Comparison of the Reversed-Phase and Ion-Exchange Contributions to Retention on Polybutadiene Coated Zirconia and Octadecyl Silane Bonded Silica Phases

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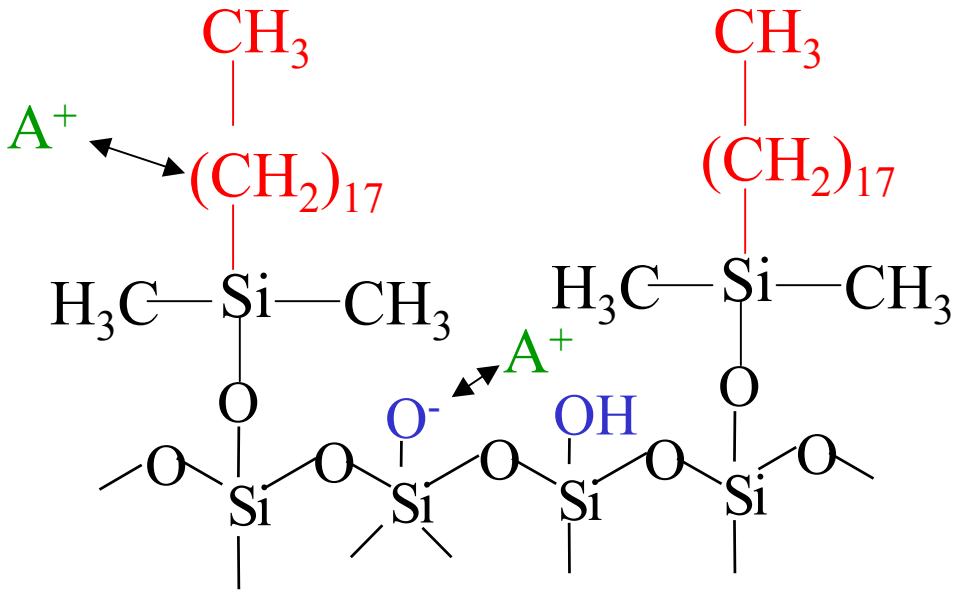
Outline

- Mixed-mode retention on silica and zirconia based stationary phases
  - Reversed-phase vs. ion-exchange interactions
- Retention models in mixed-mode retention mechanism
  - One-site vs. two-site model
  - Three plots: log k' vs. n_{CH2}, log k' vs. log $[C^+]_m$, and k' vs. $1/[C^+]$
  - Relative contribution of ion-exchange retention: k'_{IEX} / k'
- Conclusions
  - One-site model is WRONG!
  - Two-site model is more accurate.

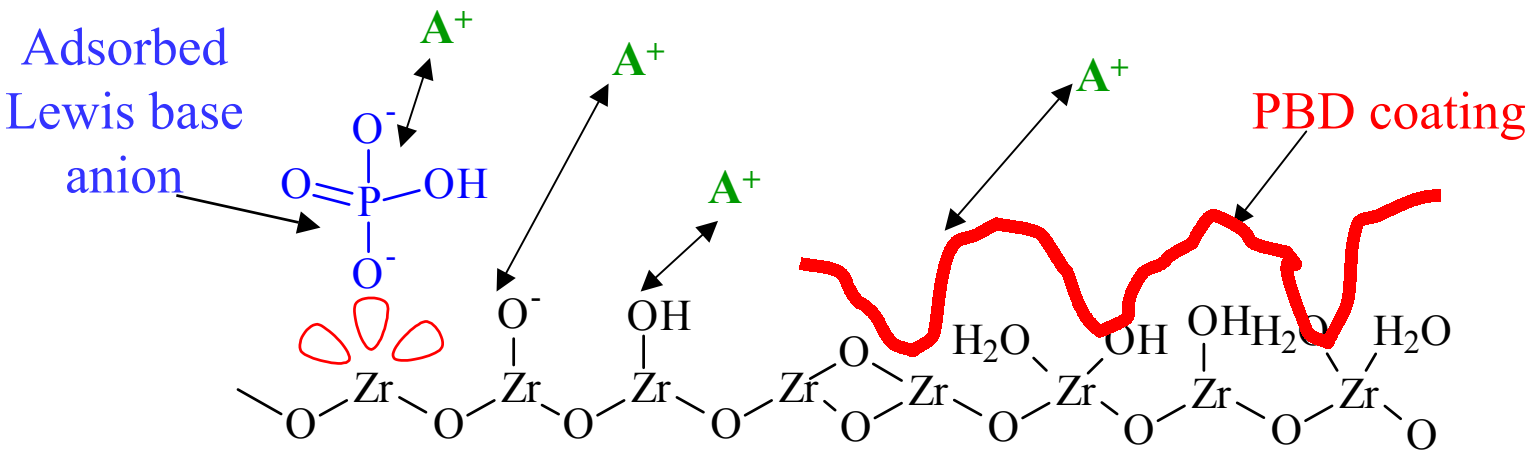
Mixed-Mode Separation on ODS Phases



- Bonded C_{18} Chains — Reversed-Phase (RP) Interactions
- Ionized Silanol Groups — Ion-Exchange (IEX) Interactions

✓ Mixed-mode retention mechanism!

