: ionic + nonionic interactions**

- nonionic interactions: single descriptors

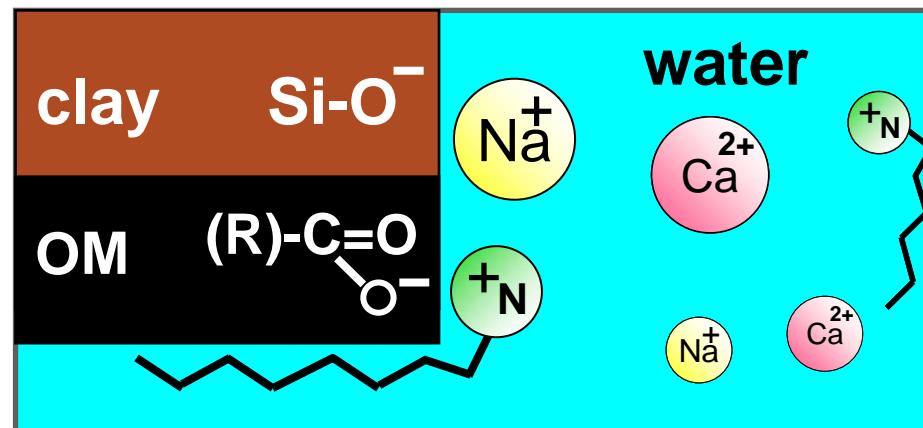
**nonionic interactions: multiple descriptors**

**(un)successful examples**

# ion-exchange for cationic surfactants

(Ishiguro et al. Colloids Surf A. 2007, pp29-39)

- Sorption **decreases** at higher salinity  
**ionic interactions**
- Sorption **increases** with longer alkyl chains  
**nonionic interactions**

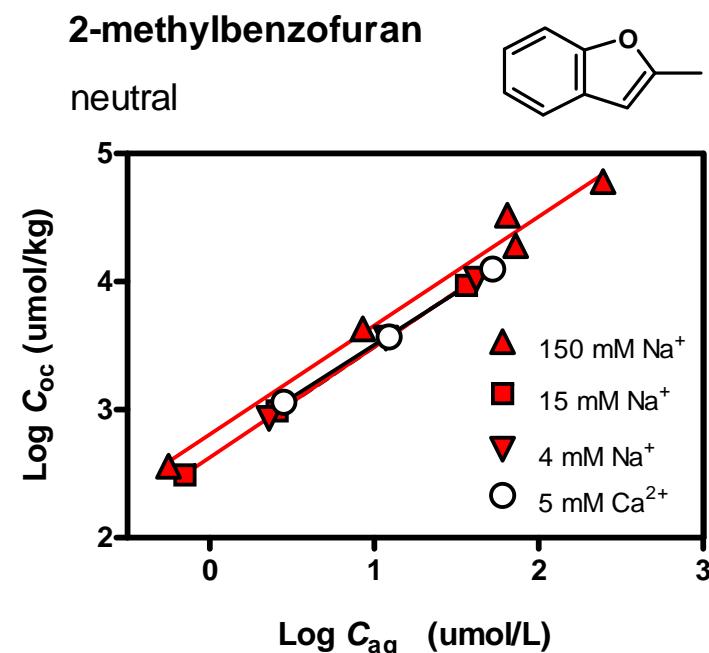


# HPLC-column experiments

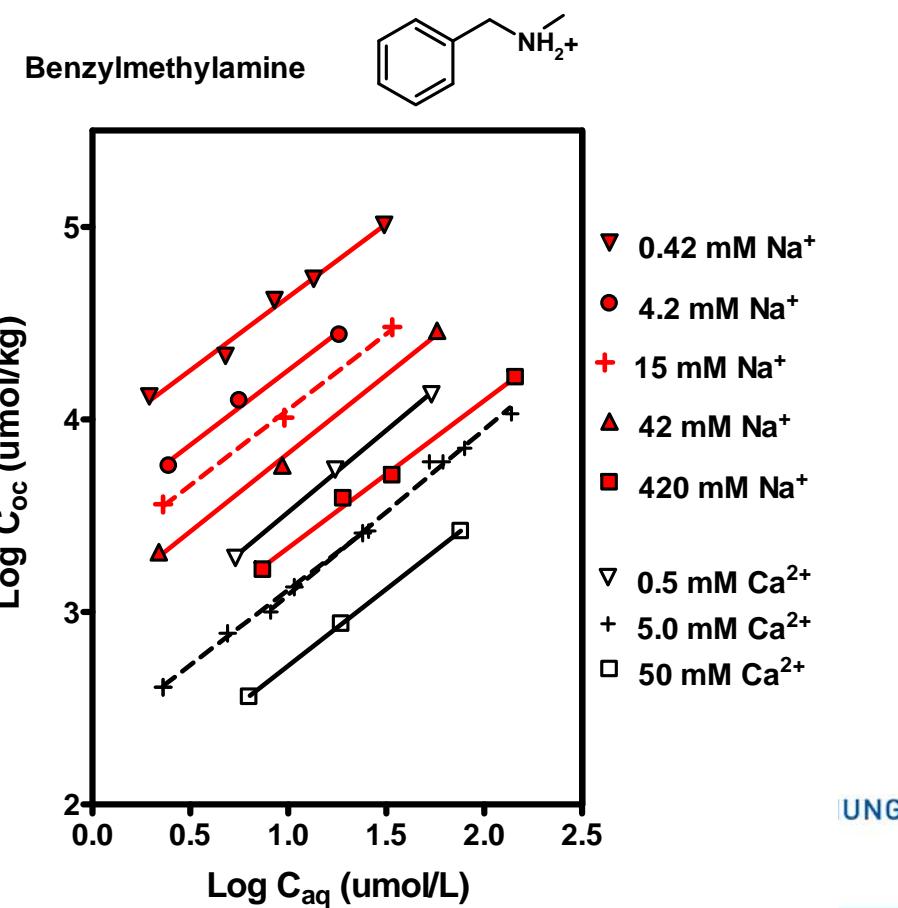
- HPLC column filled with raw NOM (pahokee peat)
  - Eluents = 100% water
- Column retention data for ~70 organic cations
  - **Retention time  $\sim \text{Log } K_d$**
- **Control eluents composition**
- **Fully condition NOM to medium**

