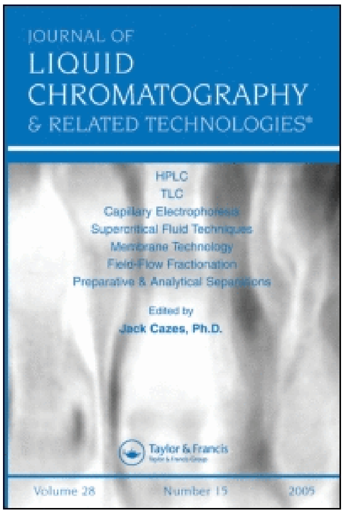

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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Yu-Ling Hu[a]; Yu-Qi Feng[a]; Jian-Di Wan[a]; Shi-Lu Da[a]
[a] Department of Chemistry, Wuhan University, Wuhan, P. R. China

To cite this Article Hu, Yu-Ling , Feng, Yu-Qi , Wan, Jian-Di and Da, Shi-Lu(2002) 'COMPARISON OF CHROMATOGRAPHIC PROPERTIES OF LEWIS BASE-MODIFIED MIXED OXIDES AS STATIONARY PHASES FOR HPLC', Journal of Liquid Chromatography & Related Technologies, 25: 1, 83 — 99

To link to this Article: DOI: 10.1081/JLC-100108541

URL: http://dx.doi.org/10.1081/JLC-100108541

J. LIQ. CHROM. & REL. TECHNOL., 25(1), 83–99 (2002)

COMPARISON OF CHROMATOGRAPHIC PROPERTIES OF LEWIS BASE-MODIFIED MIXED OXIDES AS STATIONARY PHASES FOR HPLC

Yu-Ling Hu, Yu-Qi Feng,* Jian-Di Wan, and Shi-Lu Da

Department of Chemistry, Wuhan University, Wuhan
430072, P. R. China

ABSTRACT

The chromatographic properties of stationary phases, stearic acid modified ceria-zirconia (SA$-$CeO$_2$$-ZrO_2$), alkylphosphonic acid modified ceria-zirconia (PA$-$CeO$_2$$-ZrO_2$), and alkylphosphonic acid modified magnesia-zirconia (PA$-$MgO$-$ZrO$_2$), have been investigated by reversed-phase high-performance liquid chromatography with polycyclic aromatic hydrocarbons (PAHs) and some basic compounds as probes. The retention of PAHs was quasi-homoenergetic on the three stationary phases with methanol/water as mobile phases. The retention of basic solutes was investigated on the three stationary phases over a wide range of pHs. They behave as reversed-phase packing materials at pH10.0. However, PA$-$CeO$_2$$-ZrO_2$ and PA$-$MgO$-$ZrO$_2$ exhibited dual retention mechanism at

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*Corresponding author. E-mail: yqfeng@public.wh.hb.cn

pH 4.0. These results strongly suggest that the cation-exchange sites result from the ligand of alkylphosphonic acid, rather than from the mixed oxide supports.

INTRODUCTION

Silica has the dominant position among packings used for high-performance liquid chromatography (HPLC). Its high mechanical strength, excellent pore size, ideal pore structure, and well-documented chemistry make it the material of choice for most HPLC applications. However, the main drawback of silica-based stationary phases is their limited chemical stability at extreme pH and undesirable adsorption towards basic species. (1,2) Recently, there has been an increasing interest in the use of porous metal oxides as alternative supports, such as alumina, titania, and zirconia, because of their stability in alkali-media. (3–14) Among these metal oxides, zirconia draws much interest owing to its remarkable mechanical, chemical, and thermal stability. Zirconia-based stationary phases with reversed-phase chromatographic properties have been evaluated in detail, both by modification with octadecylsilane (7–9) and coating with polymers. (10–14) Studies show polymeric octadecy-zirconia and polymer-encapsulated zirconia are stable in alkaline solution. These packing materials have been used in the separation of polycyclic aromatic hydrocarbons, amino acids, peptides, and proteins.

Although zirconia exhibits potential advantage to silica in alkaline condition, its low specific surface area and poor pore structure (15) are not expected as ideal chromatographic packing. Many efforts have been employed to improve the physicochemical properties of zirconia. (16) Shalliker (17,18) and Kaneko (19–21) have introduced silica to zirconia by surface coating and the coprecipitation method, respectively. They pointed out that the specific surface area of zirconia was increased significantly by doping with silica. The resultant mixed oxide is useful for separation of basic solutes and amino acids. However, silica doped zirconia is still not very stable in alkaline condition. Recently, two other zirconia-containing mixed oxides (magnesia-zirconia, ceria-zirconia) have been successfully prepared in our laboratory. (15,22–24) The composites exhibit a larger specific surface area, larger specific pore volume, better pore connectivity, and more uniform pore size distribution than pure zirconia. These properties result in higher column efficiency. Previously, we evaluated their chromatographic properties in normal phase mode. (15,24) However, we are actually more interested in their application in reversed-phase mode, which is more popularly used.

Similar to zirconia, the zirconia-containing mixed oxides are chemically heterogeneous on their surface. Studies have confirmed that Lewis acid sites are

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more remarkable on the surface of magnesia-zirconia and ceria-zirconia. For example, solutes with hard Lewis base moieties, such as carboxylate and phosphonate, are strongly retarded on the mixed oxides, so that they cannot be eluted even with mobile phase having great strength. This property is very troublesome for separation of these types of solutes, but the affinity of supports towards Lewis bases sets a new way for modification of the zirconia-containing oxides with Lewis bases. Carr and coworkers have modified zirconia with fluoride, (25) phosphate, (26) and ethylenediamine-N,N′-tetramethylphosphonic acid (EDTPA) (27) to create cation-exchange stationary phases, and investigated their application in the separation of proteins.