Mixed-Mode Separation on PBD-ZrO_2



- PBD Coating — Reversed-Phase (RP) Moieties
- Lewis Base Anions — Ion-Exchange (IEX) Sites

✓ Mixed-mode retention mechanism!

Columns

ODS columns

Ace

Inertsil ODS3

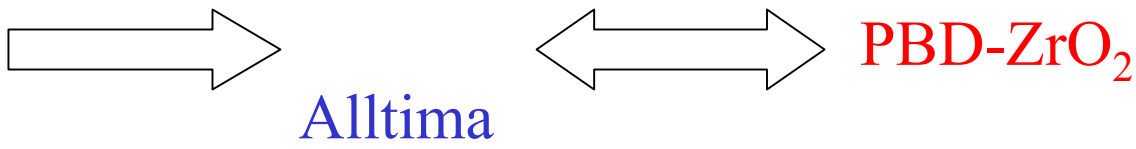
Eclipse XDB

Zorbax Extend

Zorbax SB

Zorbax Rx

Alltima

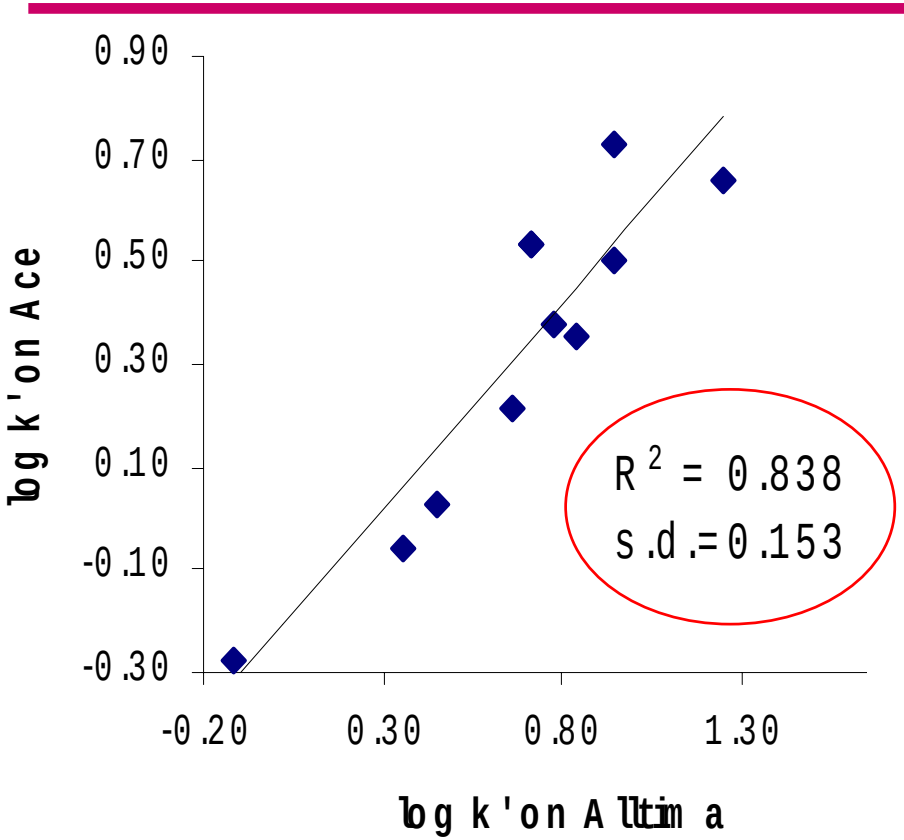


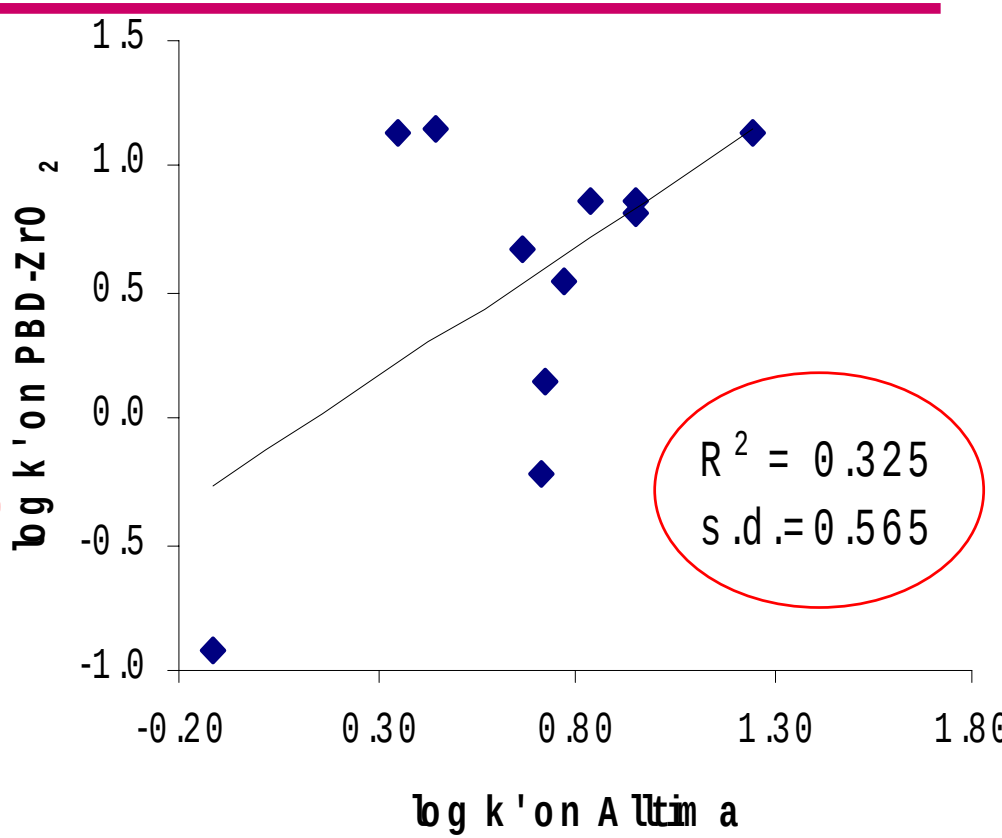
Ace: 5 µm, 100 Å, 300 m^2/g, 15.5% C

Alltima: 5 µm, 100 Å, 350 m^2/g, 16% C

PBD-ZrO_2: 4.1 µm, 500 Å, 11 m^2/g, 2.0% C

