The Effect of Amine Counterion Type on the Retention of Basic Compounds on Octadecyl Bonded Silica Based and Polybutadiene Coated Zirconia Phases

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Outline

- Background
  - Basic solutes
  - Hydrophobic vs. ion-exchange
  - ODS vs. PBD-ZrO_2
- Experimental result and discussion
  - Effect of counterion type on the retention of basic solutes
  - Reversed phase interaction contribution
  - Ion-exchange interaction contribution
- Conclusions
  - Larger effect of amine counterion on PBD-ZrO_2 than on Type B ODS
  - Both the hydrophobicity and the steric effect of the counterion matter

Basic Solutes for Mixed-Mode Retention

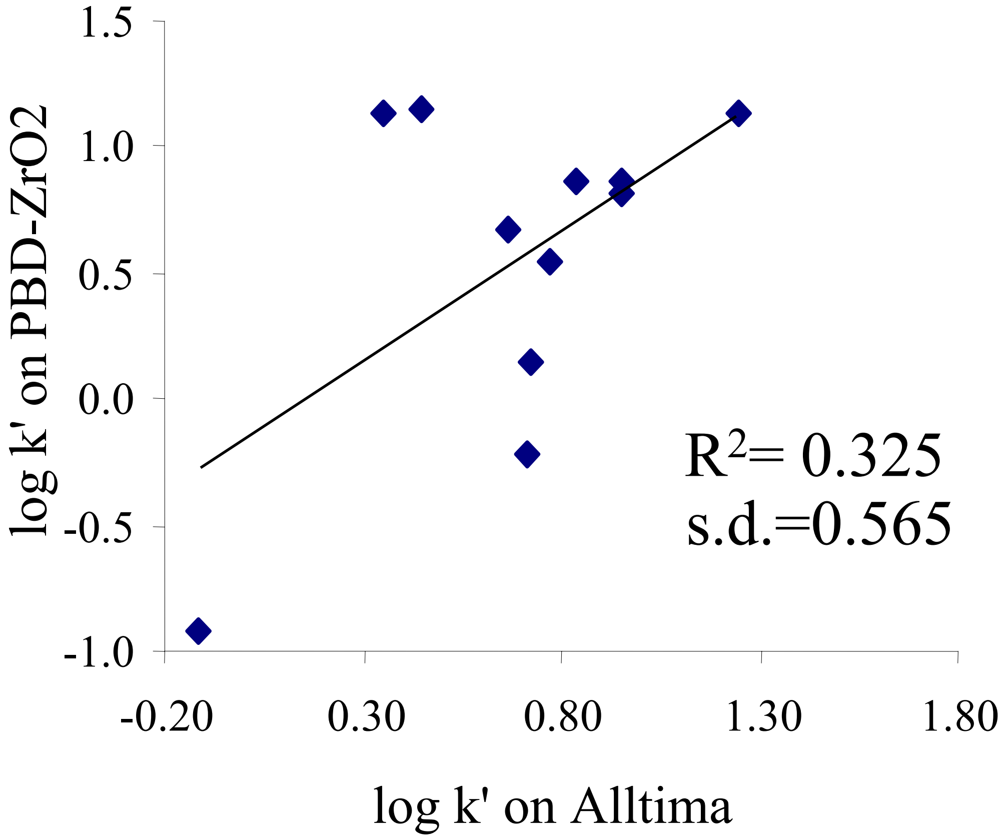
- Chromatographic interactions
  - ✓Reversed phase interaction and ion-exchange interaction

$$k' = k'_{RP} + k'_{IEX} = \phi_{RP} K_{RP} + \phi_{IEX} K_{IEX} / [C^+]_m$$

- Interaction of a basic solute with ODS
  - ✓Steric hindrance around N
  - ✓Substitution on N ($4^{th} \sim 3^{rd} > 2^{nd} > 1^{st}$)
  - ✓Hydrophobicity, chain length

- Solutions:
  - ✓Stationary phase modification
  - ✓Low pH or high pH mobile phase
  - ✓"Silanol blocker" in the eluent (type, concentration).

Motivation



Ion-exchange interactions on PBD-ZrO_2 are more than twofold of that on ODS!

