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Catalysis of an Alkaline Hydrolysis Reaction by Ionenes Immobilized on Silica

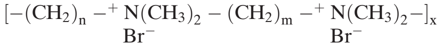
*Maria Fernanda Munhóz, Frank H. Quina**

Summary: In this work, a novel approach for the covalent coupling of ionene polyelectrolytes to chloropropyl silica surfaces is described. The immobilized ionenes catalyze the alkaline hydrolysis of N-dodecyl-4-cyanopyridinium (DCP) bromide, suggesting that, like the [3,22]-ionene in solution, these immobilized ionenes are also capable of forming micelle-mimetic microdomains.

Keywords: catalysis; ionenes; micelles; polyamines; polyelectrolytes

Introduction

The [m,n]-ionenes are linear cationic polyelectrolytes whose basic structure consists of dimethylammonium groups interconnected by alternating aliphatic chain segments containing *n* and *m* methylene groups[1,2,3,4]



$$[-(CH_2)_n-\overset{+}{N}(CH_3)_2-(CH_2)_m-\overset{+}{N}(CH_3)_2-]_x \quad \text{(under each } \overset{+}{N}\text{: } Br^-)$$

In aqueous solution, [n,m]-ionenes with short methylene segments, such as the [3,6]-ionene, exhibit behavior typical of polyelectrolytes with extended or "rodlike" conformation. In contrast, amphiphilic [n,m]-ionenes with long methylene segments, such as the [3,22]-ionene, prefer globular conformations, forming microdomains via intra- or inter polymeric aggregation of the long segments.[1,5,6]

Because of their micelle-mimetic properties, amphiphilic [n,m]-ionenes have been shown to have a variety of applications in analytical chemistry.[7–9] Because the ionenes are polymers, it is possible to immobilize them on solid supports by covalent bonding or electrostatic adsorption. In a recent work, the utilization of silica functionalized with ionenes as a new type of stationary phase for HPLC (High Performance of Liquid Chromatography)[10] was investigated.

In the present work, we report a different immobilization strategy and demonstrate that amphiphilic [n,m]-ionene polyelectrolytes immobilized on silica retain their capacity to accelerate bimolecular reactions.

Materials and Methods

The [3,22]-ionene was synthesized as previously described.[1] The [3,6]-ionene utilized was commercial hexadimethrine bromide (Aldrich). Immobilization required basically three steps: The first step is selective demethylation of the [3,m]- ionene, transforming it into a tertiary polyamine,[11] as described previously.[11] The second step is the covalent coupling of the tertiary polyamine onto chloropropyl-bonded silica. 3-Chloropropylated silica (Aldrich, 230– 400 mesh, 3.5g) was added to an acetonitrile solution (30 mL) of tertiary polyamine derived from either [3,6]- ionene (504 mg of polyamine) or the [3,22]-ionene (690 mg of polyamine). This mixture was reacted under reflux with constant stirring for 140 hours. After this period, the system was cooled and the excess solvent removed by rotatory evaporation. The silica material was washed with benzene three times (to remove the tertiary polyamine that was not immobilized). The silica was dried under low heat and constant stirring for approximately

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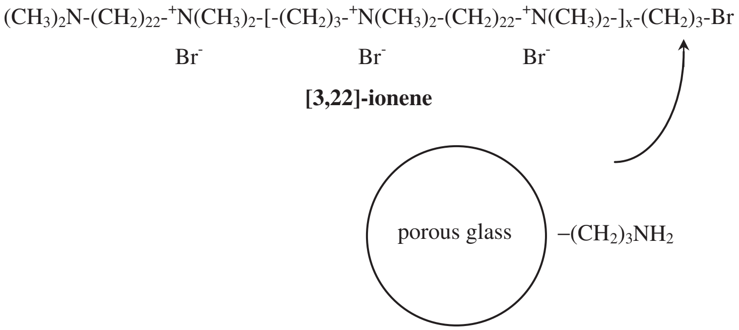
Instituto de Química – Universidade de São Paulo, CP 26077, São Paulo, 05513-970, Brasil
E-mail: quina@usp.br

4 hours on a rotary evaporator. The last step was the requaternization of the covalently bound tertiary polyamine with 1-bromopropane, 1-bromododecane or 1,3- propanesultone (all from Aldrich). The silica with the immobilized tertiary polyamine was added to an acetonitrile solution containing the bromoalkane or 1,3-propanesultone. (0.86 mmol/g silica-[3,6]-tertiary polyamine or 0.62 mmol/g silica-[3,22]-tertiary polyamine). The system was refluxed under constant stirring for 30 h. The excess acetonitrile was removed by rotatory evaporation and the silica washed with ethyl acetate. The silica was dried under low heat and constant stirring for approximately 4 hours on a rotary evaporator.