κ-κ Plot - log k' on different columns





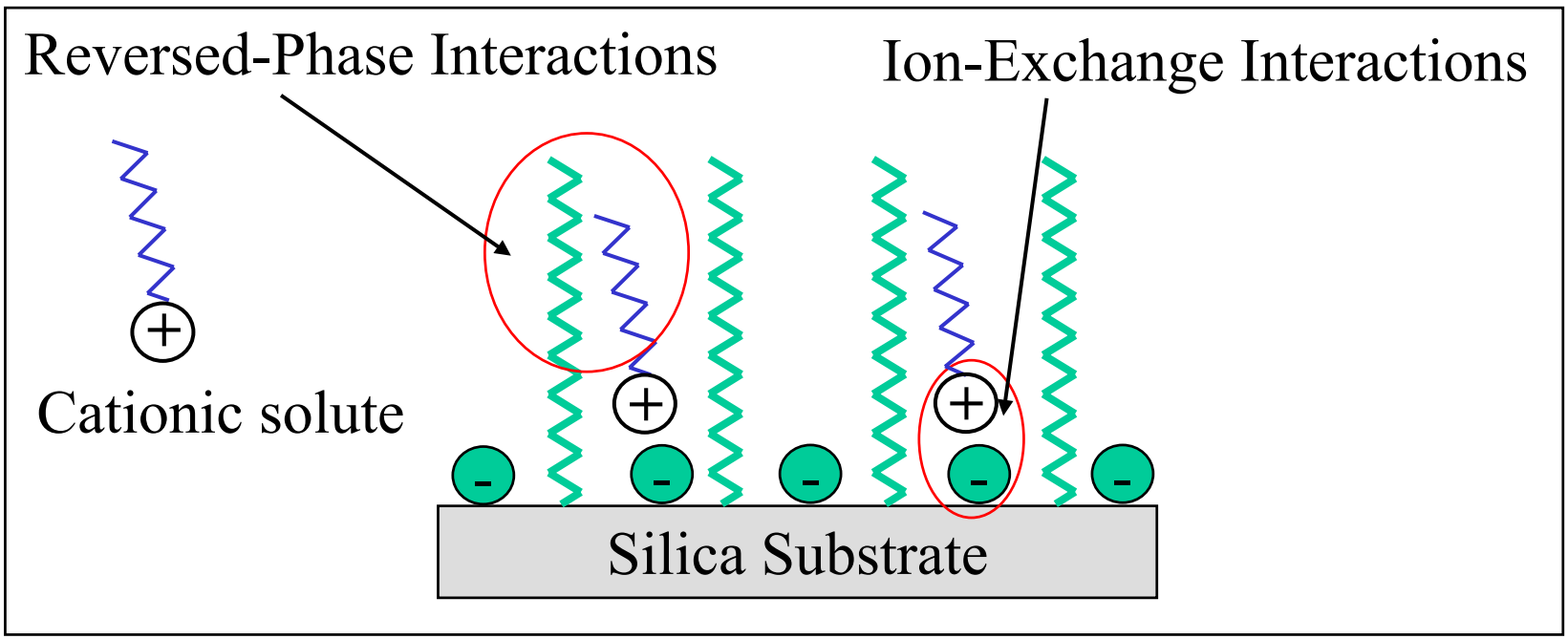
Condition: 72 % MeOH, 25 mM phosphate, pH=6, 35 °C, 1 mL/min. Solutes: 11 antidepressant drugs

- ✓ **Poor correlations in the κ–κ plot indicate changes in selectivity**
- ✓ **PBD-ZrO_2 is really different.**

One-Site Model for Mixed-Mode Retention

ADDITIVE Free Energy $\ln k'_{obs} = \ln(\phi) + \left(\frac{\Delta G^o_{RP}}{RT} + \frac{\Delta G^o_{IEX}}{RT} \right)$

ϕ: the phase ratio for the single type of site.