Condition: 72 % MeOH, 25 mM phosphate, pH=6.0, 35 °C, 1 mL/min. Solutes: antidepressant

Very different selectivity of ODS and PBD-ZrO_2

Experimental Design

Amine Counterions

Ammonium NH_4

Butylamine C_4N

Pentylamine C_5N

Hexylamine C_6N

Octylamine C_8N

Dipropylamine $(C_3)_2N$

Dimethylbutylamine $(C_2)_2NC_4$

Triethylamine $(C_2)_3N$

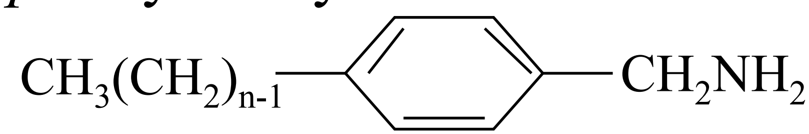
Tributylamine $(C_4)_3N$

1,6-Hexanediamine C_6N_2

phosphate buffer (pH 6.0)

Solutes and Analytical Column

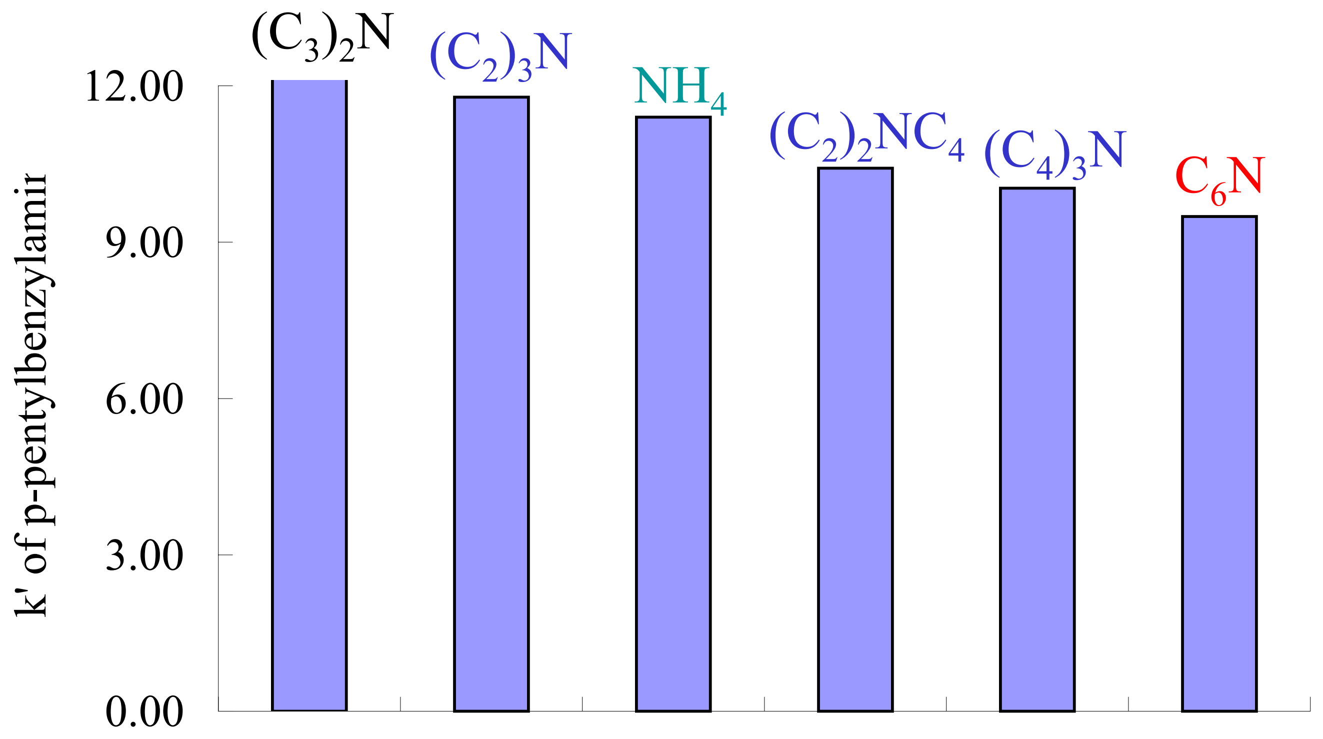
Solute:
p-alkylbenzylamines



Column:

