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Comparison of the Retention Characteristics of Modified Carbon Clad Nonporous Zirconia Micro-Spheres Using Linear Solvation Energy Relationships

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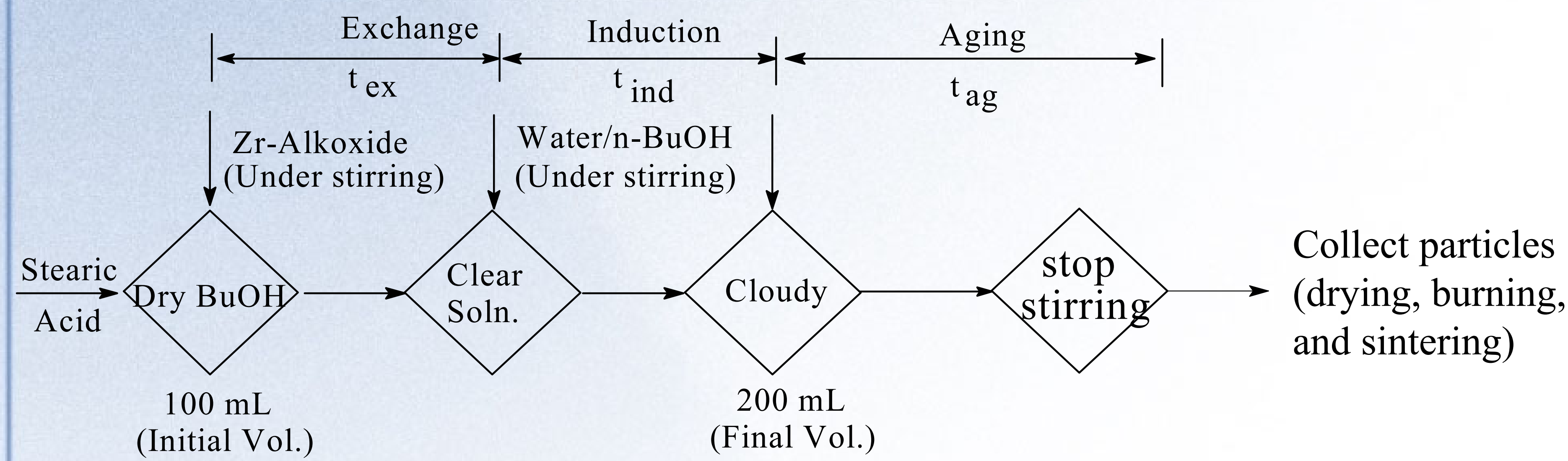
Abstract

The similarities and differences in retention characteristics of four novel nonporous modified carbon coated zirconia stationary phases by the use of linear solvation energy relationships (LSERs) is reported here. Four new modified carbon clad nonporous zirconia stationary phases were produced by the use of diazonium coupling chemistry including C18, C18 amide, cyano and a C34 polar embedded phase. These stationary phases can be applied to nonporous zirconia particles in the size range of 1-3 microns. This surface modification method is chemically flexible and plays the same role in carbon-based HPLC as silane chemistry does for silica-based phases. The retention of these new phases was correlated with solute descriptors of cavity formation/dispersion, dipolarity/polarizibility, and hydrogen bond donar-acceptor interactions. The carbon-based phases showed large contributions from the dipolarity/polarizaibility term indicating significant pi-pi interactions between solutes and the stationary phase. The effects of the different bonded phases on the LSER coefficients for the modified carbon clad nonporous zirconia phases is compared to unmodified carbon clad nonporous zirconia. These new carbon based bonded phases phases offer highly chemically and thermally stable nonporous HPLC supports of different selectivity for ultrafast analytical separations.