In our study, we chose Lewis bases with long alkyl-chain moieties as support modifier, in order to create a reversed-phase stationary phase. Previous study on the alkylphosphonic acid modified magnesia-zirconia ($PA-MgO-ZrO_2$), suggested that the stationary phase was of high column efficiency and was stable within the pH range of 2 to 12. (28–30) Afterwards, we synthesized the alkylphosphonic acid modified ceria-zirconia ($PA-CeO_2-ZrO_2$) and the stearic acid modified ceria-zirconia ($SA-CeO_2-ZrO_2$) stationary phases, following the similar procedure. (24–31) $PA-CeO_2-ZrO_2$ also showed satisfactory stability over the pH range of 2 to 10. (31). The stability of $SA-CeO_2-ZrO_2$ was acceptable within pH 2 to 8, but was less stable after elution with 1000 mL of methanolic buffer solution at pH 10.0. In chromatography, the organic ligands, as well as, the nature of the support can both affect the chromatographic properties of the stationary phases; therefore, it is necessary to have a detailed knowledge of their chromatographic performance.

The purpose of this work was to elucidate the retention mechanism of solutes on Lewis base modified mixed oxides. The three selected stationary phases, the stearic acid modified ceria-zirconia, alkylphosphonic acid modified ceria-zirconia, and alkylphosphonic acid modified magnesia-zirconia, were compared chromatographically under various conditions.

EXPERIMENTAL

Chemicals

All reagents were obtained from commercial sources and were of reagent grade or better. Zirconyl chloride ($ZrOCl_2.8H_2O$), cerium nitrate, magnesia chloride, polyoxyethylenesorbitan trioleate (Tween 85), sorbitan monooleate (Span 80), light petroleum, methanol, and stearic acid were all purchased from Shanghai Reagent Company. Alkylphosphonic acid was synthesized in our laboratory, as reported previously. (28)

Preparation of Lewis Bases Modified Mixed Oxides

Ceria-zirconia and magnesia-zirconia spherical particles were synthesized according to the modified procedures of our previous method. (23) Briefly, zirconyl chloride and cerium nitrate, or zirconyl chloride and magnesia chloride, were dissolved in distilled water and the mixture was then poured into light petroleum containing Span 80 and Tween 85 with stirring at the rate of 1800 rpm. After 10 min, pH was adjusted to approximately 10 by introducing NH_3 slowly. The reaction mixture was stirred for at least 48 h. Then, the hydrogel particles of the mixed oxides obtained were subjected to a multi-stage washing procedure. After a classification procedure, the collection of the particles was heated at 12°C for 1.5 h to turn the hydrogels to xerogels. Thereafter, the xerogels were calcinated at 60°C for 1 h to remove the organic residues. Some of the physicochemical characteristics of ceria-zirconia and magnesia-zirconia are shown in Table 1. The data have been discussed in detail in our previous papers. (15,24)

The Lewis bases modified mixed oxides were made by equilibration of the ceria-zirconia or magnesia-zirconia with 800 mL of stearic acid or alkylphosphonic acid solution, then washed thoroughly with methanol and distilled water to remove unadsorbed modifier. The amount of organic modifier adsorbed was determined by elemental analysis performed with a MOD-1106 elemental analyzer (Italy). It was found to be 2.9 $\mu mol . m^{-1}$ for $SA-CeO_2-ZrO_2$, 3.0 $\mu mol . m^{-1}$ for $PA-CeO_2-ZrO_2$, and 6.1 $\mu mol . m^{-1}$ for $PA-MgO-ZrO_2$, respectively.

Comparison Study

A comparison study of $SA-CeO_2-ZrO_2$, $PA-CeO_2-ZrO_2$, and $PA-MgO-ZrO_2$ stationary phases was carried out under the same chromatographic condition.

Table 1. Physicochemical Properties of Zirconia, Ceria-Zirconia, and Magnesia-Zirconia

Composite	Mole Ratio of Ce/Mg to Zr	Average Particle Size, μm	Pore Volume, $cm^3.g^{-1}$	Specific Surface Area, m^2g^{-1}	Acidity at pH 10, $mmol\ g^{-1}$	Basicity at pH 3.5, $mmol\ g^{-1}$	pH of p.z.c.
Zirconia	—	5	0.128	21	0.082	0.10	7.00
Ceria-zirconia	0.315	5	0.136	112	0.178	0.158	7.74
Magnesia-zirconia	0.129	5	0.205	62	not detected	1.00	> 11.0

The HPLC equipment consisted of a Shimadzu 10A liquid chromatographic pump, SPD-10A UV-Vis photometric detector, a Rheodyne 7125 injection system, and a Shimadzu C-R6A integrator.

The packing materials were slurry-packed into 150 × 4.6 (i.d.) mm stainless-steel columns. The column temperature was controlled at $28 \pm 1^\circ C$ through a water bath.

Methanol-water mixture, containing 50 mM sodium chloride, 5 mM acetic acid-sodium acetate buffer at pH 2.0, 4.0, 6.0, and 5 mM Tris-HCl buffer at 8.0, 10.0 were used as mobile phases. The flow rate of the mobile phase was set at $0.5\,\mathrm{mL}\,.\,\mathrm{min}^{-1}$.