# HPLC-column experiments: salt

$K_d$  for neutral compounds  
not affected by salt

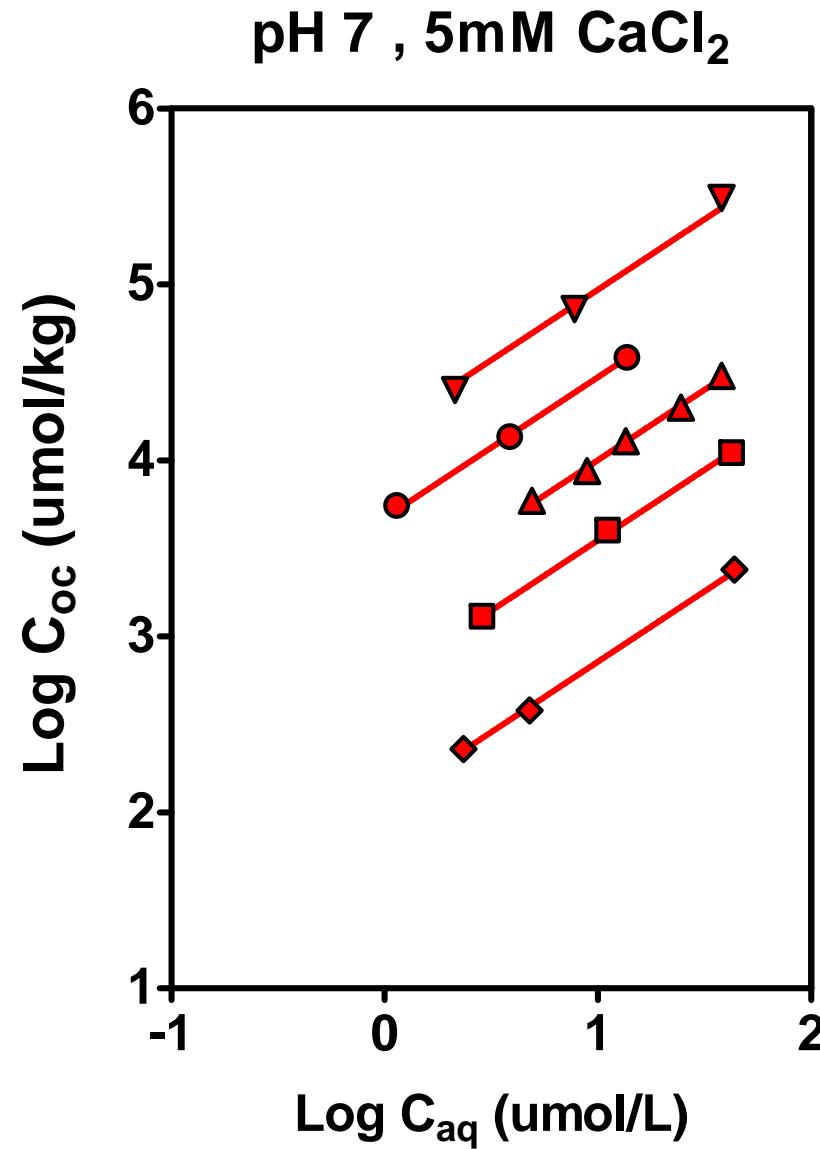
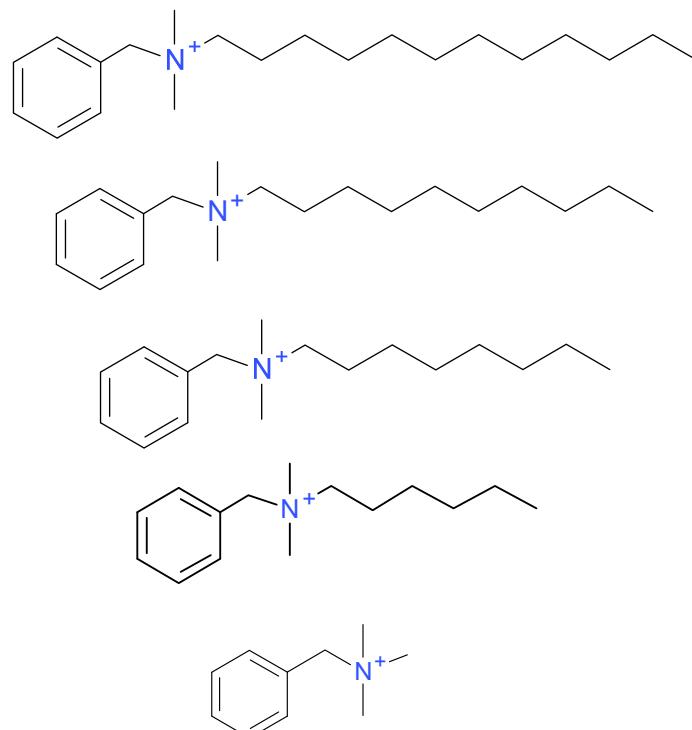