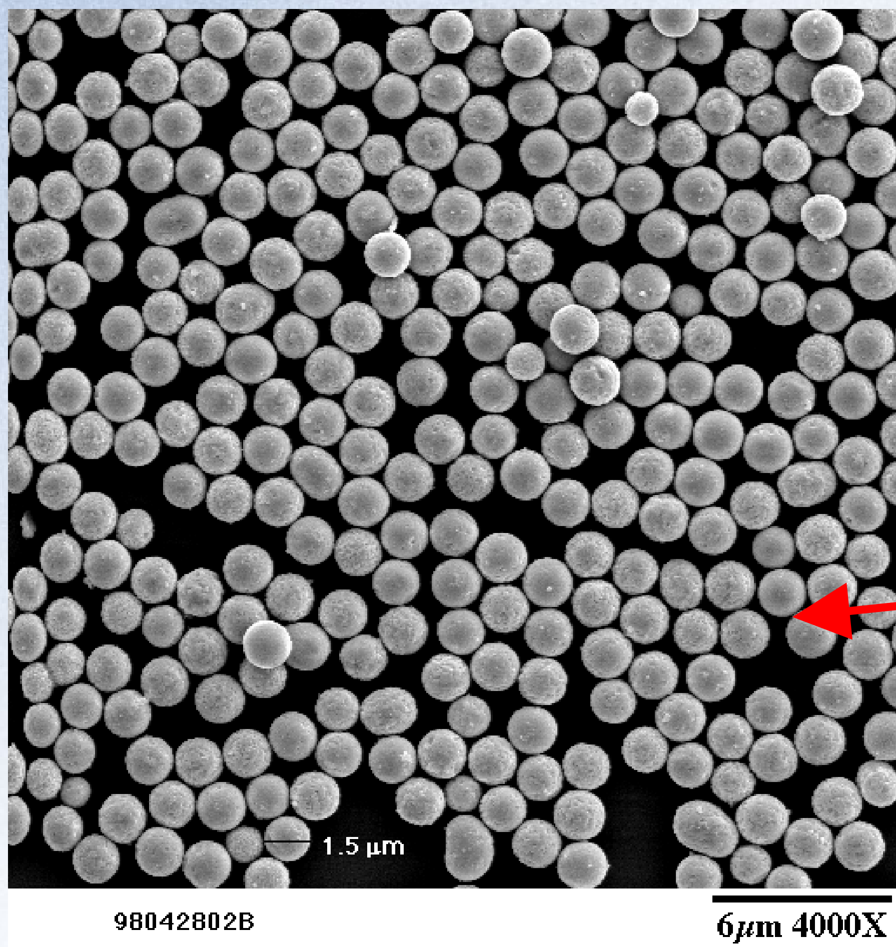
Outline

- A General Method to Make Nonporous Zirconia
- A General Method to Make Carbon Clad Nonporous Zirconia
- A New Way to Modify the Carbon Clad Nonporous Zirconia Surface by the Use of Diazonium Coupling Chemistry
- LSER Comparison of Retention Mechanism on Carbon, C18-Carbon, C18 Amide-Carbon, C34 Amide-Carbon, Cyano-Carbon Nonporous Zirconia
- Conclusions:
  - Different selectivity