The detection wavelength was set at 254 nm. Prior to the study, the columns were always equilibrated with 100 mL of the mobile phase.

RESULTS AND DISCUSSION

Retention Characteristics of PAHs

The reversed-phase chromatographic properties of $SA{-}CeO_2{-}ZrO_2$, $PA{-}CeO_2{-}ZrO_2$, and $PA{-}MgO{-}ZrO_2$ were evaluated with polycyclic aromatic hydrocarbons as test solutes. Figure 1 depicts plots of logarithmic capacity factors of toluene on the three stationary phases against the methanol content in the mobile phase. As is apparent from Fig. 1, the plots are linear with a correlation coefficient about -0.999. Similar plots have also been obtained for other PAHs under the same mobile phase conditions. These results are consistent with those on silica-based reversed-phase stationary phases.

In reversed-phase chromatography, both the surface ligand and the support probably contribute to the retention of solutes. In order to understand the physicochemical basis of the similarities and differences in the retention characteristics of these Lewis bases modified stationary phases, the energetics of the retention of PAHs on different phases, have been compared. It was known that the capacity factor (k) comprises of contributions from both the intrinsic equilibrium constant, or Gibbs free energy for the retention process, and the phase ratio of the column. Methods have already been described for comparison of intrinsic retention free energy of stationary phase, with plots of log k obtained on one stationary phase, versus that obtained on another, with the same mobile phase. (32)

Linear correlation with unit slope for such a plot, is indicative of identical Gibbs free energy in retention behavior for the two stationary phases. Such identical behavior is referred as “homoenergetic” retention and is predicted by the solvophobic theory. The intercept of the plots is the logarithmic quotient of the two column phase ratios. Linear correlation, with slope different from unity, indicates a similar but not identical retention mechanism, which is termed as

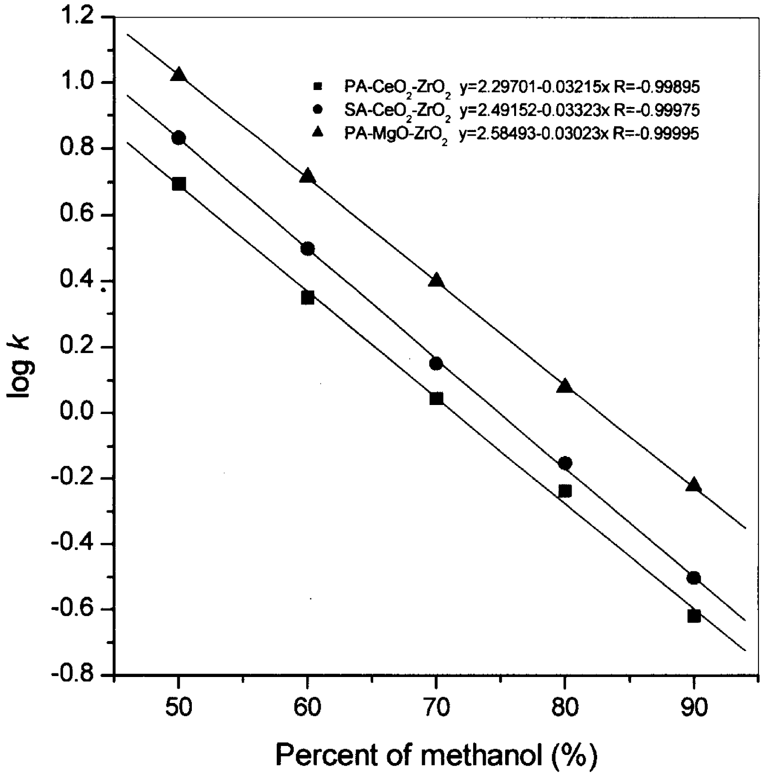


Figure 1. Plots of logarithmic capacity factor of toluene versus the methanol content in the mobile phase. Columns: PA$-$CeO$_2$$-ZrO_2$, SA$-CeO_2$$-ZrO_2$ and PA$-$MgO$-$ZrO$_2$, 150×4.6 mm I.D.; Mobile phases: methanol-water mixture; Flow rate: 0.5 mL/min.

"homeoenergetic" retention. If no correlation exists, retention is presumed to be a function of other interactions, besides purely solvophobic ones.

Figure 2 shows the log *k*-log *k* plots of seven PAHs on SA$-$CeO$_2$$-ZrO_2$ vs. PA$-$CeO$_2$$-ZrO_2$ and PA$-$MgO$-$ZrO$_2$ vs. PA$-$CeO$_2$$-ZrO_2$, respectively, with methanol/water (70/30, v/v) as the mobile phase. As can be seen from Fig. 2, both of the plots are linear, but their slopes are different. The slope of log *k*-log *k* plot of seven PAHs on SA$-$CeO$_2$$-ZrO_2$ vs. PA$-$CeO$_2$$-ZrO_2$, is slightly larger than unity, which implies that "homeoenergetic" retention exists. Whereas, for PA$-$MgO$-$ZrO$_2$ and PA$-$CeO$_2$$-ZrO_2$, the slope of the log *k*-log *k* plot is almost equal to unity, indicating that retention of PAHs is homoenergetic. This result suggests, that the inorganic supports do not contribute to the retention of PAHs,