$K_d$  for cationic compounds  
differs factor 100 due to salt

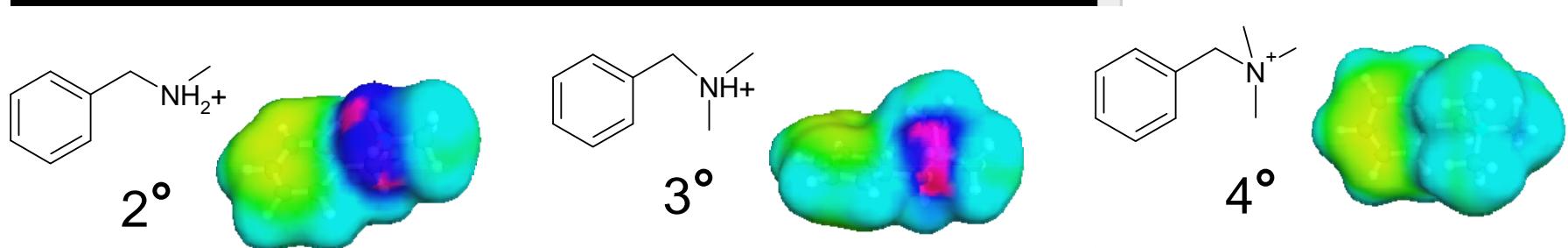
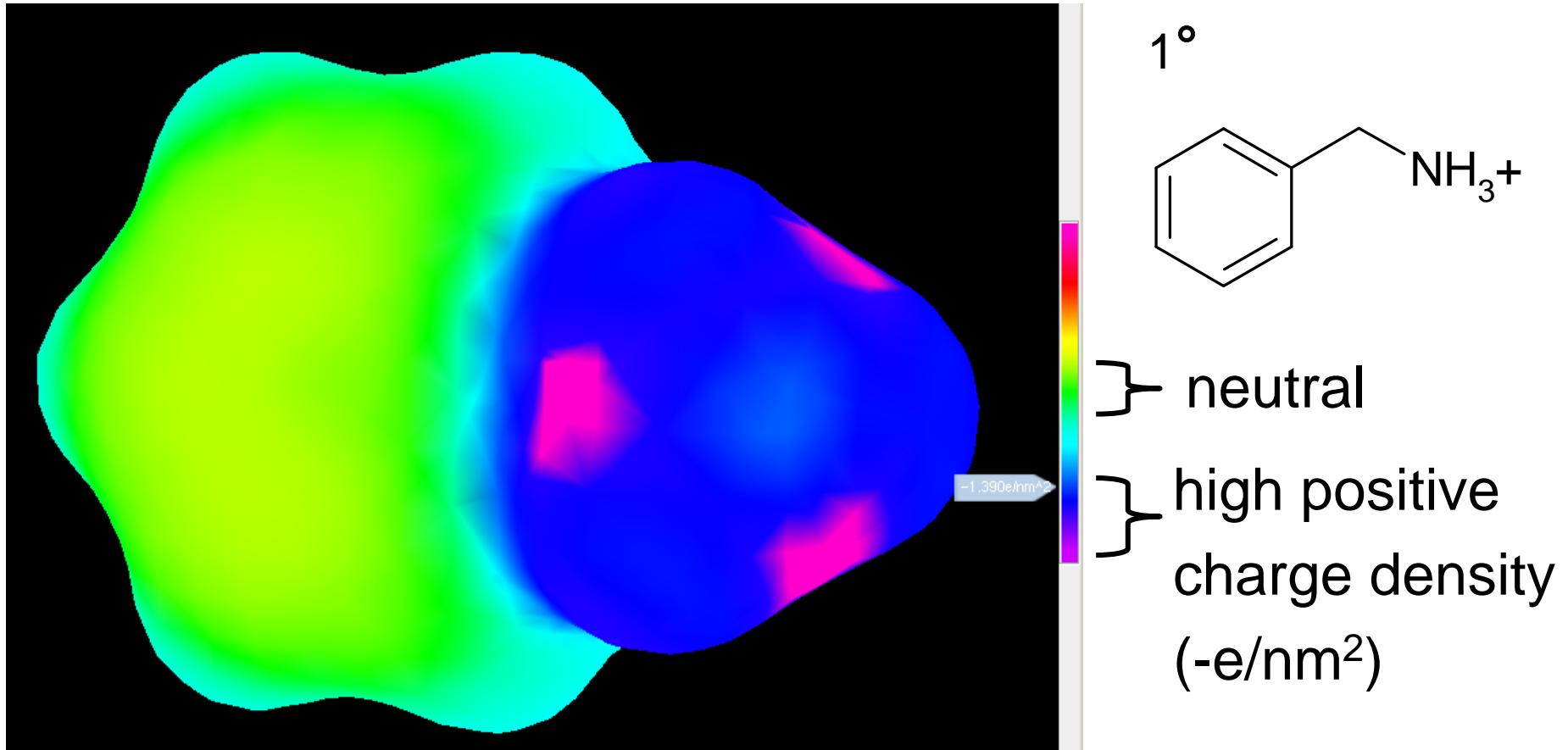


# HPLC-column experiments: alkyl chain

$\log K_d$  increases  
with longer alkyl chain



# Type of amine: charge density differences



# ion-exchange model

How to model ion-exchange affinity of organic cations?

Aim: predictive model based on meaningful parameters

$$\text{Log } K_d = \text{ionic term} + \text{non-ionic term}$$

dissolved salts      molecular descriptors

type of amine

(acidic groups)      (structure of sorbent)

**ionic (metals): NICA-Donnan**

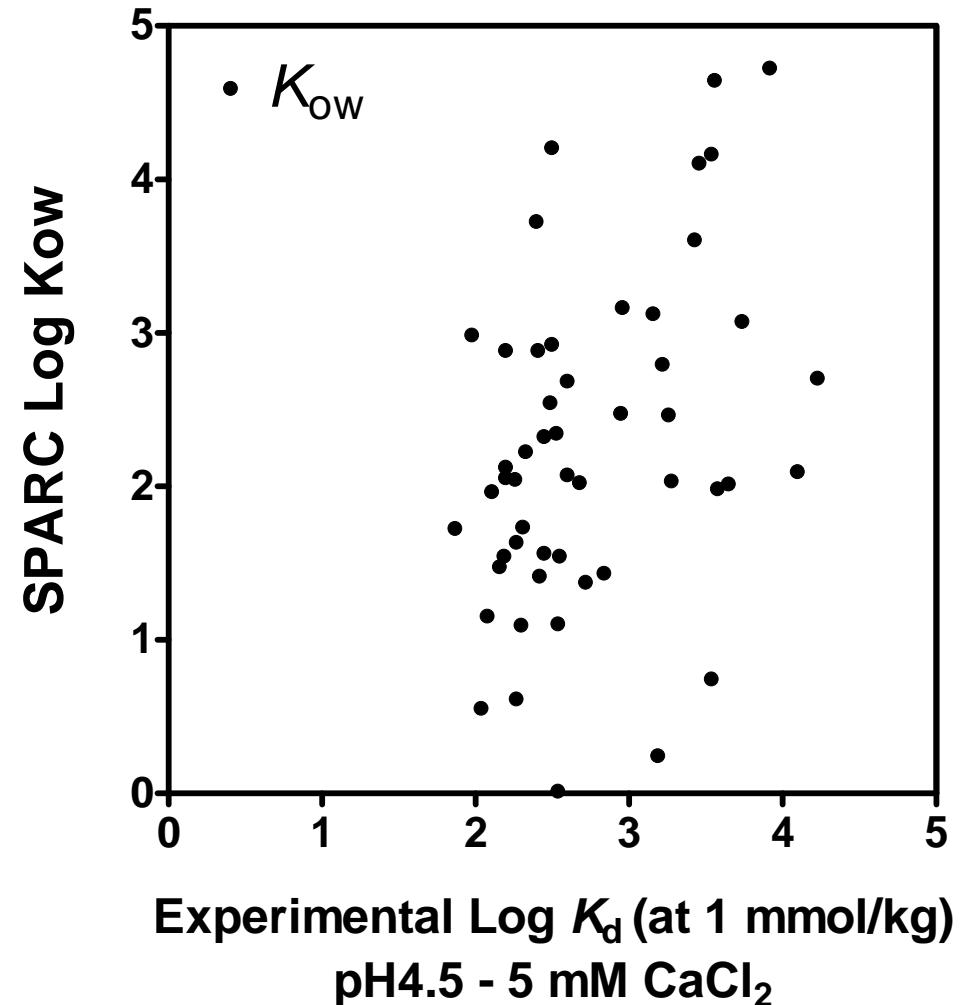
**nonionic:  $K_{ow}$ , pp-LFER, COSMOtherm**

# Single parameter ion-exchange model

Can't we just use  $K_{\text{OW}}$  to model the nonionic-term ?