- Alltima ODS phase
- PBD-ZrO_2

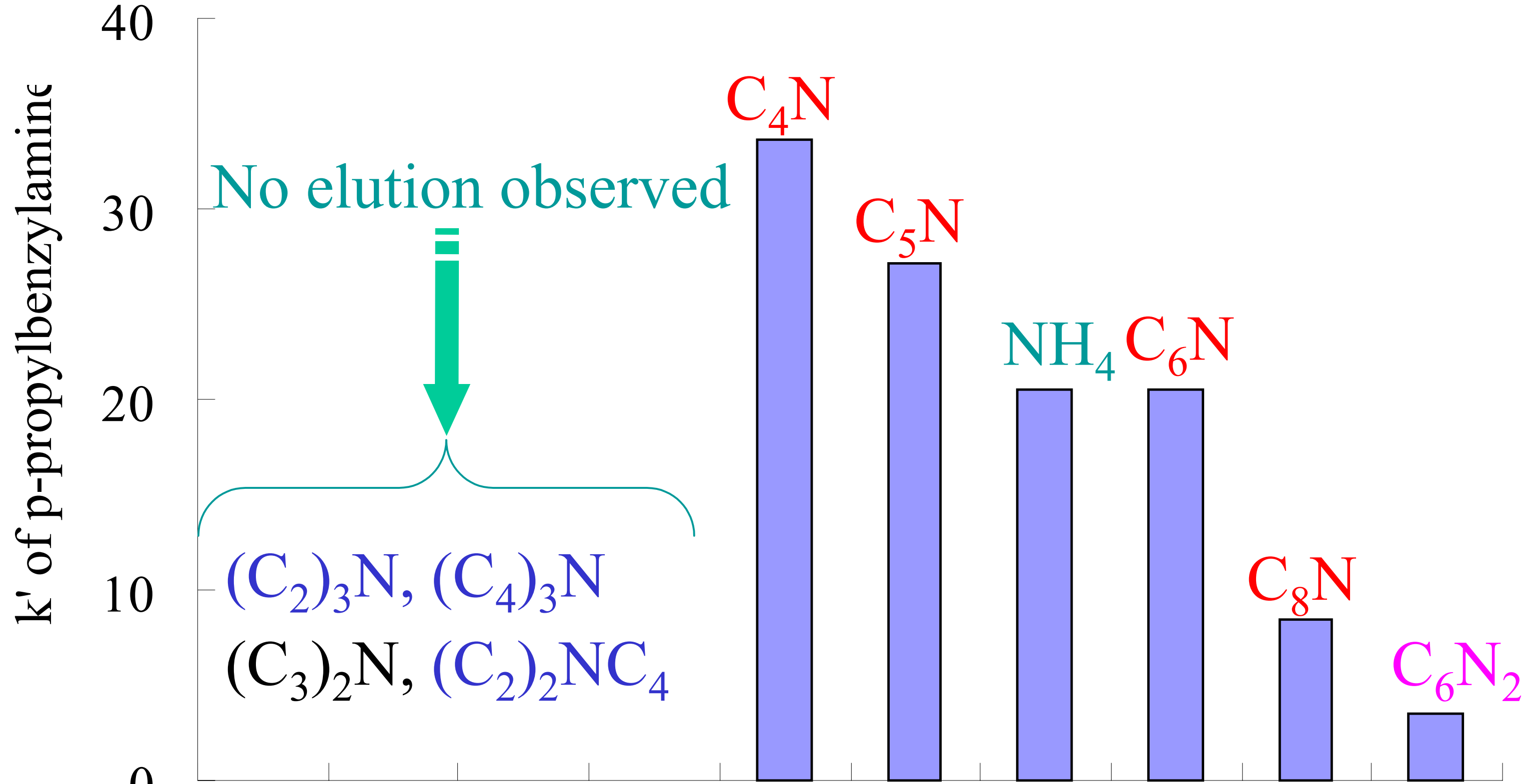
Effect of Amine Counterion on Retention of Basic Solutes on ODS



Condition: 55/45 MeOH/25 mM phosphate, pH 6, 35 ºC, 1 mL/min.