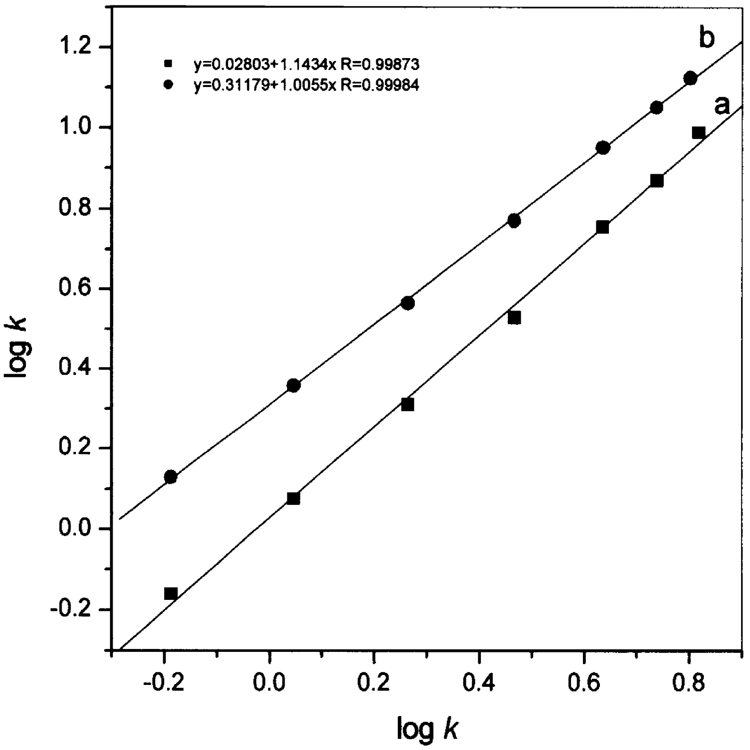
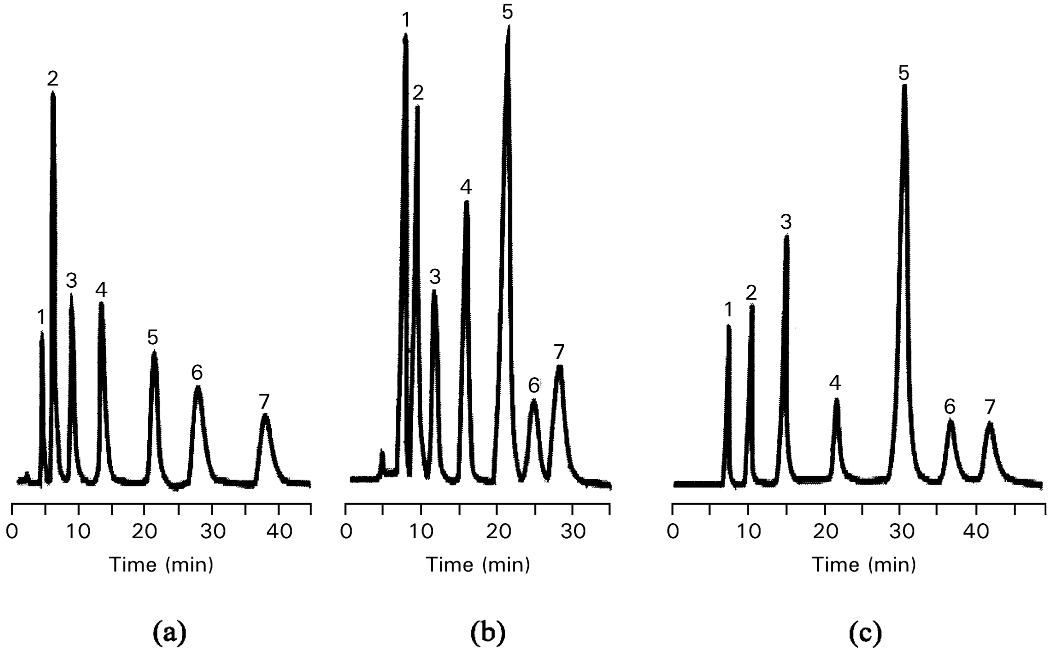


Figure 2. Plots of logarithmic capacity factor of PAHs on the SA$-$CeO$_2$$-ZrO_2$ phase versus that on the PA$-$CeO$_2$$-ZrO_2$ phase (a), and on the PA$-$MgO$-$ZrO$_2$ phase versus that on the PA$-$CeO$_2$$-ZrO_2$ phase (b). Mobile phase: methanol-water (70/30, v/v); Flow rate: 0.5 mL/min. PAHs are benzene, toluene, naphthalene, biphenyl, fluroene, phenanthrene and anthracene.

as was observed on both of the bare CeO$_2$$-ZrO_2$ and MgO$-$ZrO$_2$ from the result of our previous study. (24)

It should be mentioned, that quotient of the two column phase ratios (PA$-$MgO$-$ZrO$_2$ to PA$-$CeO$_2$$-ZrO_2$) was found to be 2.05 by calculation from the antilog of intercept of the curve (b) in Fig. 2. The value indicates that PA$-$MgO$-$ZrO$_2$ has a phase ratio of two times higher than that of PA$-$CeO$_2$$-ZrO_2$, although, the specific surface area of CeO$_2$$-ZrO_2$ is slightly larger than that of MgO$-$ZrO$_2$. This may be ascribed to stronger affinity of MgO$-$ZrO$_2$ towards Lewis bases than that of CeO$_2$$-ZrO_2$, leading to higher surface coverage of alkylphosphonic acid on MgO$-$ZrO$_2$ than its counterpart.