- Column retention data for ~70 organic cations
- **Constant eluents:**  
**Constant ionic interactions**

SPARC:  
<http://archemcalc.com/>

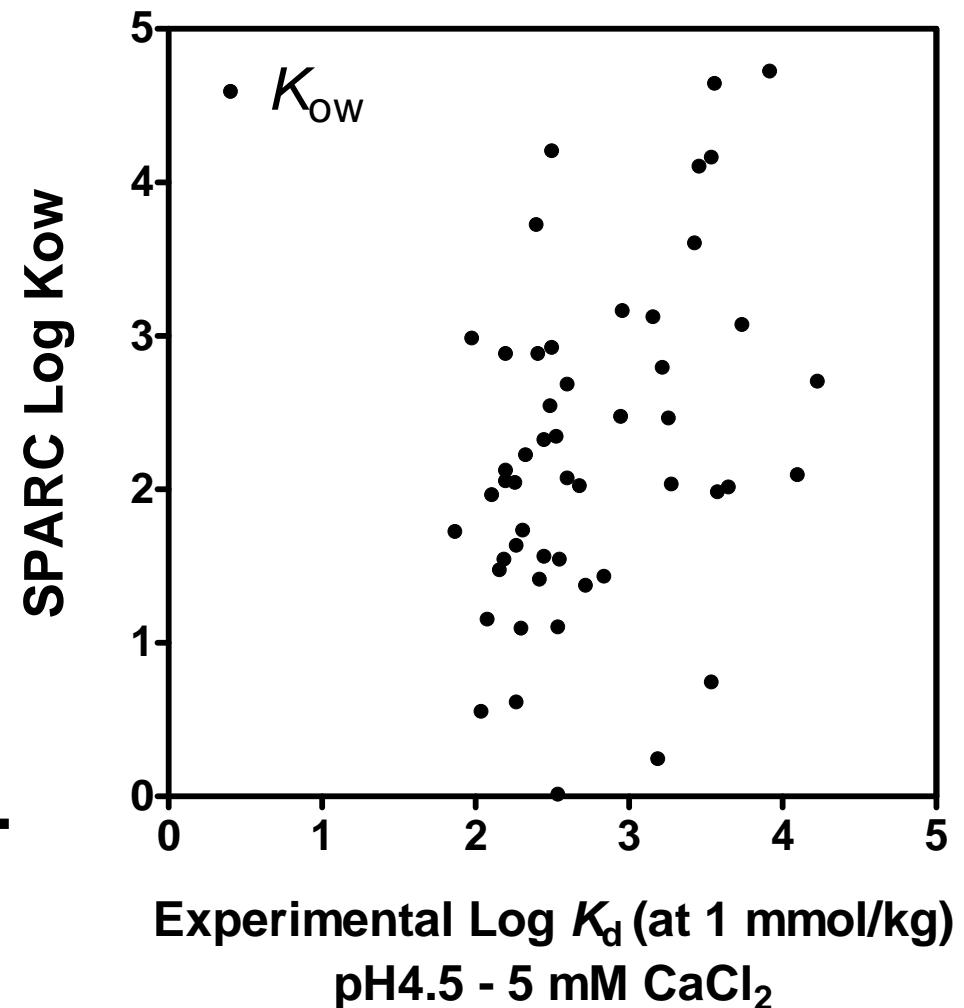
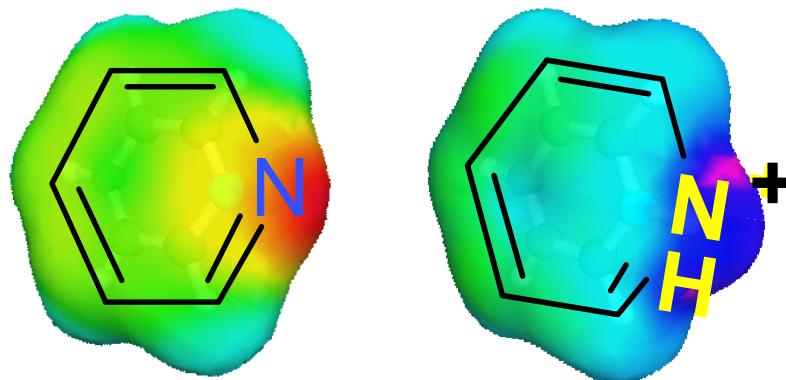


# Single parameter ion-exchange model

$K_{\text{OW}}$  as a single descriptor:

not adequate

- No quaternary compounds:  
permanently charged
- $K_{\text{OW}}$  only for Neutrals:  
influence highly polar N

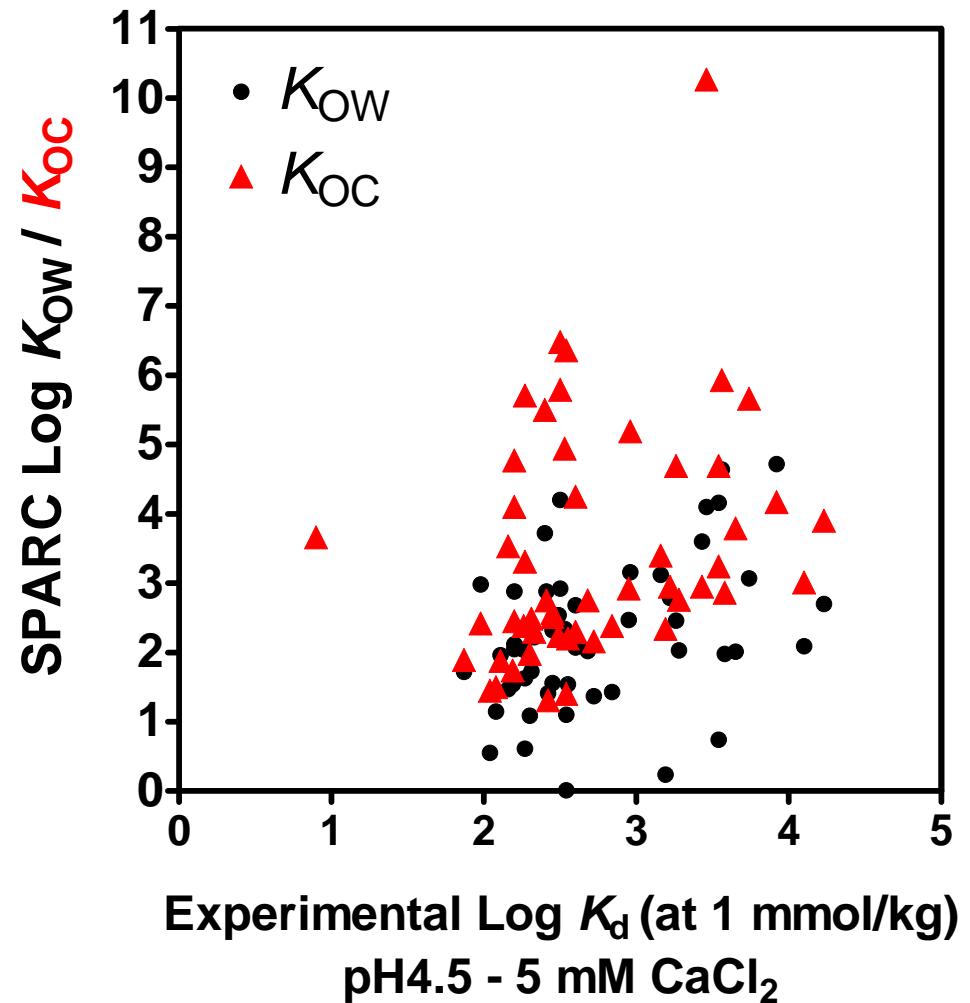
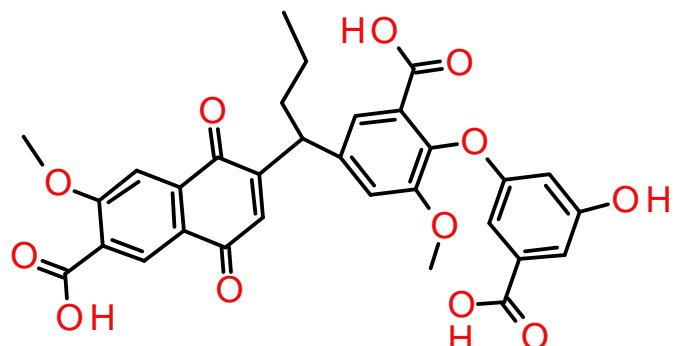