Type of amine counterion only has small effect on Type B ODS columns

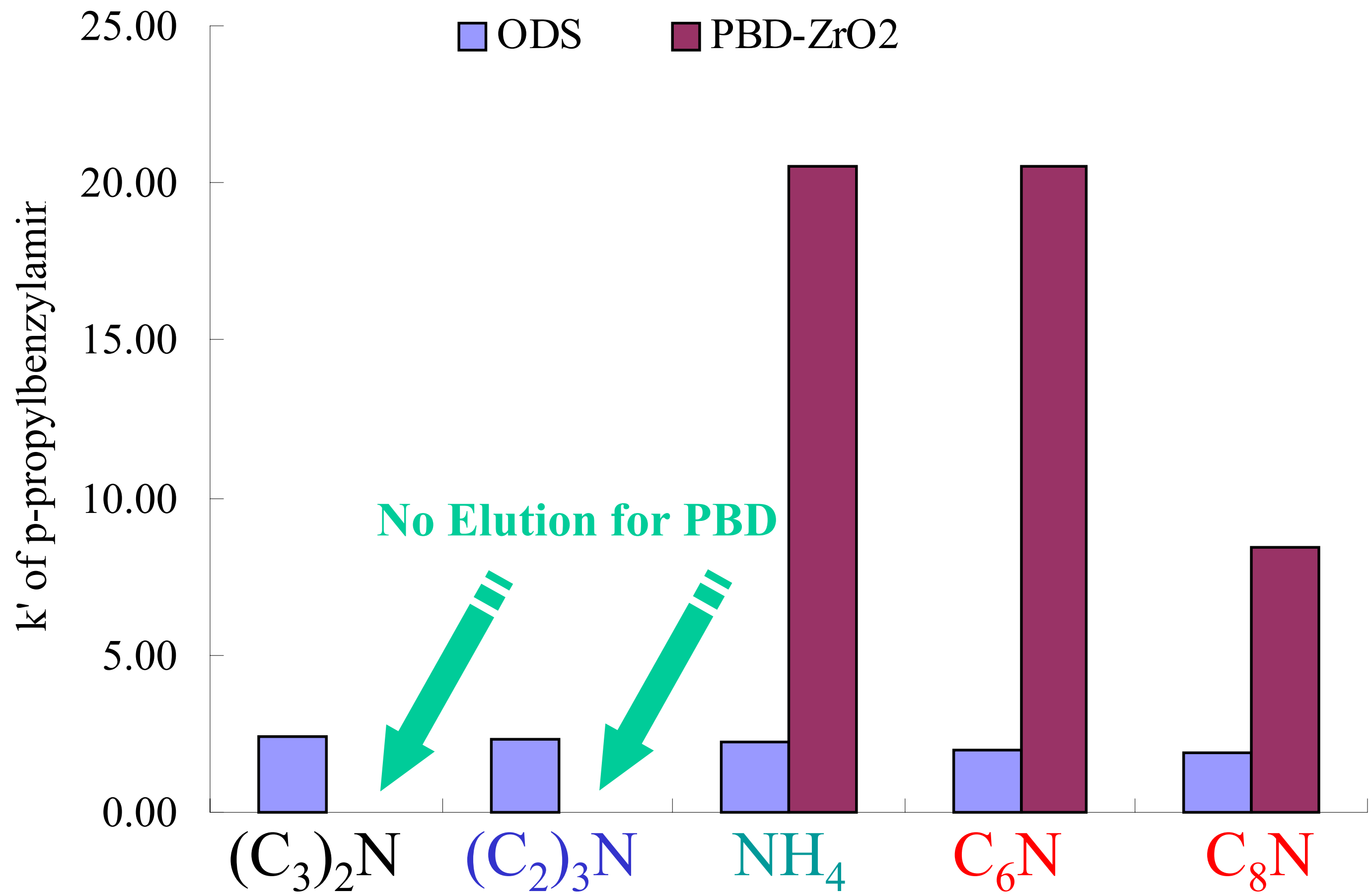
Effect of Amine Counterion on Retention of Basic Solutes on PBD-ZrO_2



Condition: 55/45 MeOH/25 mM phosphate, pH 6, 35 ºC, 1 mL/min.

The molecular geometry of the amine counterion has a big effect.
Diamine gives the best "blocking" effect.