Nonporous Zirconia Synthesis



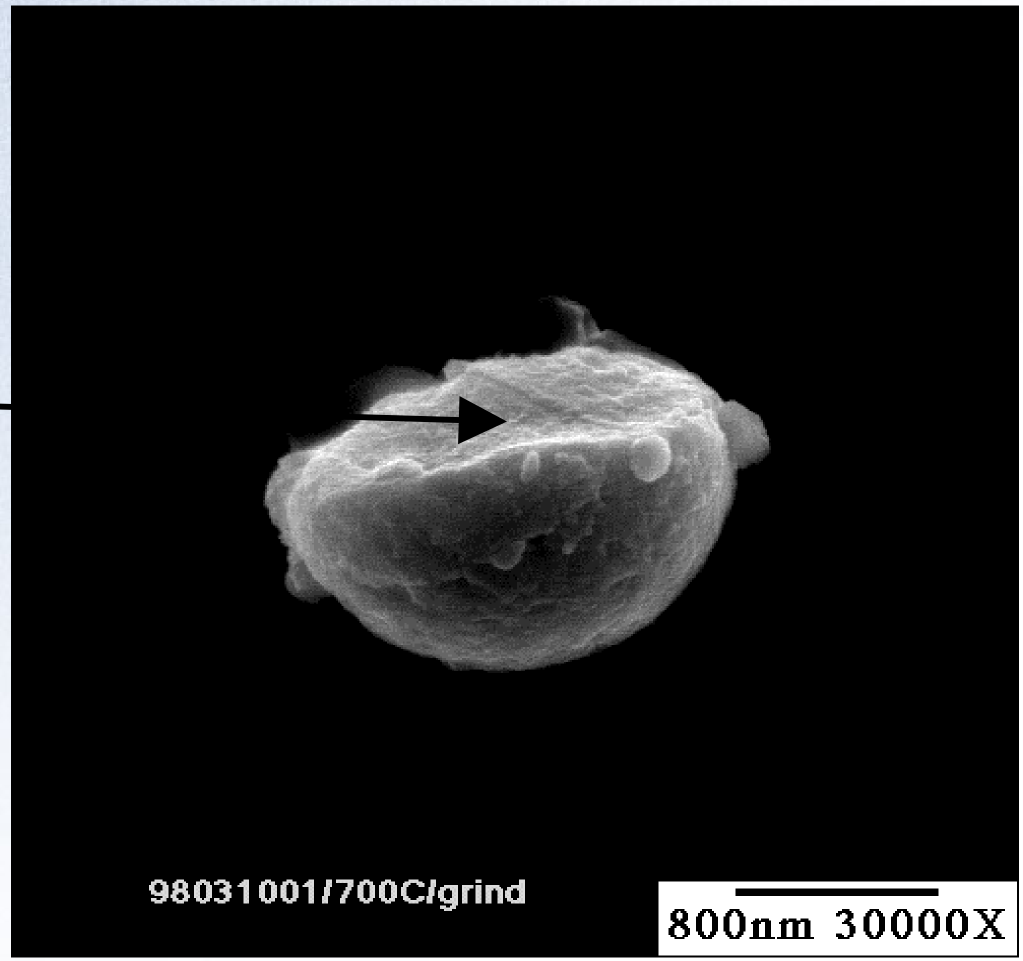
SEM of Nonporous Zirconia Particles



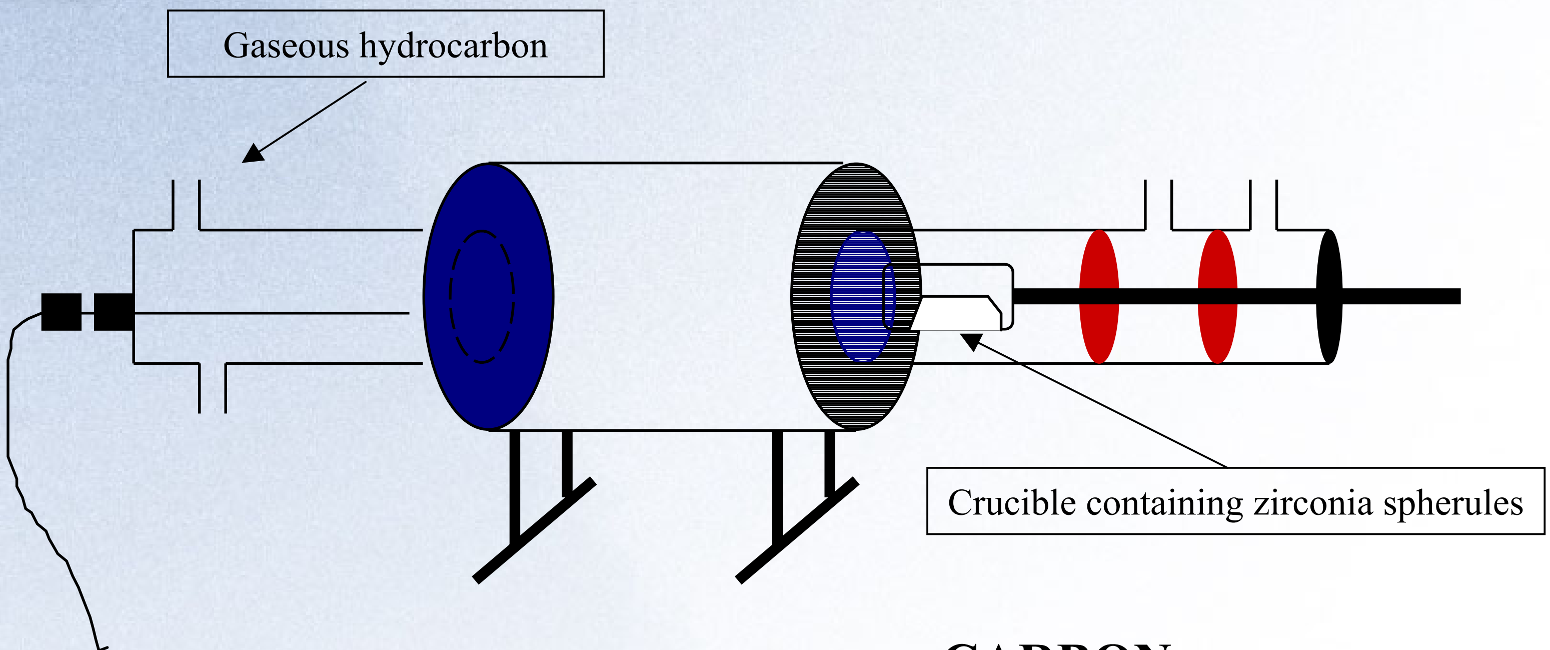
The particles are monodisperse, spherical and nonaggregated.