# Single parameter ion-exchange model

*neutral NOM model instead of  $K_{OW}$*

is not adequate

- SPARC only for neutral
- No quaternary compounds: permanently charged
- Neutral NOM : polarity ?
- Adequate NOM model ?



# Single parameter ion-exchange model

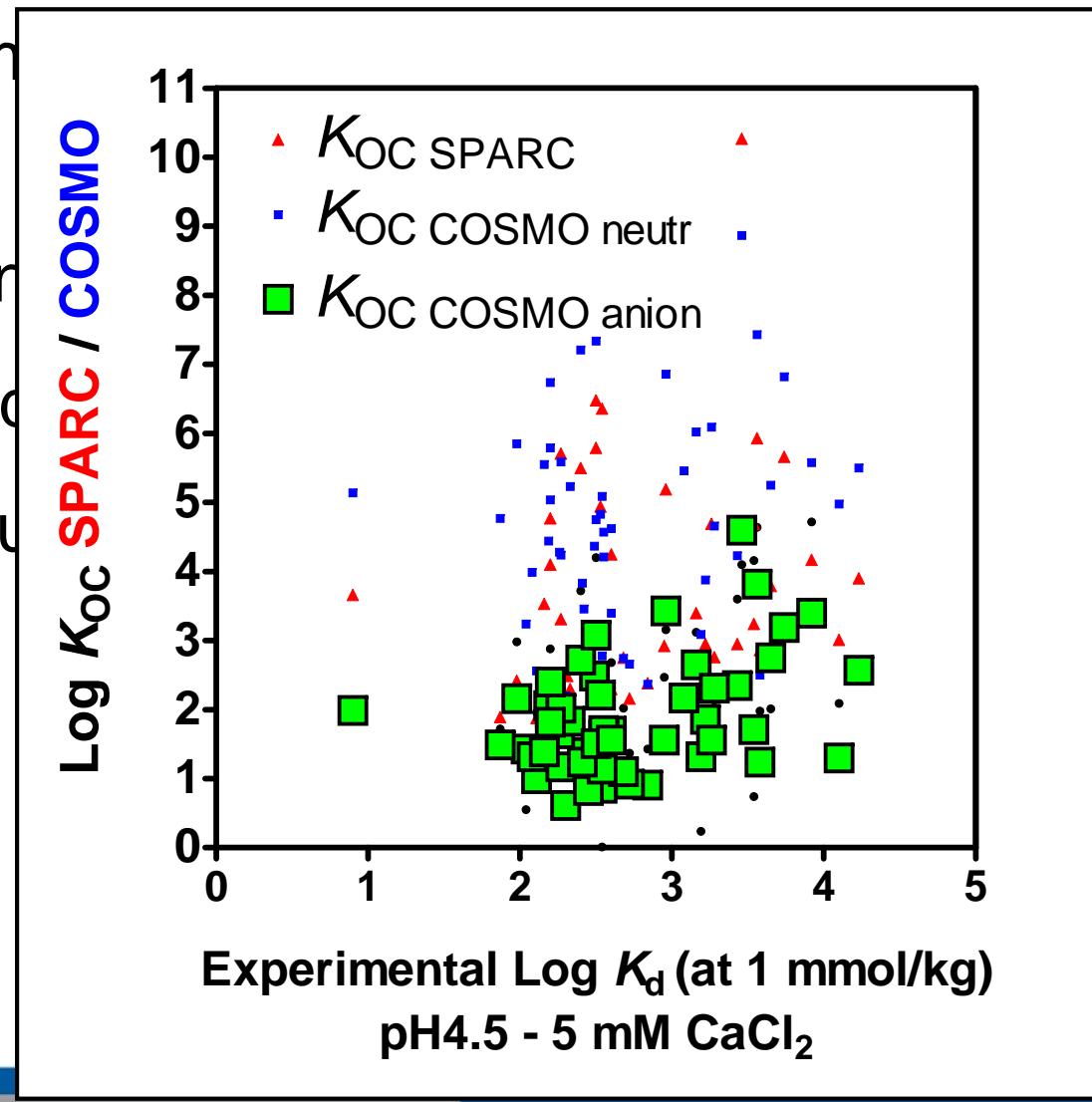
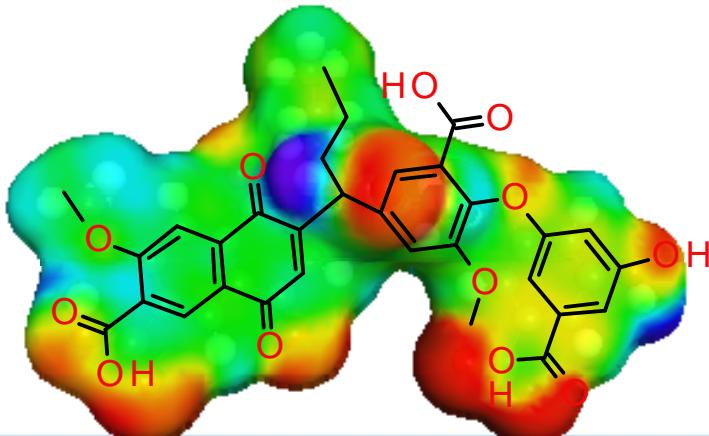
Can we simulate sorption of cations ?