(a) (b) (c)

Figure 3. Separation of seven PAHs on (a) SA$-$CeO$_2$$-ZrO_2$, (b) PA$-CeO_2$$-ZrO_2$ and (c) PA$-$MgO$-$ZrO$_2$, respectively. Mobile phase: methanol-water (70/30, v/v); Flow rate: 0.5 mL/min. PAHs are 1-benzene, 2-toluene, 3-naphthalene, 4-biphenyl, 5-fluroene, 6-phenanthrene and 7-anthracene.

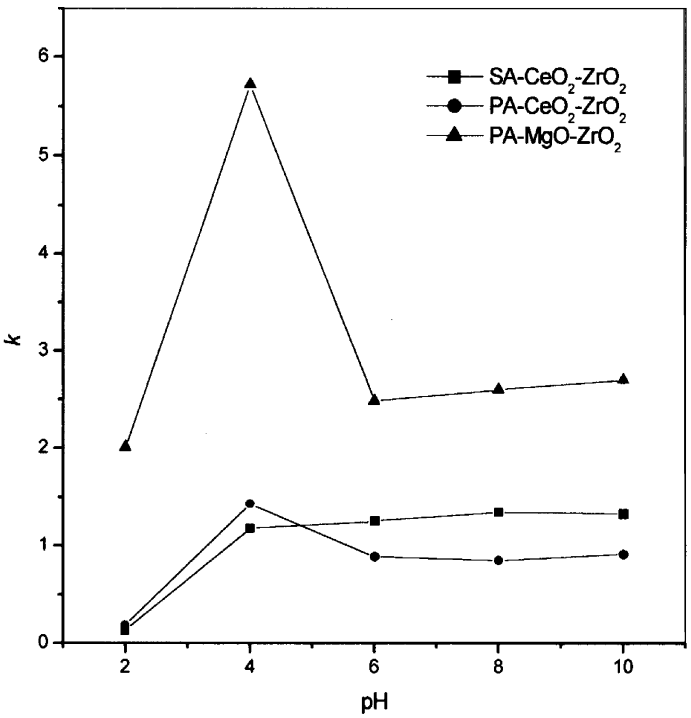


Figure 4. Plots of capacity factor of aniline versus the pH of the mobile phase on the SA$-$CeO$_2-$ZrO$_2$, PA$-$CeO$_2-$ZrO$_2$, and PA$-$MgO$-$ZrO$_2$ stationary phase. Mobile phase: methanol-buffer (30/70, v/v) containing 50 mM sodium chloride, 5 mM acetate for pH 2.0, 4.0, 6.0 and 5 mM Tris for pH 8.0, 10.0; flow rate: 0.5 mL/min.

Figure 3 illustrates the separation performance of PAHs on SA$-$CeO$_2-$ZrO$_2$, PA$-$CeO$_2-$ZrO$_2$ and PA$-$MgO$-$ZrO$_2$, respectively. They are well separated on both columns, with the same elution sequence that is typical for most reversed phase modes.

Retention Characteristics of Basic Compounds

To further evaluate the chromatographic properties of the stationary phases under investigation, the retention behavior of basic compounds was studied at different pH. For simplicity, aniline and N-methylaniline were chosen as the representatives of primary amine and secondary amine, respectively. The plots of

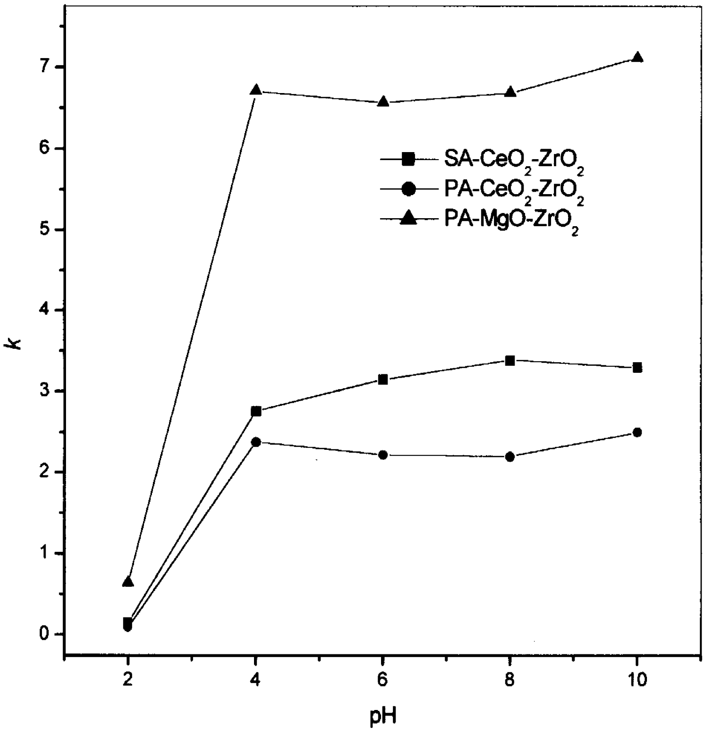


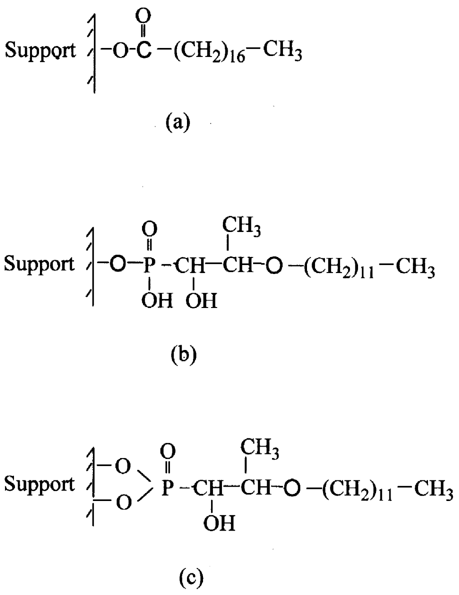
Figure 5. Plots of capacity factor of N-methylaniline versus the pH of the mobile phase on the SA$-$CeO$_2-$ZrO$_2$, PA$-$CeO$_2-$ZrO$_2$, and PA$-$MgO$-$ZrO$_2$ stationary phase. Chromatographic conditions: see Figure 3.

their capacity factors versus pH value of mobile phases were demonstrated in Fig. 4 and Fig. 5.