SEM of the Interior of a Nonporous Zirconia Particle

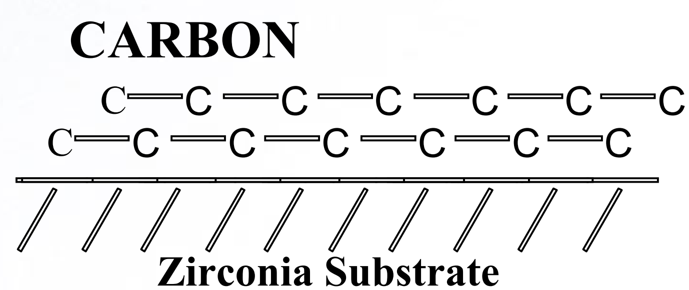
The nonporous nature of the particles was verified by grinding a sample and looking at the interior of a broken particle.



Synthesis of Carbon Clad Nonporous Zirconia Substrate



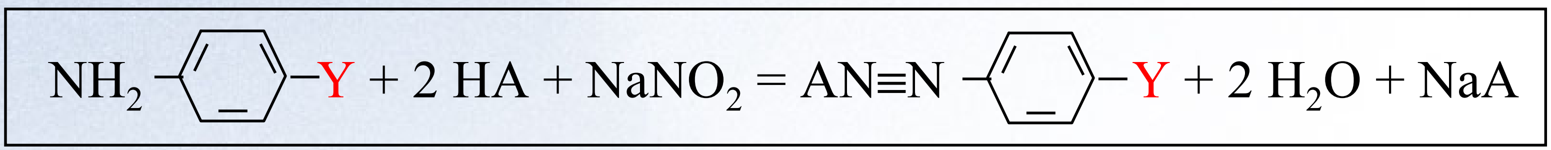
$$C_6H_{14} \rightarrow 6C + 7H_2$$

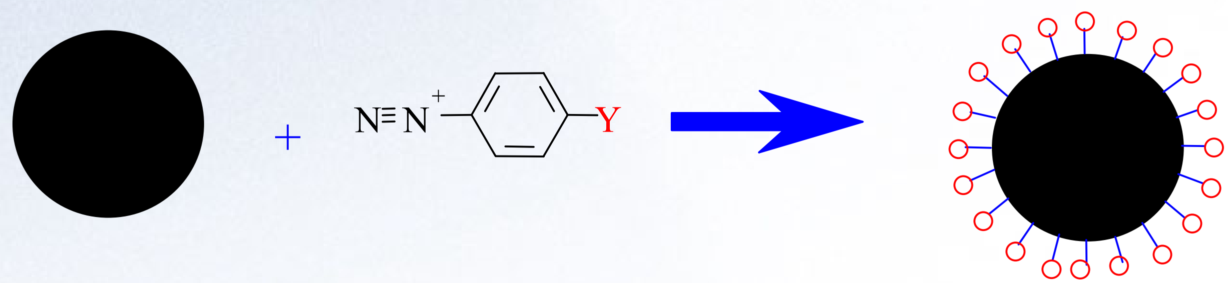


P. T. Jackson, M. R. Scheme, T. P. Weber, and P. W. Carr, *Anal. Chem.*, 1997, 69, 416-425

Diazonium Chemistry for Nonporous Stationary Phase Synthesis

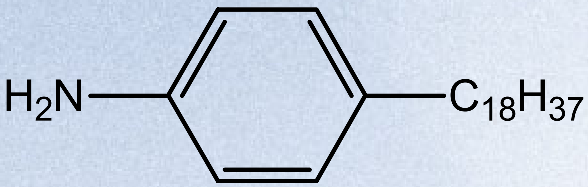
- General approach - Cabot Corporation (Billerica, MA):
  - functionalizing agent X-R-Y
  - X reacts with surface
  - Y = functional group
- X is typically a diazonium salt



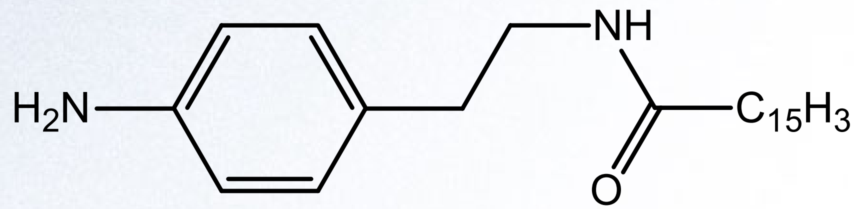


Carbon Clad Nonporous Zirconia Diazonium Salt Modified Carbon Clad Nonporous Zirconia