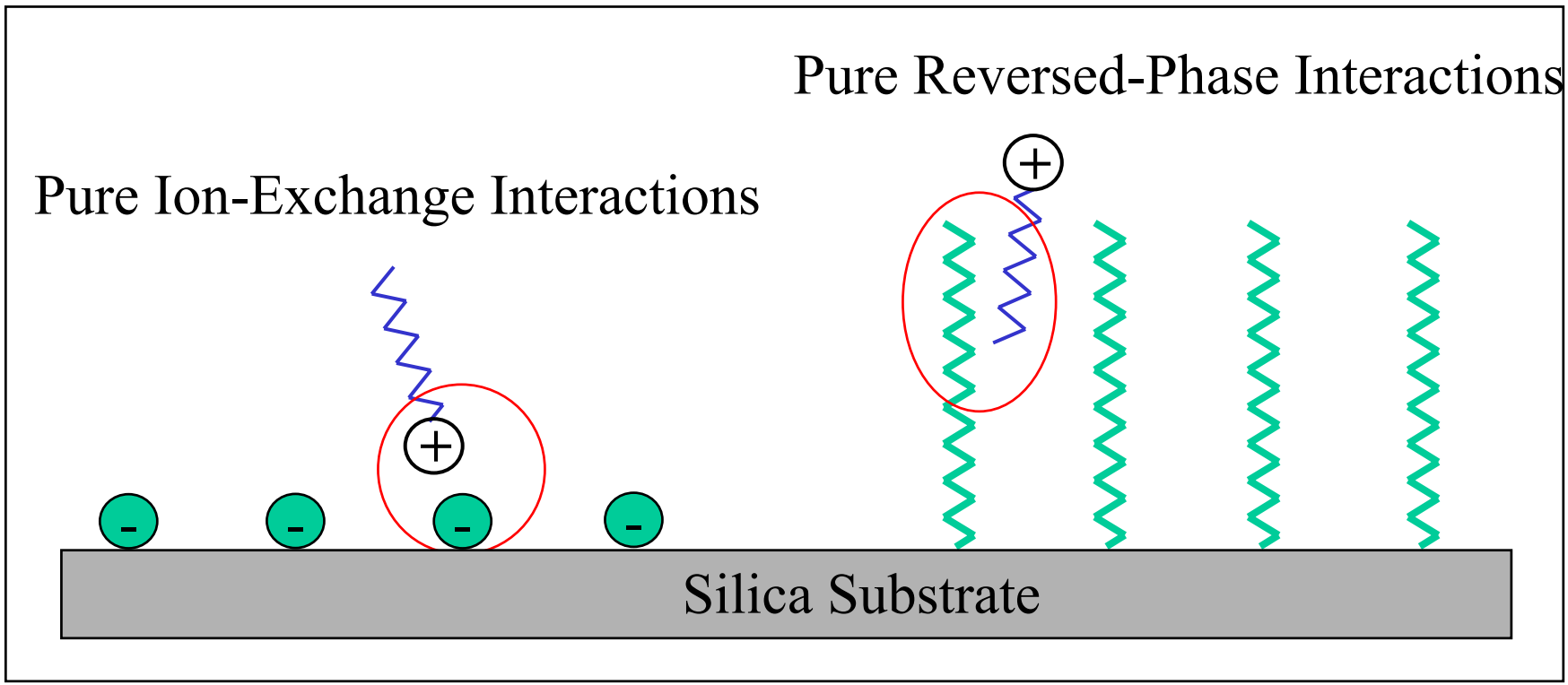


U. D. Neue et al. *J. Chromatogr. A*, 925(2001), 49-67

Two-Site Model for Mixed-Mode Retention

Two INDEPENDENT Interaction Sites

$$k'_{obs} = k'_{RP} + k'_{IEX}$$



Sokolowski, A.; Wahlund, K. G. *J. Chromatogr.* 189 (1980), 299
A. Nahum and C. Horvath, *J. Chromatogr.* 203 (1981), 53-63

Ion-Exchange Retention Characteristics

$$\log k'_{IEX} = \text{Constant} - \log[C^+]_m$$

- One-site model $\log k'_{obs} = A' + \log k'_{RP} - \log[C^+]_m$
- Two-site model $\log k'_{obs} = \log(k'_{RP} + k'_{IEX})$