COSMOthermX: quantum

COSMOthermX allows ion

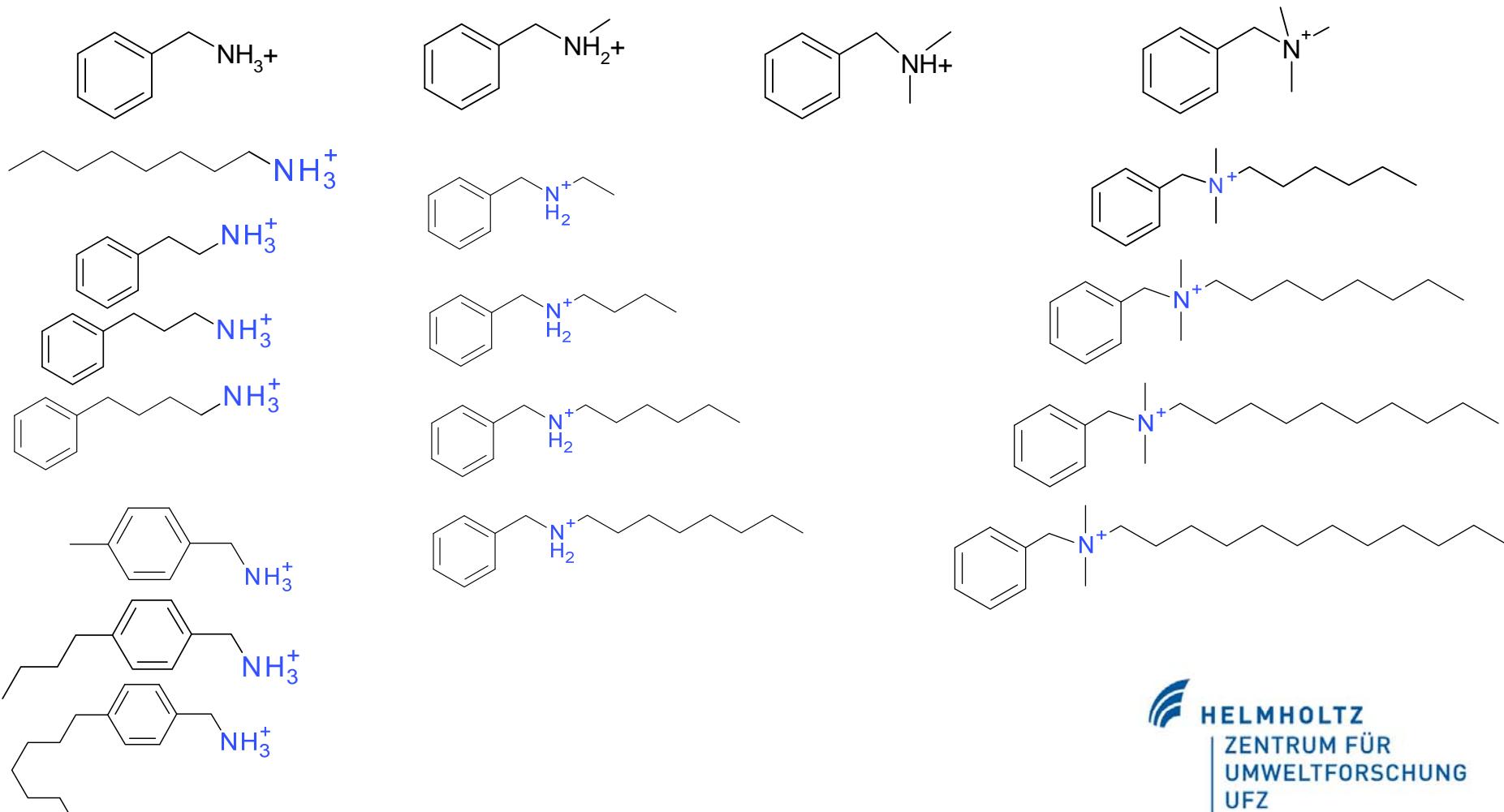
and charged NOM mod

NOM models available, bu

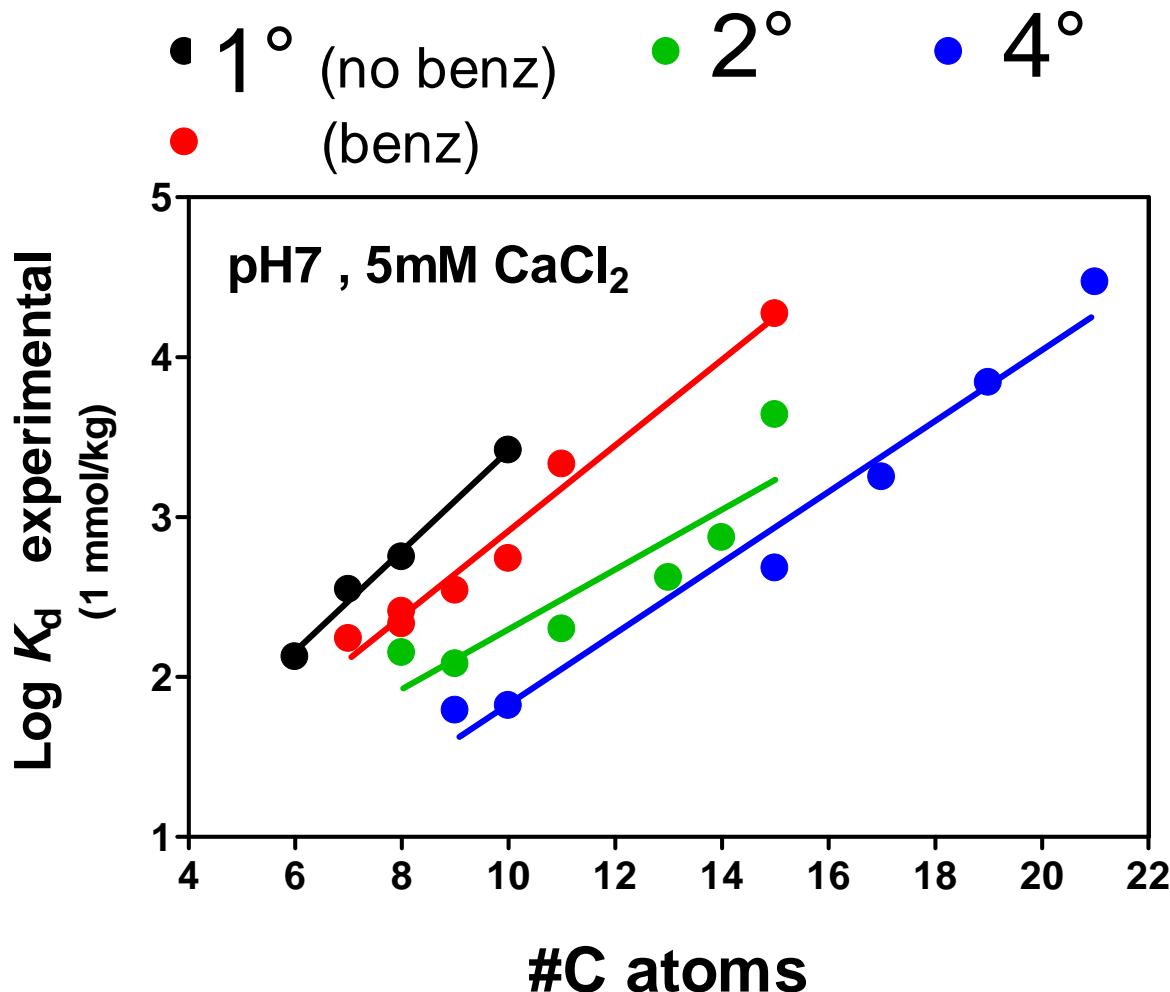


# Multi-parameter nonionic term: Step 1 „Non-specific“ organic cation structures

only various types of N+, alkyl chains and/or benzene