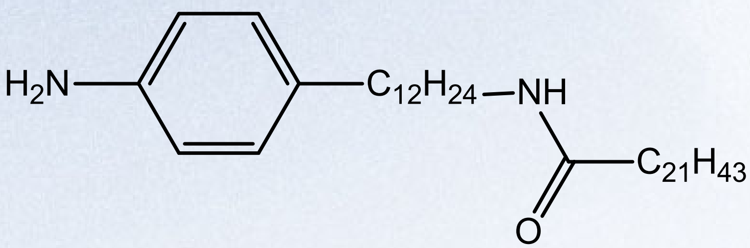
Structures of Stationary Phases



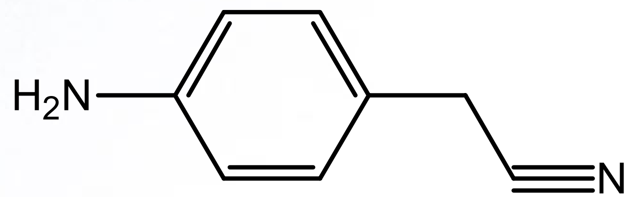
4-octadecylaniline (C18)



4-aminophenethyl palmitoyl amide
(C18 amide)

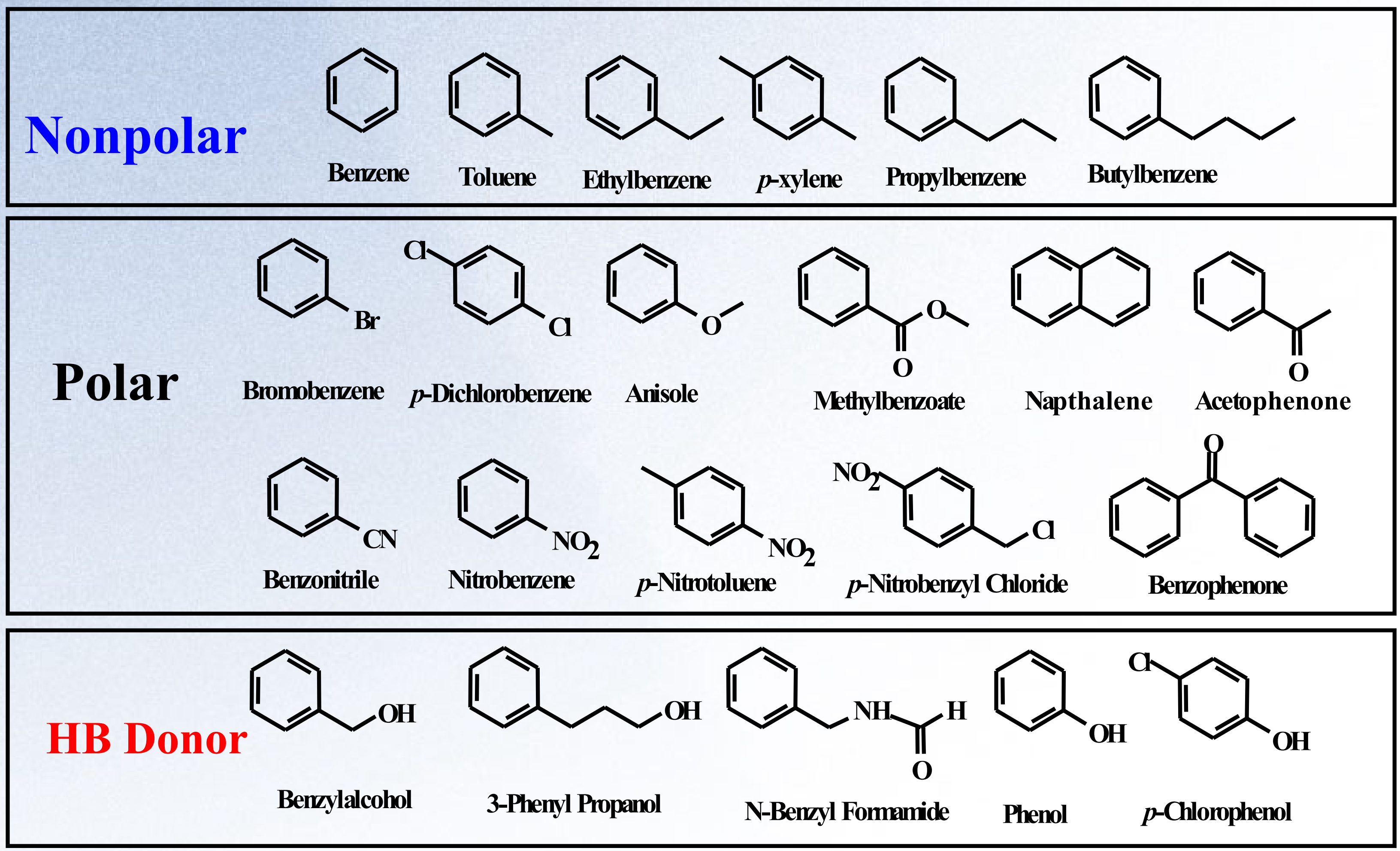


4-aminophenyl dodecylbehenoyl amide
(C34 amide)