Slope of $\log k'_{obs}$ vs. $\log [C^+]_m$

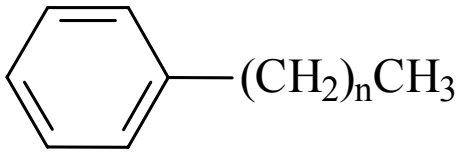
Retention Mechanism	One-site	Two-site
RP only	0	0
IEX only	-1	-1
RP dominant	-1	~ 0
IEX dominant	-1	~ -1

Reversed-Phase Retention Characteristics

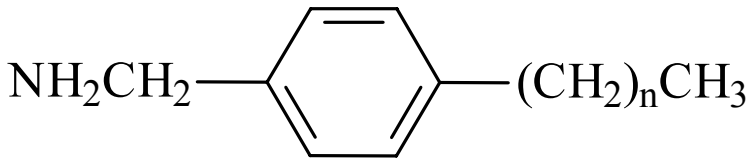
For a homologous series of solutes:

$$\log k'_{RP} = A + Bn_{CH_2}$$

B: independent of the homologous used



Alkylbenzenes



p-Alkylbenzylamines

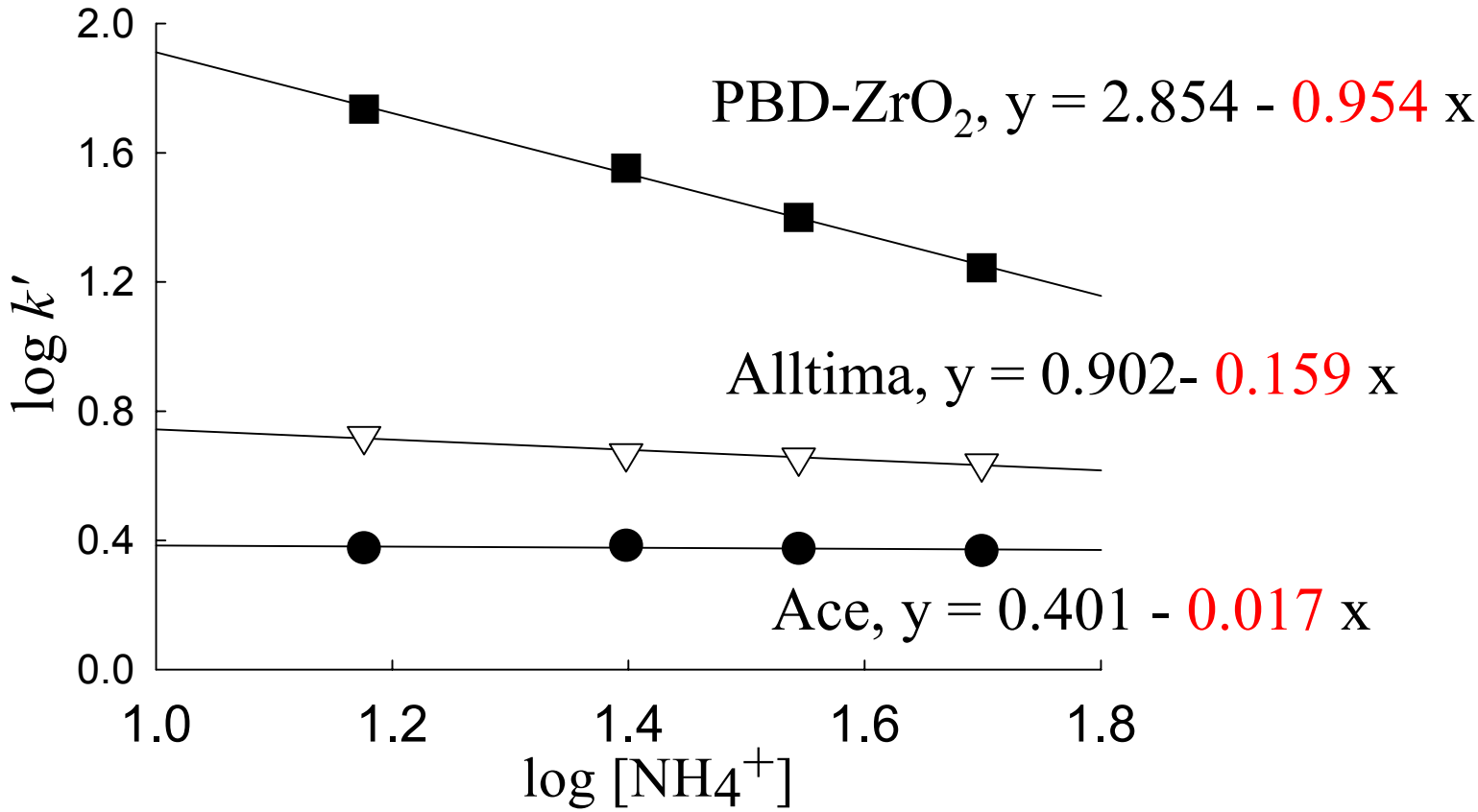
One-site model $\log k'_{obs} = \log k'_{RP} + \log k'_{IEX}$