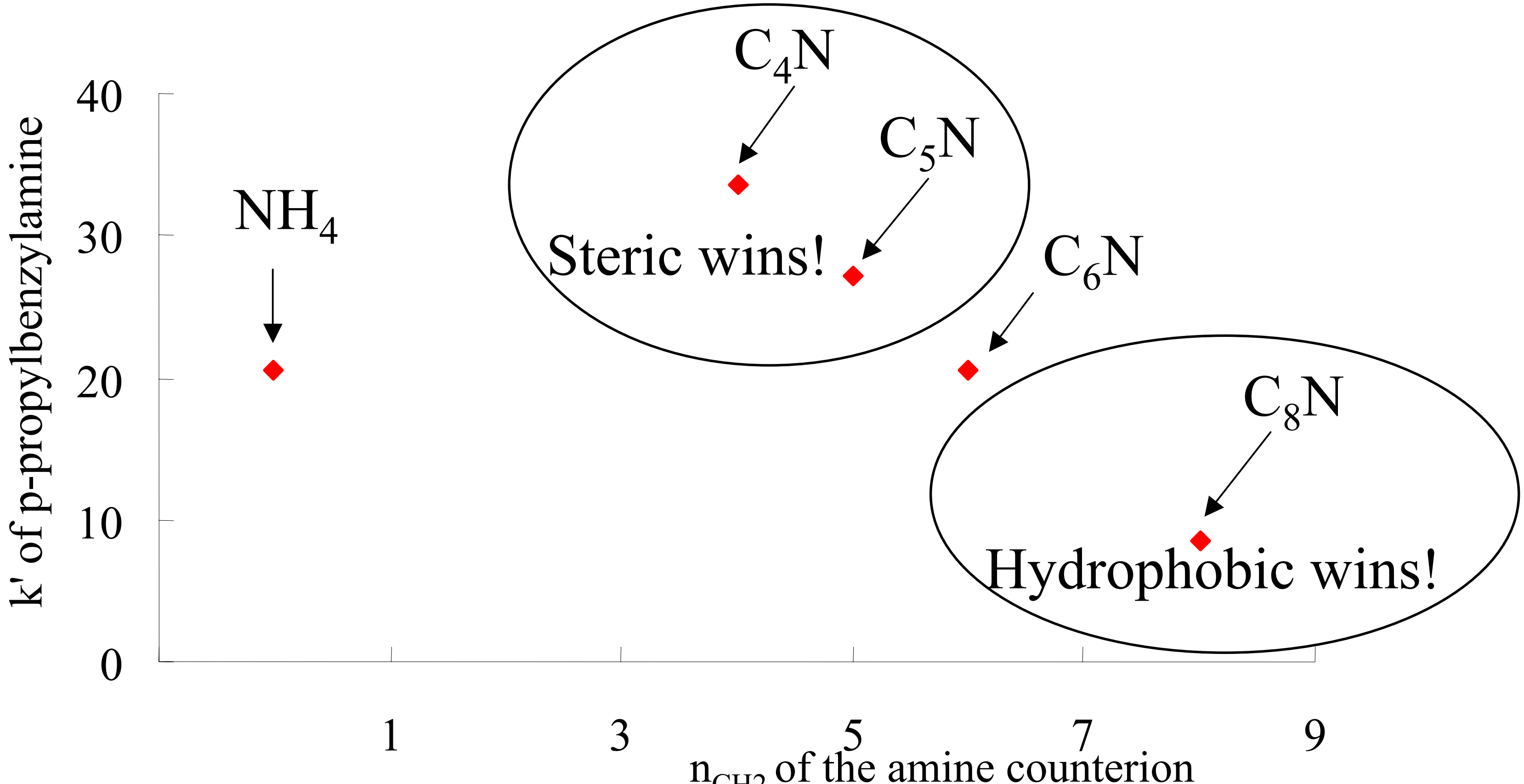
Counterion Effect on ODS and PBD-ZrO_2



Condition: 55/45 MeOH/25 mM phosphate, pH 6, 35 ºC, 1 mL/min

Radically different effect of amine counterion on ODS and PBD-ZrO_2.