4-aminobenzyl cyanide
(CN)

22 Solutes


Nonpolar
Benzene
Toluene
Ethylbenzene
p-xylene
Propylbenzene
Butylbenzene
Polar
Br
Bromobenzene
Cl
Cl
p-Dichlorobenzene
O
Anisole
O
O
Methylbenzoate
Napthalene
O
Acetophenone
CN
Benzonitrile
NO2
Nitrobenzene
NO2
p-Nitrotoluene
NO2
Cl
p-Nitrobenzyl Chloride
O
Benzophenone
HB Donor
OH
Benzylalcohol
OH
3-Phenyl Propanol
NH
H
O
N-Benzyl Formamide
OH
Phenol
Cl
OH
p-Chlorophenol

Linear Solvation Energy Relationships

log k' = **unfavorable** cavity formation + Σ **favorable** interactions

$$= \log k_0' + \boxed{m V_2} + \boxed{s\pi_2^* + a\Sigma\alpha_2^H + b\Sigma\beta_2^H}$$

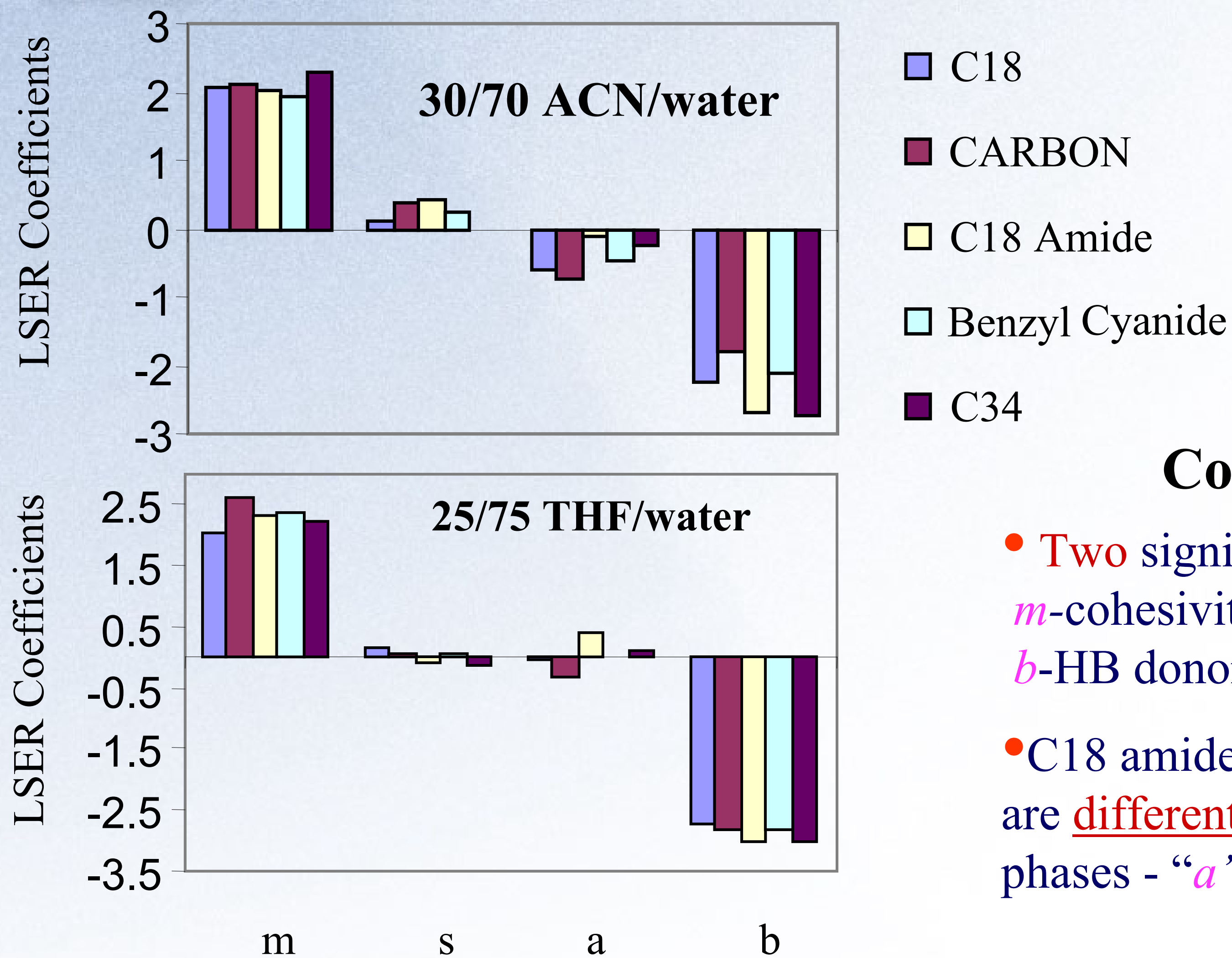
Solute descriptors

V_2	molecular size
π_2^*	dipolarity/polarizability
$\Sigma\alpha_2^H$	hydrogen bond acidity