B: independent of the homologous used

Two-site model $\log k'_{obs} = \log(k'_{RP} + k'_{IEX})$

B: NOT independent of the homologous used

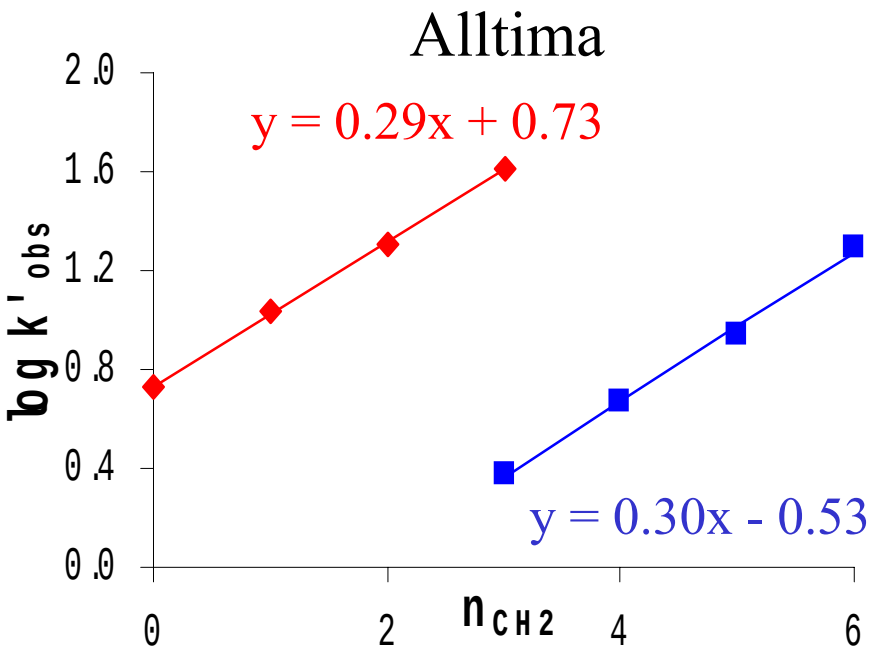
Effect of Counterion Concentration

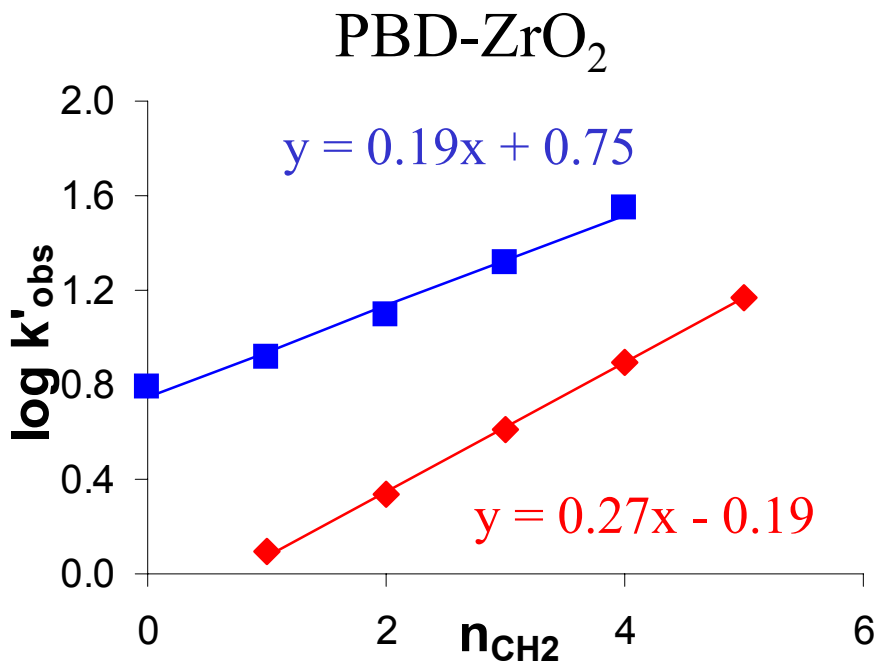


Conditions: 55/45 MeOH/ammonium phosphate buffer, pH = 6.0, T= 35 °C
Solute: p-butylbenzylamine

- ✓ One-site model is WRONG (slope is NOT –1)!
- ✓ Ion-exchange contribution is not large on ODS phases!