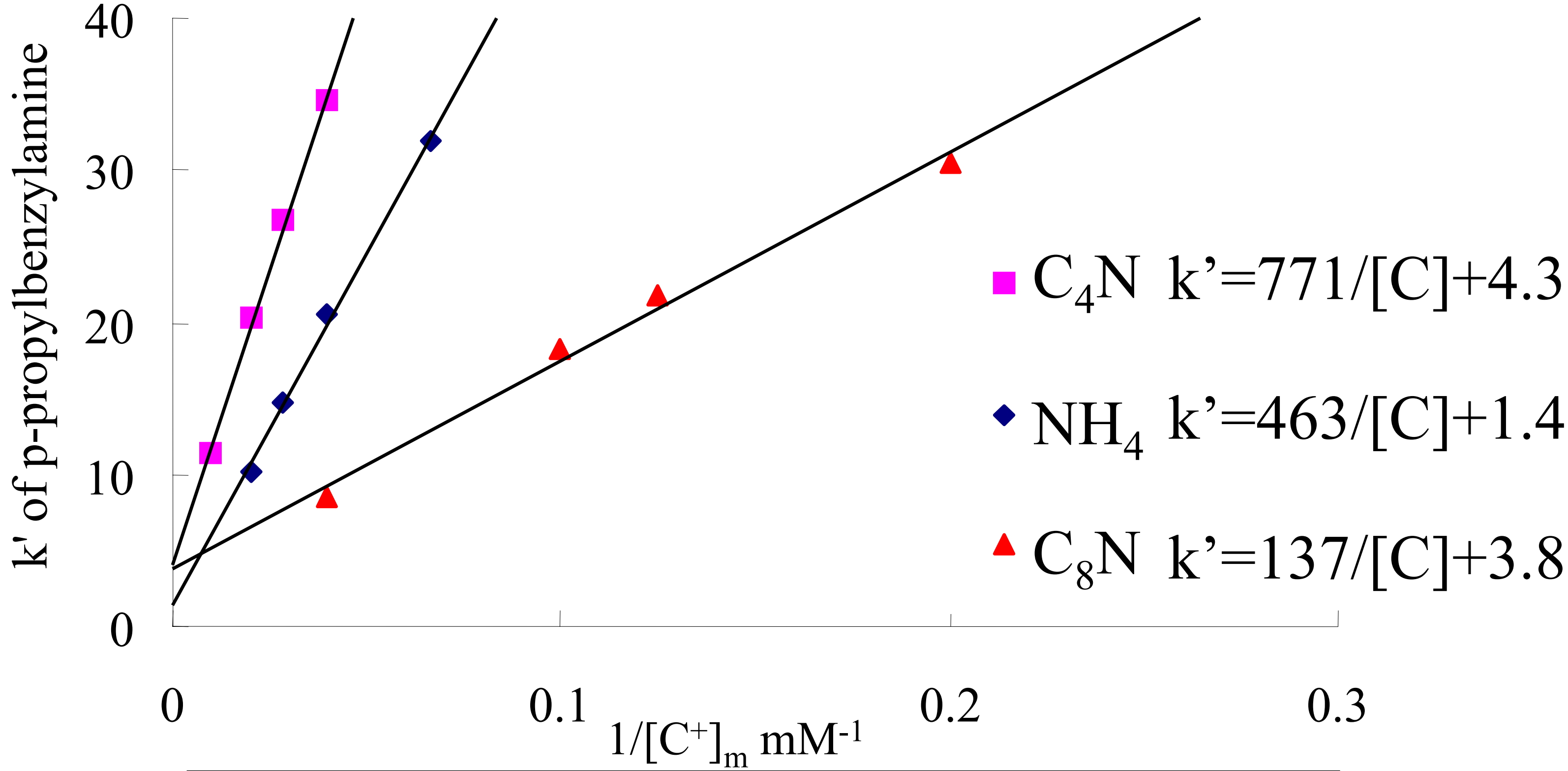
Effect of Amine Counterion on Retention of Basic Solutes on PBD-ZrO_2



Condition: 55/45 MeOH/25 mM phosphate, pH 6, 35 ºC, 1 mL/min

The blocking effect is a balance between steric hindrance and hydrophobicity.