$\Sigma\beta_2^H$	hydrogen bond basicity

Mobile-stationary phase

m	cohesiveness/dispersiveness
s	dipolarity/polarizability
a	HB acceptor basicity
b	HB donor acidity

LSER Coefficients for RPLC Phases



Conclusions:

- Two significant coefficients: *m*-cohesivity/dispersivity *b*-HB donor acidity
- C18 amide and CARBON are different from other phases - "*a*".

Comparison of Selectivity by κ–κ Plots:

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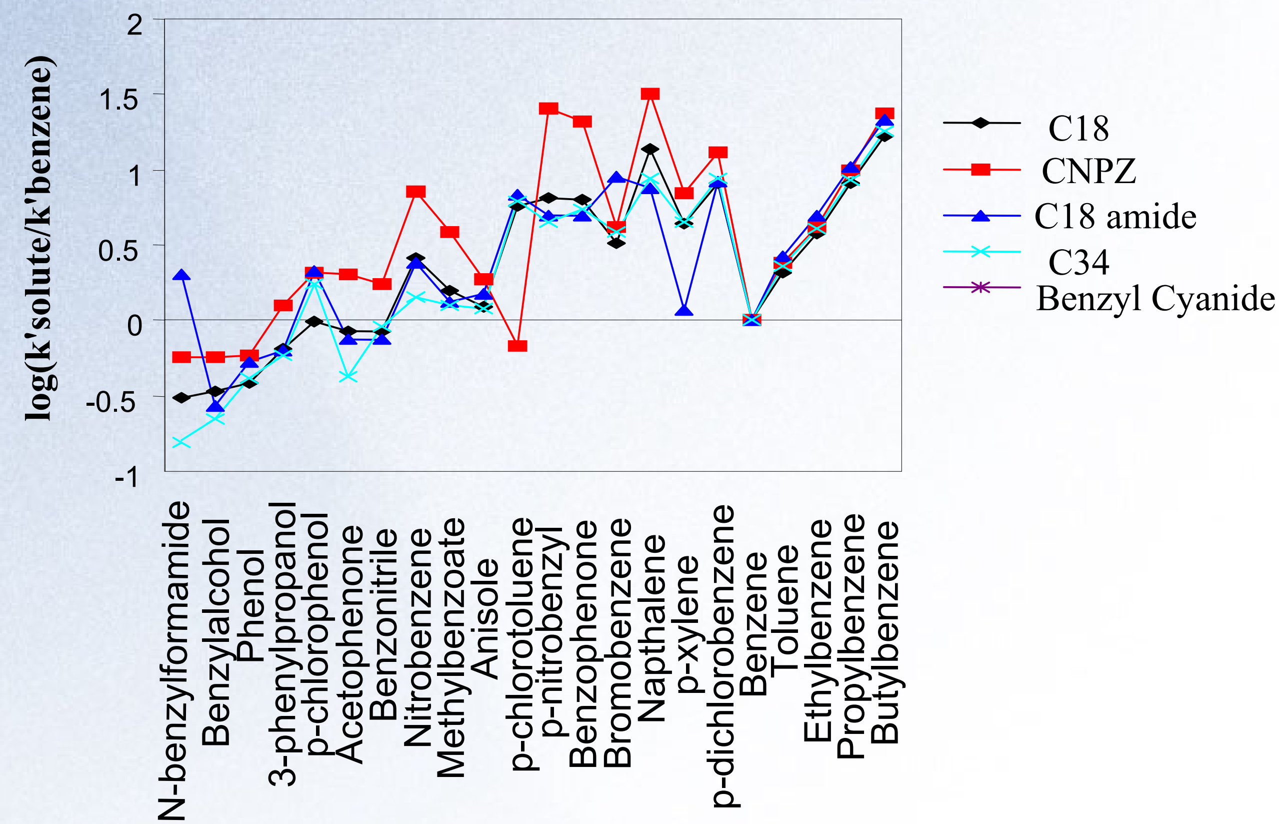
	C18	CARBON	C18 amide	C34	CN
C18	1				
CARBON	0.7707	1			
C18 amide	0.7537	0.4795	1		
C34	0.945	0.6287	0.7429	1	
CN	0.92	0.757	0.7602	0.8621	1

Mobile phase: 30/70 ACN/water

Low R^2 shows that C18 amide and CARBON are distinctly different from each other and other phases.