As can be seen in Fig. 4, the retention of aniline increases slowly with increasing pH of the mobile phases and, then, becomes almost constant on SA$-$CeO$_2-$ZrO$_2$, as expected for most reversed-phase modes. At pH 2.0, aniline was completely ionized and exhibited very weak hydrophobic interaction with SA$-$CeO$_2-$ZrO$_2$, resulting in weak retention. As the eluent pH increased, aniline was deprotonated gradually, therefore, exhibing stronger hydrophobic interaction with the stationary phase until the pH is above its pKa. However, the retention behavior of aniline varied on PA$-$CeO$_2-$ZrO$_2$ and PA$-$MgO$-$ZrO$_2$. The difference was prominent at pH 4.0, where aniline exhibited the highest retention, especially on PA$-$MgO$-$ZrO$_2$.

Similar results were obtained for other primary amine. In addition, all the primary amine under investigation showed very broad, or even abnormal, peaks at pH 4.0. This may be explained by a dual mode retention mechanism, i.e., reversed-phase mechanism and cation-exchange mechanism. We have supposed, in the previous study of PA$-$MgO$-$ZrO$_2$ stationary phase, that the cation-exchange interaction was mainly ascribed to the supports incompletely covered by organic layer. (30) However, the explanation was not sufficient for the apparent fact that ceria-zirconia and magnesia-zirconia are protonated at pH 4.0 and have positive charges. The positively charged aniline may undergo electrostatic exclusion from the pores of the positively charged supports, leading to weaker retention. Thereafter, the unusual large capacity factor of aniline on PA$-$CeO$_2-$ZrO$_2$ and PA$-$MgO$-$ZrO$_2$ at pH 4.0, probably resulted from the interaction between the solute and the alkylphosphonic acid adsorbed on the support.

Although the ion-exchange interaction was notable on PA$-$CeO$_2-$ZrO$_2$ and PA$-$MgO$-$ZrO$_2$ at pH 4.0, it was not observed on SA$-$CeO$_2-$ZrO$_2$, that has the same support as PA$-$CeO$_2-$ZrO$_2$. Accordingly, we proposed likely forms, as shown in Fig. 6(a) and Fig. 6(b), respectively, in which stearic acid and alkylphosphonic acid adsorbed on the supports. Stearic acid is carboxylic acid



(a)

(b)

(c)

Figure 6. Proposed models for the adsorption forms of stearic acid (a), and alkylphosphonic acid (b), and (c) on the supports.

with the sole hydroxyl group. As seen in Fig. 6(a), there was no hydroxyl group exposed on the surface after stearic acid adsorbed on the support, which results in no cation exchange interaction. The adsorption of alkylphosphonic acid onto supports may be in terms of form as shown in Fig. 6(b) rather than Fig. 6(c). One of the hydroxyl groups of phosphonic acid was exposed and deprotonated above pH 4.0, making the stationary phase behave as a cation exchanger. The presumption was in accordance with the result observed in the capillary electrochromatography (CEC) study of PA$-$MgO$-$ZrO$_2$. (33) The electroosmotic flow of PA$-$MgO$-$ZrO$_2$ increased significantly, compared to the bare MgO$-$ZrO$_2$ at relatively higher pH, owing to the exposed oxyanions provided by