Effect of Number of Methylene Units





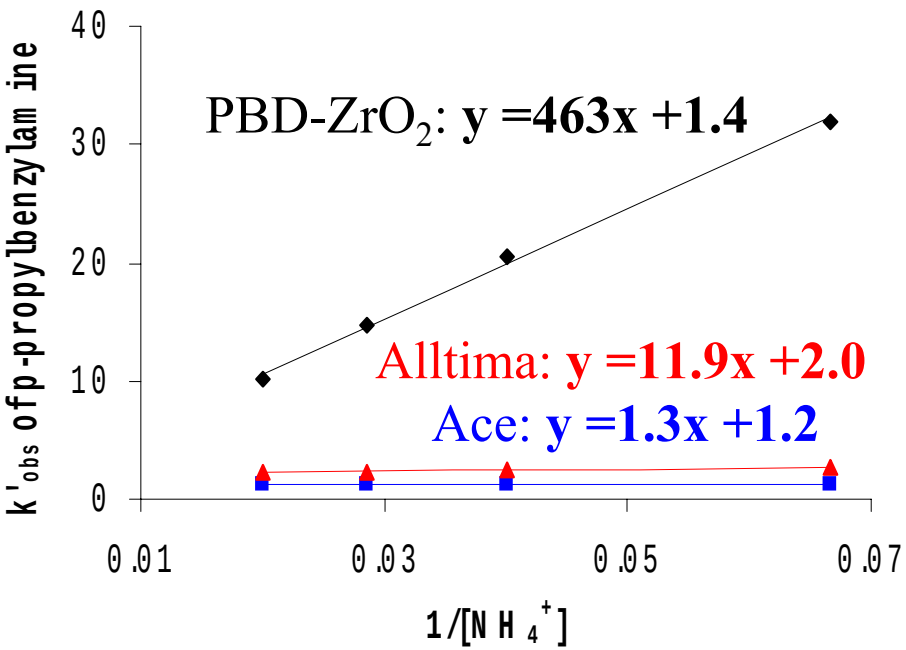
◆: alkylbenzenes; ■: p-alkylbenzylamines

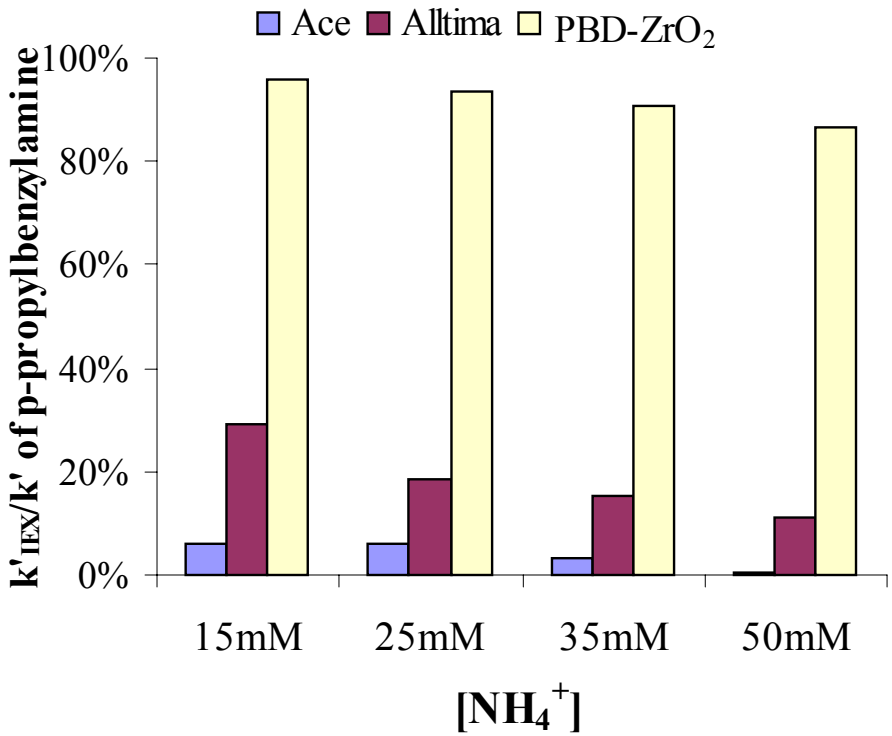
Mobile phase: 55 % MeOH, 25 mM ammonium phosphate, pH 6.0.
Other experimental conditions: 1 mL/min; 35 °C; 254 nm.

- ✓ One-site model is WRONG
- ✓ Two-site model is more accurate
- ✓ Ion-exchange retention dominates on PBD-ZrO_2

Two-Site Model

$$k'_{obs} = k'_{RP} + \frac{\text{Constant}}{[C^+]_m} \qquad Intercept = k'_{RP};\ k'_{IEX} = k' - k'_{RP}$$