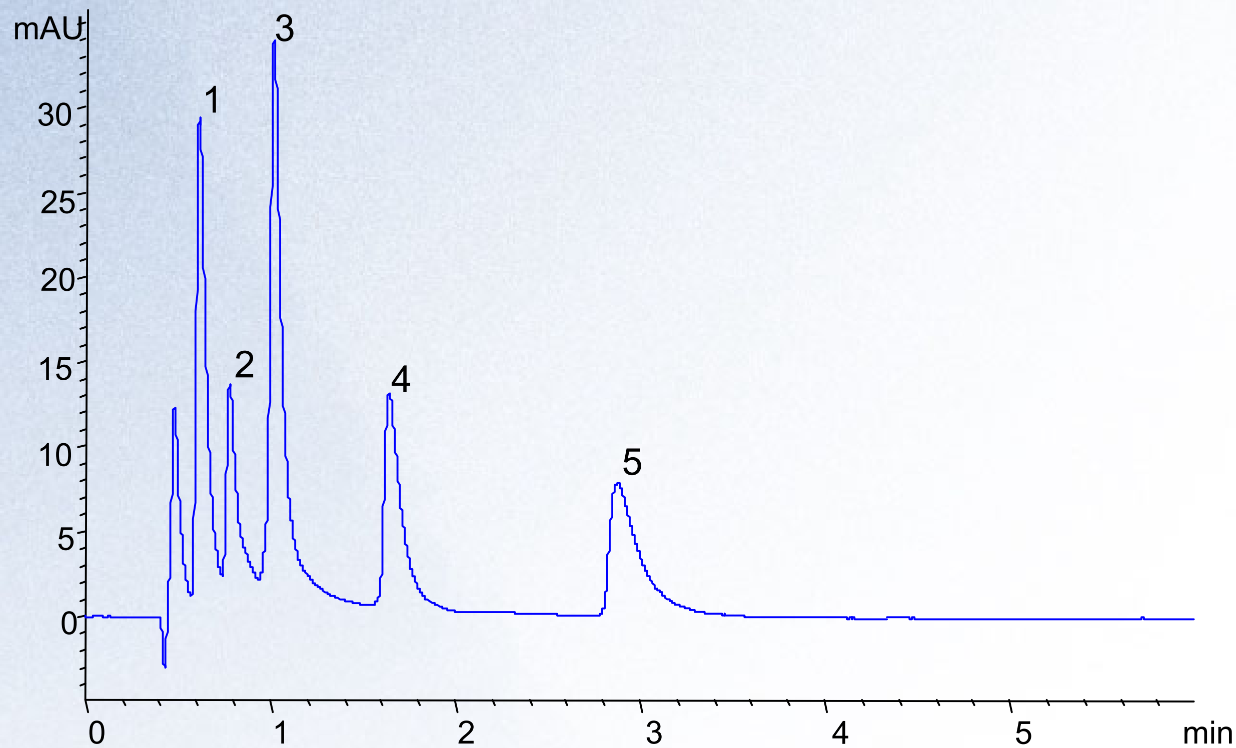
Melander, W.; Stoveken, J.; Horvath, C, *Journal of Chromatography A,* 1980, 199, 35-56.

Comparison of Selectivity Factor



Conclusions:
- All phases are reversed stationary phases.
- C18, C34 and benzyl Cyanide are very similar.
- CARBON and C18 amide are different from the other phase.

Separations Using C18 Bonded Carbon Coated NPZ



LC Conditions:

Column: C18 Modified CNPZ-C18 50x4.6 mm; Mobile Phase: 35/65 Acetonitrile/Water; Flow rate: 1.0 mL/min.; Temperature: 30 ºC; Injection volume: 1µL; Solutes: 1 benzene, 2 toluene, 3 ethylbenzene, 4 propylbenzene, 5 butylbenzene.

Conclusions

- Nonporous zirconia particles can be synthesized to be monodispersed, nonaggregated, and spherical.
- Five carbon based nonporous zirconia reversed stationary phases were successfully synthesized.
- Based on LSER studies, all five phases are reversed stationary phases. C18, C34, and CN are similar. CARB and C18 amide are different from the other reversed stationary phases.
- Acknowledgements: National Science Foundation (Grant # DMI-990871)