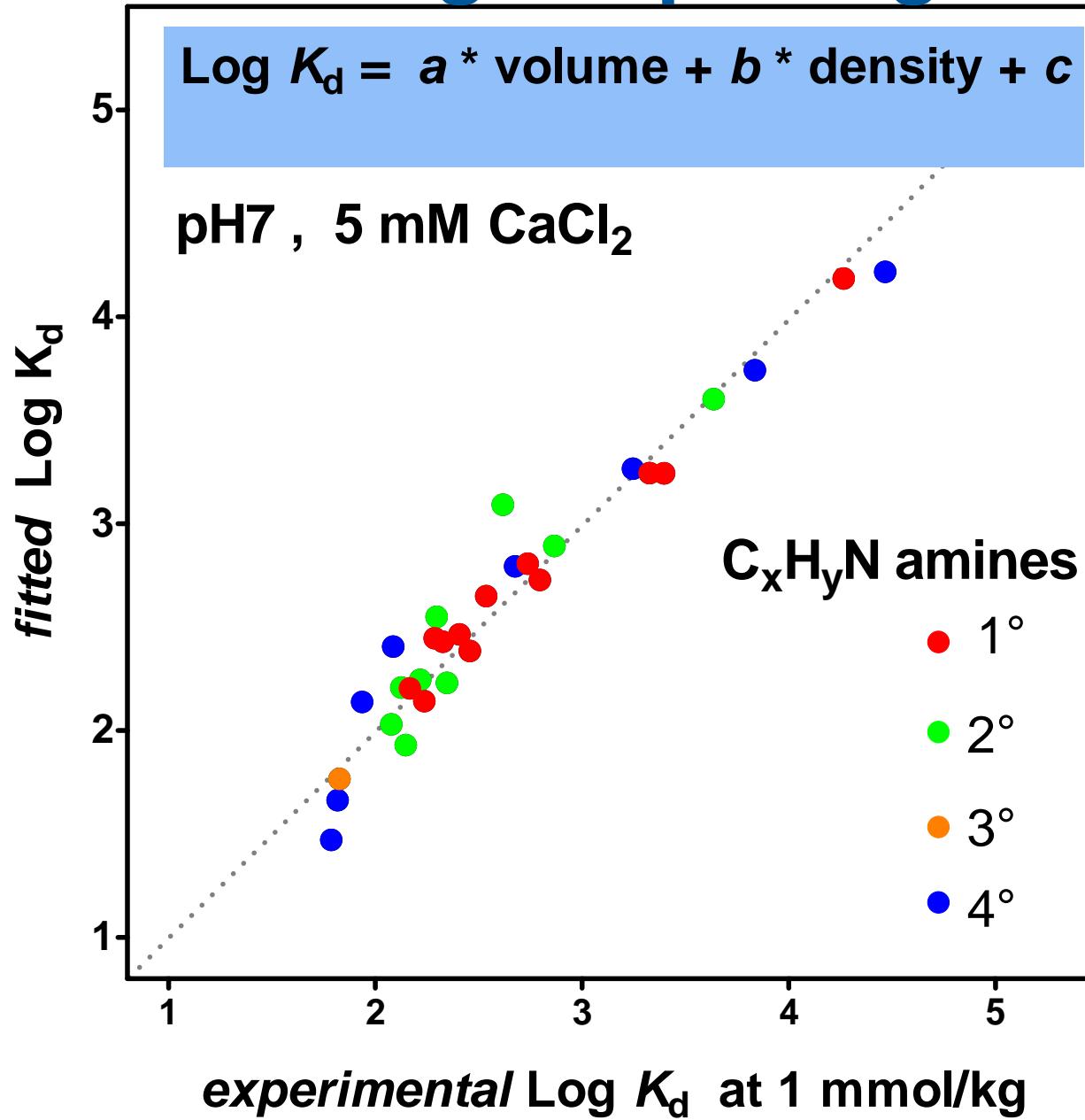


# Modeling simple organic cations



Type of amines:  
 $\text{Log } K_d \text{ 1}^\circ > \text{2}^\circ > \text{4}^\circ$   
charge density  
Higher  $\text{Log } K_d$   
for more #C  
mol. volume