k' vs. $1/[C^+]_m$ on PBD-ZrO_2



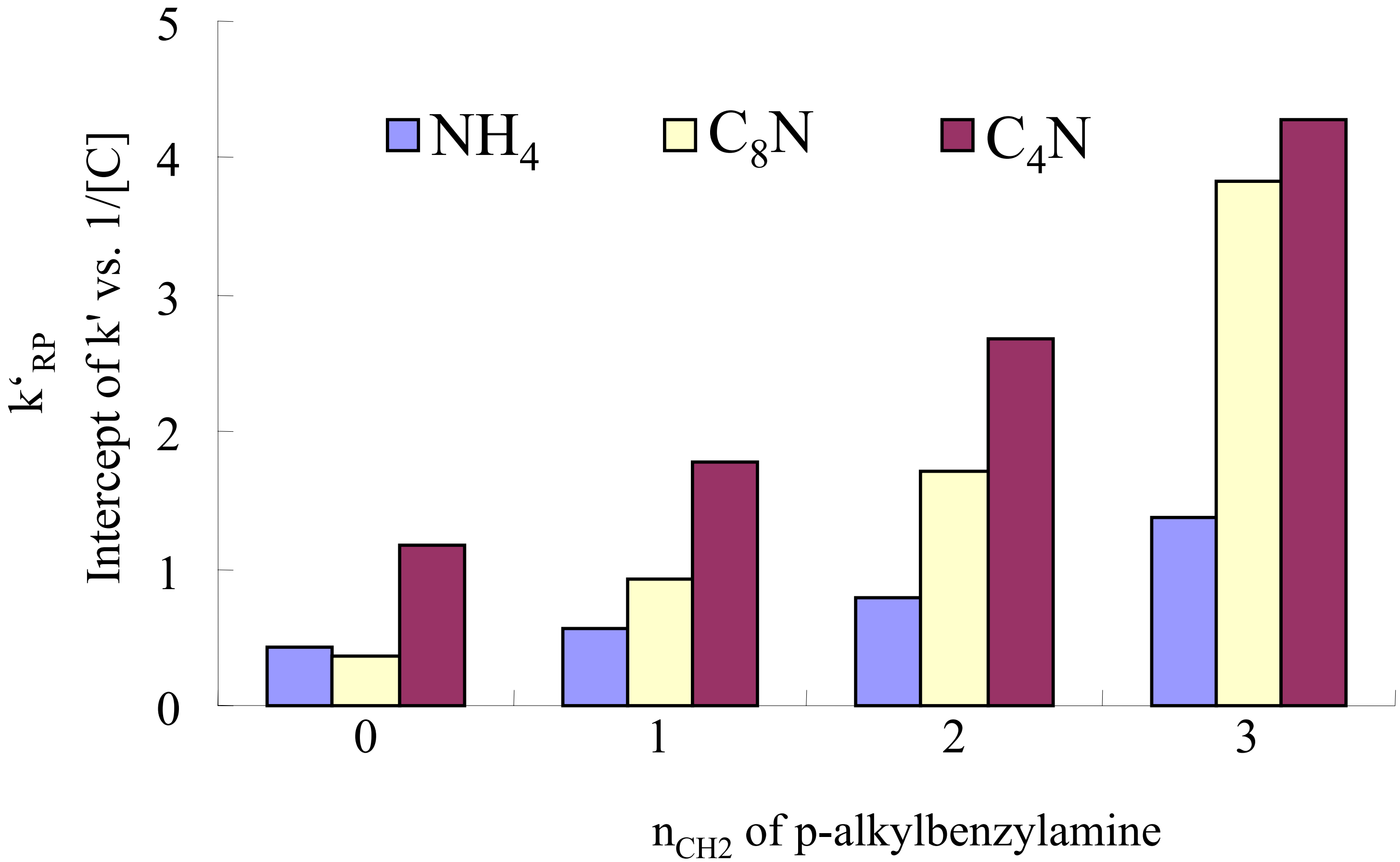
Condition: 55/45 MeOH/ phosphate, pH 6, 35 ºC, 1 mL/min