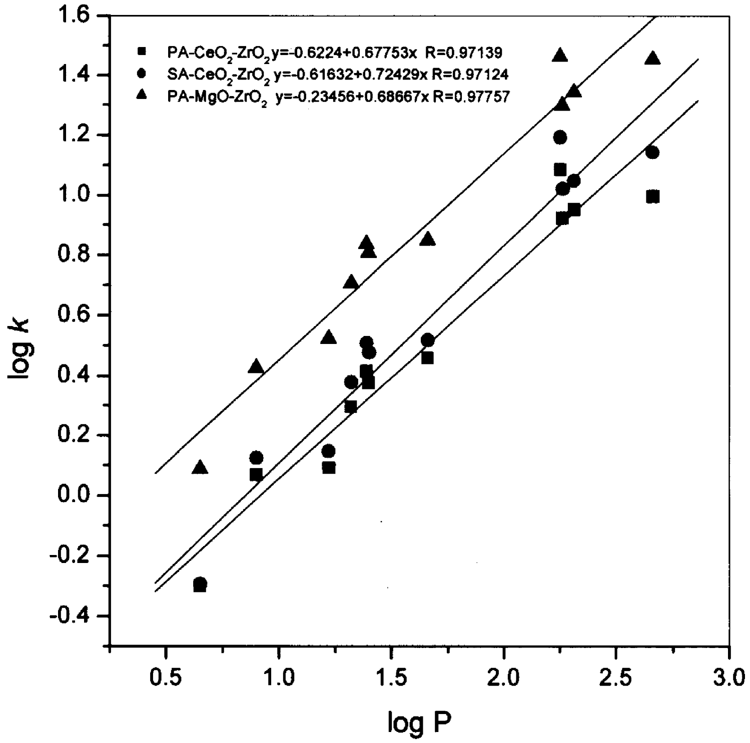


Figure 7. Plots of capacity factor of basic solutes versus their hydrophobic parameter at pH 10.0 on the PA$-$CeO$_2-$ZrO$_2$, SA$-$CeO$_2-$ZrO$_2$, and PA$-$MgO$-$ZrO$_2$ stationary phases. Mobile Phase: methanol-5 mM acetate buffer (30/70, v/v) containing 50 mM sodium chloride. Flow rate: 0.5 mL/min. Basic compounds are pyridine, aniline, 3-methylpyridine, o-toluidine, m-toluidine, p-toluidine, N-methylaniline, p-bromoaniline, N,N′-dimethylaniline, 2-naphthylamine, N-ethyl-m-toluidine.

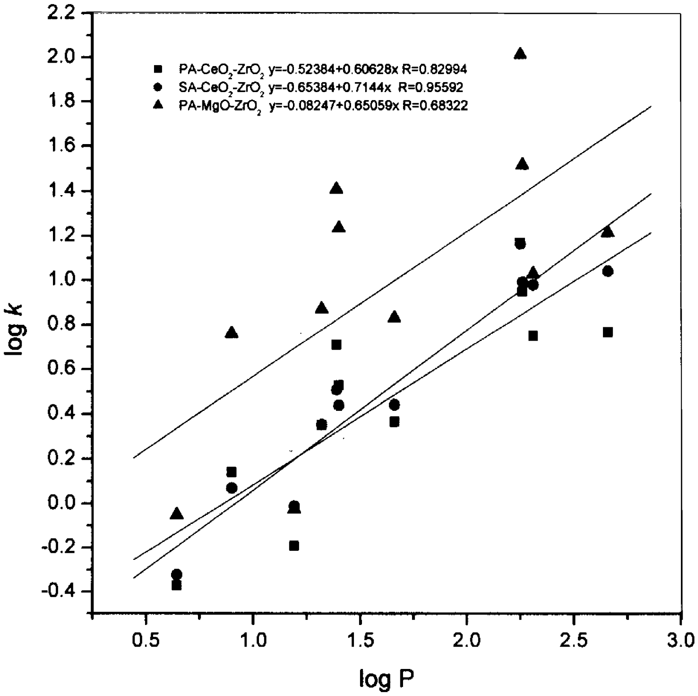


Figure 8. Plots of capacity factor of basic solutes versus their hydrophobic parameter at pH 4.0 on the PA–CeO_2–ZrO_2, SA–CeO_2–ZrO_2, and PA–MgO–ZrO_2 stationary phases. Mobile Phase: methanol-5 mM Tris buffer (30/70, v/v) containing 50 mM sodium chloride. Flow rate: 0.5 mL/min. Basic solutes are the same as those in Figure 7.

alkylphosphonic acid. However, it decreased significantly from pH 5.0 to pH 4.0 because of protonation of the oxyanions.

Although the different behavior of primary amines on stationary phases is interesting, secondary amines, such as N-methylaniline, exhibited the same chromatographic behavior regardless of the stationary phases (see Fig. 5). The ion-exchange interaction of the solute was not apparent at pH 4.0 on all the stationary phases, which may be ascribed to the cation-exchange site of the solutes being shielded by non-polar groups.

Since the partition coefficient, log P, of a solute between octanol and water is known to be related to its capacity factor, (34) if only hydrophobic interactions are responsible for the retention of the analyte, the dependence of log P on log *k* should approximately be linear. In order to better understand the retention mechanism of basic compounds on the stationary phases, the logarithmic capacity

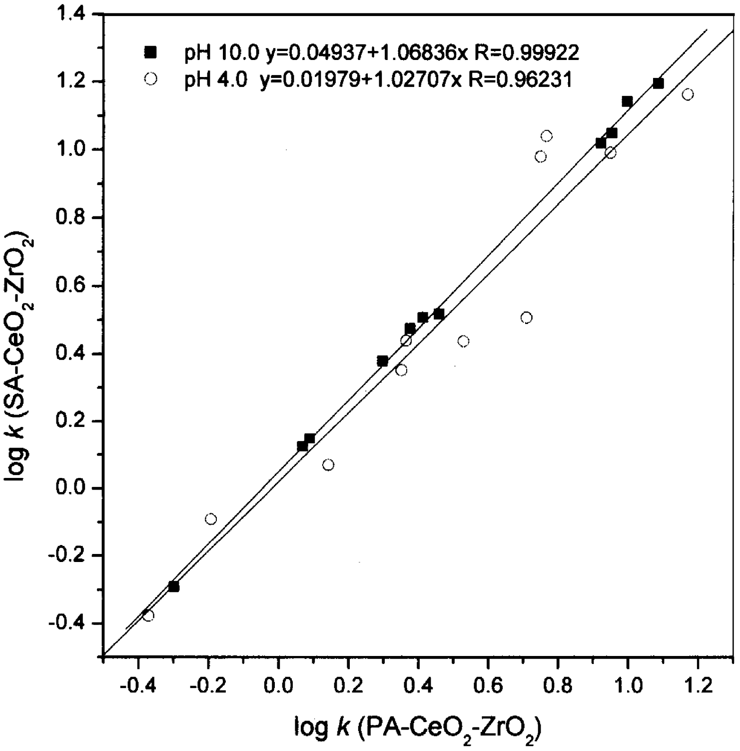


Figure 9. Plots of logarithmic capacity factor of basic solutes on the SA–CeO_2–ZrO_2 versus that on the PA–CeO_2–ZrO_2 stationary phase at pH 10.0 and pH 4.0, respectively. Mobile phase: methanol-buffer (30/70, v/v) containing 50 mM sodium chloride, 5 mM acetate for pH 4.0 and 5 mM Tris for pH 10.0; Flow rate: 0.5 mL/min. Basic solutes are the same as that in Figure 7.