# Modeling simple organic cations



$R^2=0.94$   
RMSE = 0.17

# **nonionic term: Step 2**

## **Complex organic cation structures**

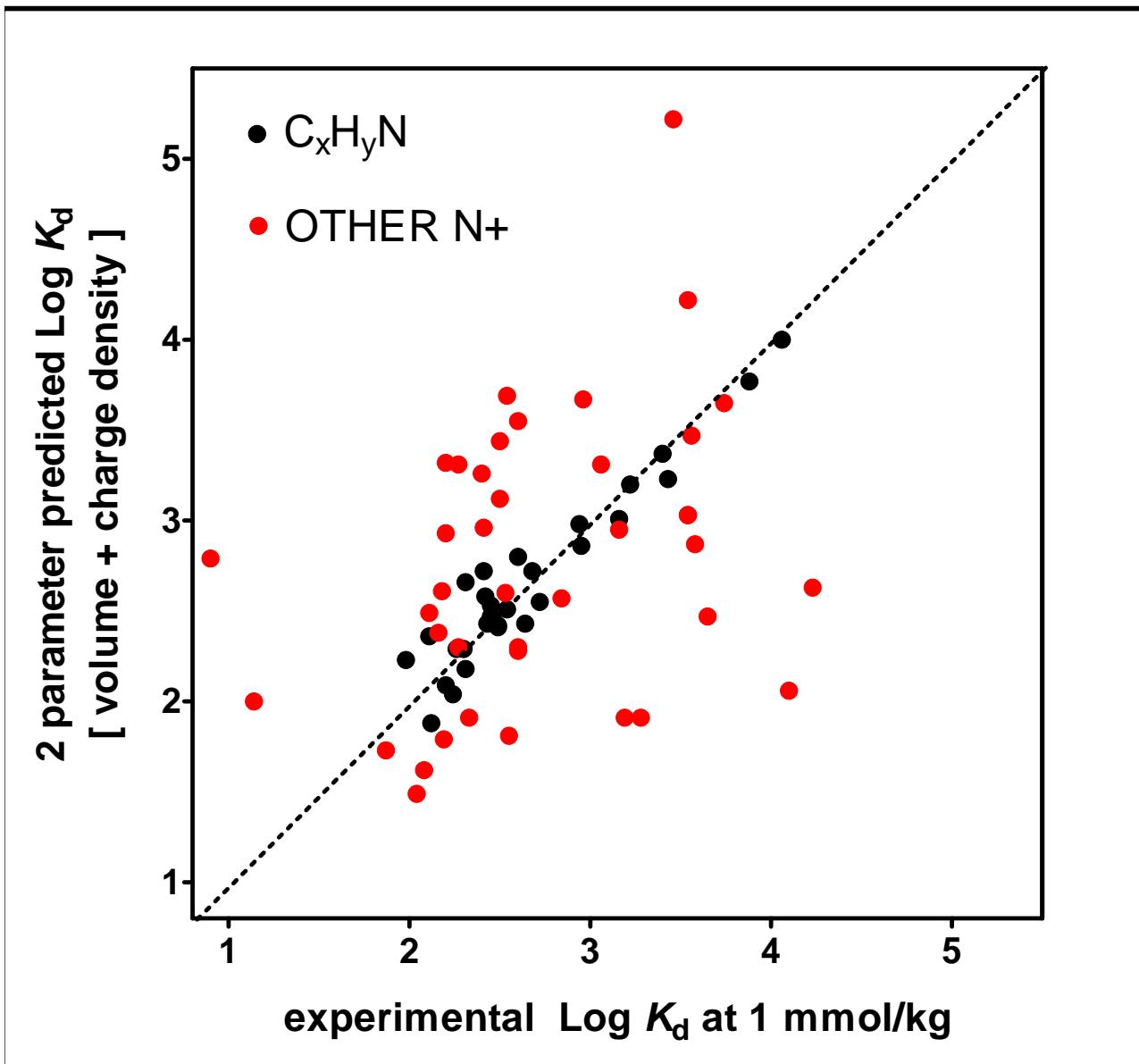
- pharmaceuticals
  - beta-blockers
  - anaesthetics
- drugs of abuse
- pesticides
- neurotransmitter

**calculate non-specific interaction term: volume + charge density**

**explain specific interaction term: descriptors X, Y, Z**

# nonionic term: Step 2

## Complex organic cation structures

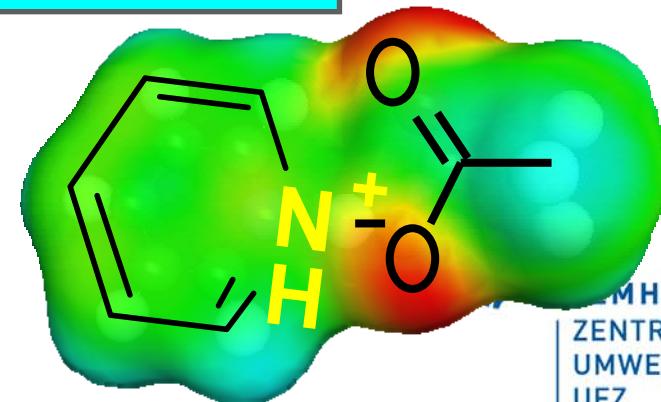
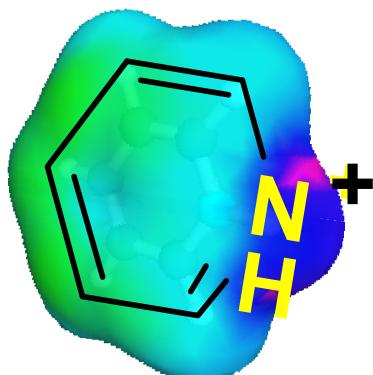
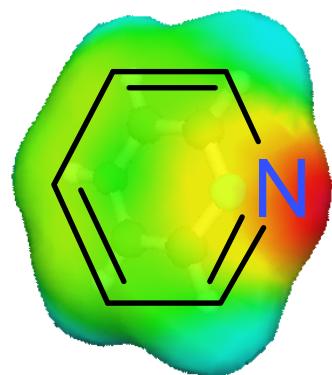
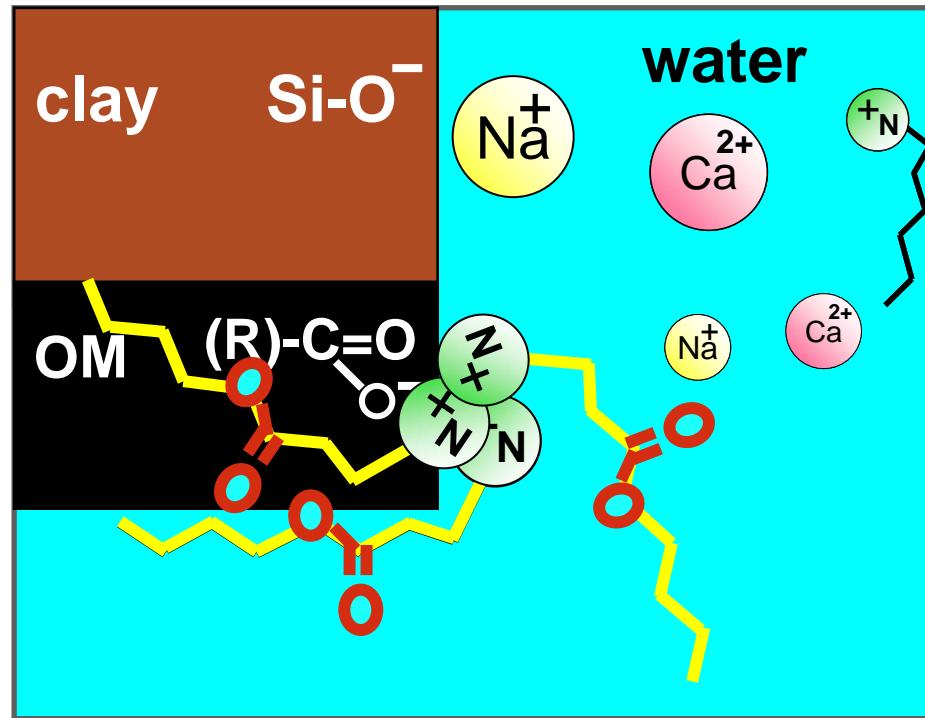


# Multi parameter ion-exchange model

- empirical fitting  
CODESSA software: 104 molecular descriptors
- Neutrals: meaningful descriptors covering all interactions  
pp-LFER: 5 descriptors
  - Volume
  - Refractive index
  - Dipolarity
  - Hydrogen bond acceptor
  - Hydrogen bond donor

} non-specific  
} specific

# where is the nonionic interaction site ?



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# Conclusions

Highly consistent diverse data set available

$\text{Log } K_d$  range is limited

Successful in modeling simple organic cations

Unsuccessful in modeling specific interactions

Molecular-scale insight needed (3D simulations)