$$k' = k'_{RP} + k'_{IEX} = k'_{RP} + \phi_{IEX} K_{IEX} / [C^+]_m$$

Intercept: Reversed phase contribution k'_{RP}

Slope: Ion-exchange contribution K_{IEX}

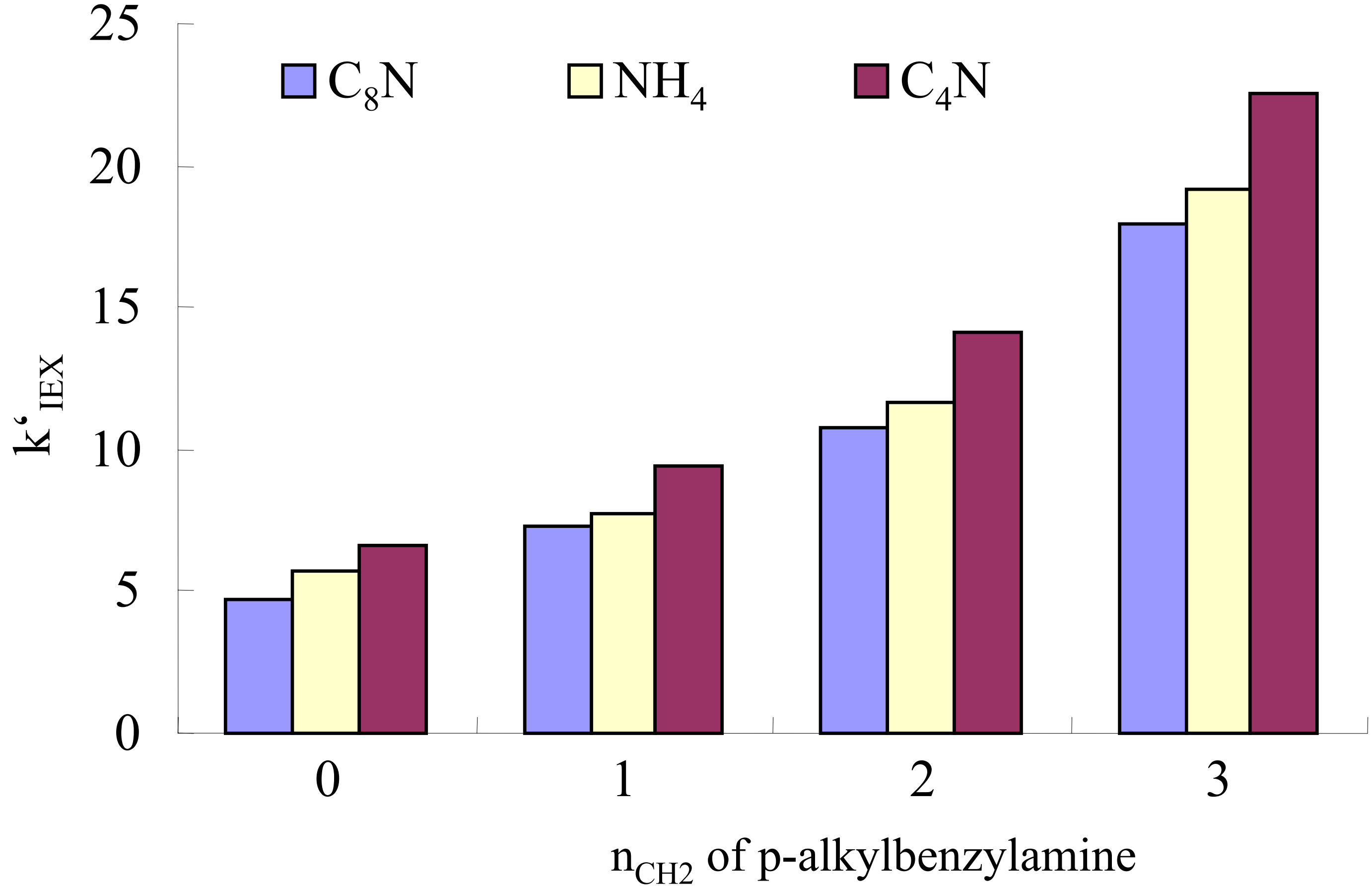
Contribution of Reversed Phase Interactions on PBD-ZrO_2



Condition: 55/45 MeOH/ phosphate, pH 6, 35 ºC, 1 mL/min

A weaker counterion butylamine leads to larger reversed phase interactions for basic solutes.

Contribution of Ion-Exchange Interactions on PBD-ZrO_2



Condition: 55/45 MeOH/25 mM phosphate, pH 6, 35 ºC, 1 mL/min

The stronger the counterion, the smaller the ion-exchange interactions.

Conclusions

1. Counterion is more useful for selectivity adjustment on PBD-ZrO_2.
2. Relatively small effect of the type of the amine on Type B silica column.
3. Big effect of the type of the amine counterion on PBD-ZrO_2.
4. Both steric hindrance and hydrophobicity of the amine counterion influence the retention of basic solutes.
5. Doubly charged diamine is much more effective than the singly charged amine.

Acknowledgments

National Institute of Health

University of Minnesota

Alltech Associates, Inc

ZirChrom Separation