factors of solutes, log *k versus* their hydrophobic parameter, log P, (35) were plotted at pH 10.0 and pH 4.0, respectively (see Fig. 7 and Fig. 8). As presented in Fig. 7, the linearity of log *k*-log P curves at pH 10.0 is acceptable with the correlation coefficient above 0.97, which implies that the reversed-phase mechanism is dominant under this condition. The information obtained from Fig. 8 was a completely different case. The linearity of curves was poor at pH 4.0 on PA–CeO_2–ZrO_2 and PA–MgO–ZrO_2 with the corresponding coefficient of 0.83 and 0.68, respectively, which provides further evidence for the assumption of dual mode retention mechanism. It should be noted, that the plot of log *k*-log *P* on SA–CeO_2–ZrO_2 presents a relatively good linear relationship at pH 4.0, although, the correlation coefficient decreased somewhat compared to that at pH

10.0. This suggests that ion-exchange interaction of basic solutes is weak on SA$-$CeO$_2$$-ZrO_2$.

Finally, comparison of retention energetic of basic solutes on the stationary phases, was carried out by the method as mentioned above. Figure 9 and Fig. 10 illustrate the log *k*-log *k* plots obtained on the corresponding stationary phases at pH 10.0 and pH 4.0, respectively. Referring to Fig. 9 and Fig. 10, log *k*-log *k* plots were linear at pH 10.0, indicating that the retention energetic of basic solutes was the same on the stationary phases. Whereas, the linear correlation of log *k*-log *k* plots was rather poor at pH 4.0, illustrating different retention mechanism were present on the stationary phases. The capacity factors of basic solutes, therefore, comprise contribution both from the intrinsic equilibrium constant for the retention process and the phase ratio of the column.

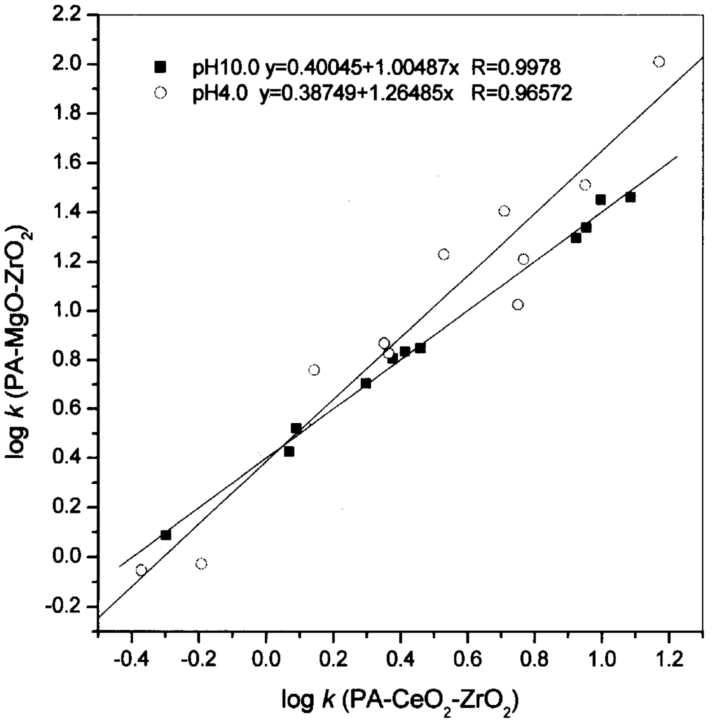


Figure 10. Plots of logarithmic capacity factor of basic solutes on the PA$-$MgO$-$ZrO$_2$ versus that on the PA$-$CeO$_2$$-ZrO_2$ stationary phase at pH 10.0 and pH 4.0, respectively. Chromatographic conditions see Figure 9. Basic solutes are the same as those in Figure 7.

CONCLUSIONS

PAHs and basic compounds were used as probes for chromatographic comparison of Lewis bases-modified mixed oxide-based support as reversed-phase stationary phases. The modified stationary phases exhibited similar chromatographic behavior towards PAHs in methanol-water eluents and basic solutes in eluents at pH 10. Under this condition, the Gibbs free energy for the retention process was identical or similar, and difference in capacity factors of solutes ascribed to different phase ratio. When the chromatographic behavior was carried out at pH 4.0, the capacity factors of basic solutes comprise contribution, both from the variation of Gibbs free energy and the phase ratio, i.e., dual retention mechanism occurred. It was apparent that the secondary interaction, other than hydrophobic interaction, was provided by the alkylphosphonic acid covered on the supports.

ACKNOWLEDGMENTS

Financial support of this research by a grant (No. 2987520) from the National Nature Science Foundation of China and Hubei Provincial Nature Science Foundation of China is gratefully acknowledged.

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Received April 7, 2001
Accepted July 5, 2001
Manuscript 5553

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