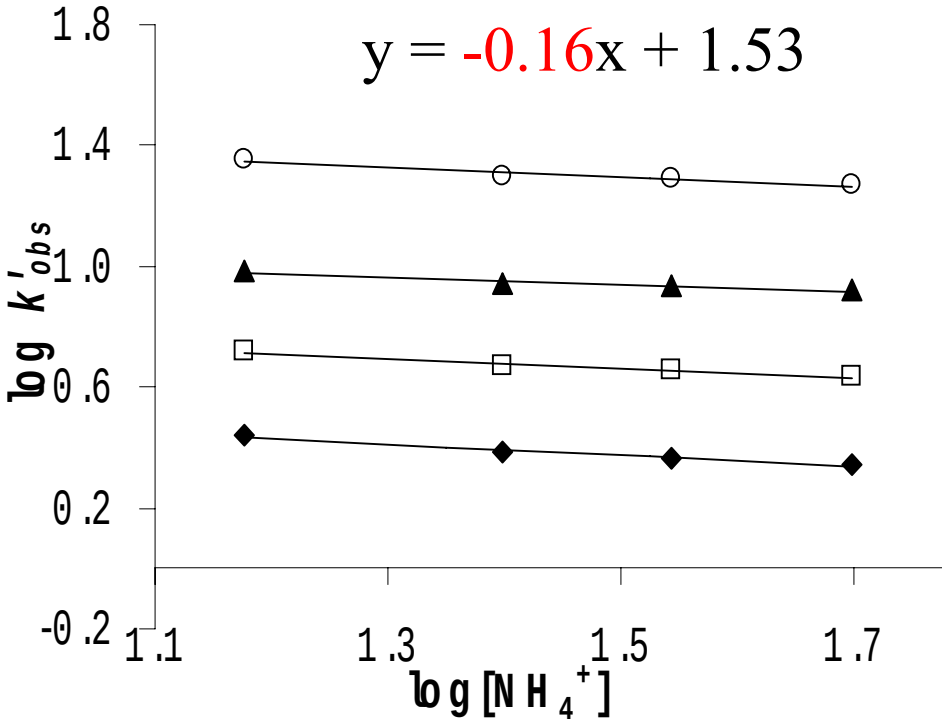
55 % MeOH, ammonium phosphate, pH =6, 1 mL/min, 35 ºC

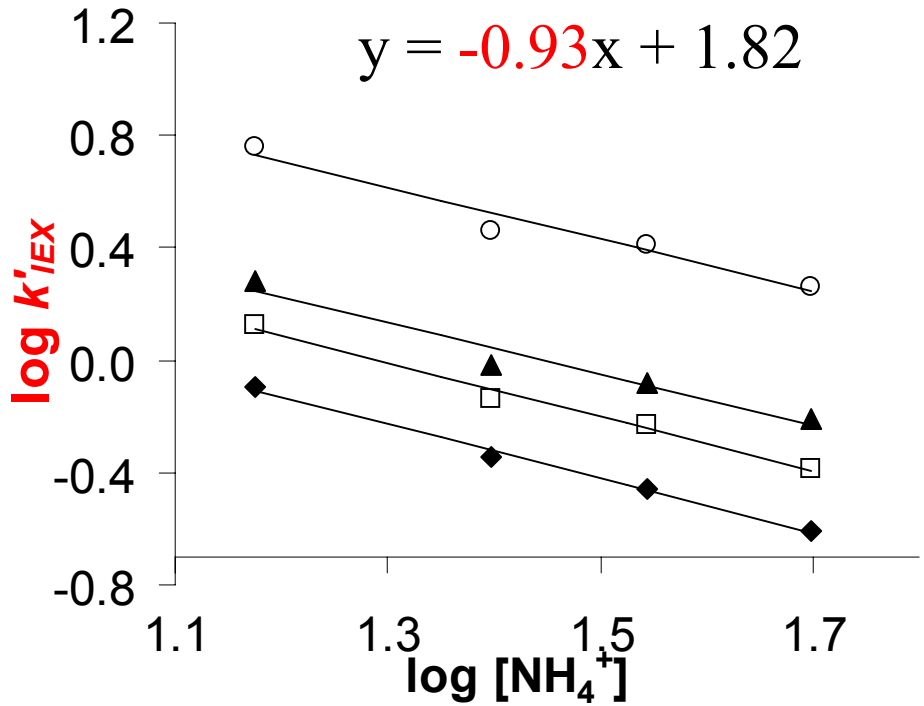
✓**Quantitative estimation of the relative contributions of RP and IEX**

✓**Much more IEX on PBD-ZrO_2 causes selectivity difference**

log k'_{IEX} vs. log [NH_4^+] —Alltima

log k'_{obs} vs. log [NH_4^+] ⟶ $k'_{IEX} = k'_{obs} - k'_{RP}$ ⟶ log k'_{IEX} vs. log [NH_4^+]





◆: propylbenzylamine; □: butylbenzylamine; ▲: pentylbenzylamine; ○: hexylbenzylamine

✓ Estimation of k'_{IEX} by using two-site model is good!

Conclusions

- ✓ One-site free energy addition retention model is incomplete
- ✓ Two-site mixed-mode retention model is more correct
- ✓ The dominant of IEX on PBD-ZrO_2 accounts for the dramatic different selectivity towards basic solutes compared to ODS phases.
- ✓ A plot of *k*' vs. $1/[C^+]_m$ is a very useful tool for quantitatively estimating relative contributions of reversed-phase and ion-exchange interactions to the retention of basic solutes.

Acknowledgements

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ZirChrom Separations