Kinetic measurements were performed at 30.0 °C and constant stirring in a Hewlett-Packard Model 8452A UV-VIS diode array spectrophotometer. A monolayer of the ionene bonded silica spheres (20 × 5 mm in size) was spread onto a strip of conventional transparent tape. The tape with the adhered monolayer spheres was immersed into 3 mL of 20 mM sodium borate buffer, pH 9.4, containing 10 μL of a 2.5 mM stock solution of DCP to initiate the reaction. The alkaline hydrolysis of N-dodecyl-4-cyanopyridinium (DCP) was followed by monitoring the decrease in absorbance at 232 nm or the increase in absorbance at 266 nm due to the appearance of N-dodecyl-pyridone. DCP was prepared by the procedure of Landquid[12] and purified by recrystallization from acetonitrile/benzene.



Results and Discussion

In recent work, the [3,16]- and [3,22]-ionenes were directly immobilized onto the surface of porous silica functionalized with aminopropyl groups.[10] This material exhibited interesting properties as a multimodal stationary phase for HPLC. However, the immobilization of the ionenes onto the solid support in that work was, rather inefficient probably due to two factors: (a) strong electrostatic adsorption of the cationic ionenes onto the glass surfaces of the spheres; (b) the intrinsically low probability of covalent union of the ionene with an aminopropyl group on the surface of silica, since the reactive bromopropyl groups are present only at the extremities of the polymer.

In this study, we report an alternative strategy for covalent coupling of the ionenes onto solid supports. This strategy takes advantage of the fact that the [m,n]-ionenes can be selectively and quantitatively demethylated to give the corresponding tertiary polyamine by refluxing in ethanolamine [12]

$$[-(\mathrm{CH_2})_n -^{+} \mathrm{N(CH_3)_2} - (\mathrm{CH_2})_m -^{+} \mathrm{N(CH_3)_2}-]_x \rightarrow [-(\mathrm{CH_2})_n - \mathrm{N(CH_3)} - (\mathrm{CH_2})_m - \mathrm{N(CH_3)}-]_x.$$

Unlike ionenes, the tertiary polyamines are soluble in a variety of organic media, are less prone to adsorb on surfaces and

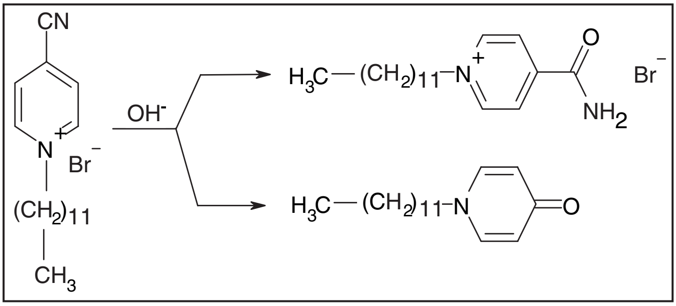


Figure 1.

Representation of the alkaline hydrolysis reaction of DCP, which gives two main products, amide and pyridone, in water, but only the pyridone in micellar media.[13]

have multiple reactive sites (the tertiary amine groups) distributed along the polymeric chain. Once immobilized on the surface of interest, the tertiary polyamine can then be requaternized with a variety of reagents. In the present study, we have covalently attached the tertiary polyamines derived from the [3,6]- and [3,22]-ionenes to chloropropyl silica spheres and then requaternized the bound polyamine with 1-bromopropane, 1-bromododecane or 1, 3- propanesultone to give either cationic ionenes with short (1-propyl) or long (1-dodecyl) alkyl or zwitterionic (ammoniopropane sulfonate) side chains.

The amphiphilic [3,m]-ionenes that form microdomains in water catalyze alkaline hydrolysis reactions because they solubilize organic substrates and concentrate the hydroxide ion on the surface of the microdomains.[1] To study the catalytic efficiency of microdomains formed by the requaternized [3,m]-ionenes immobilized on silica., we utilized the rate of alkaline hydrolysis of the 1-dodecyl-4-cyanopyridinium ion (DCP) (Figure 1).

Figure 2 compares the values of the absorved first order rate constants, k_{obs}, for the alkaline hydrolysis of DCP in the presence of silica functionalized with six different ionenes (three [3,6]-ionene derivatives and three [3,22]-ionene derivatives) compared with k_{obs} for the reaction carried out in aqueous buffer solution under the same conditions in the absence of ionene.

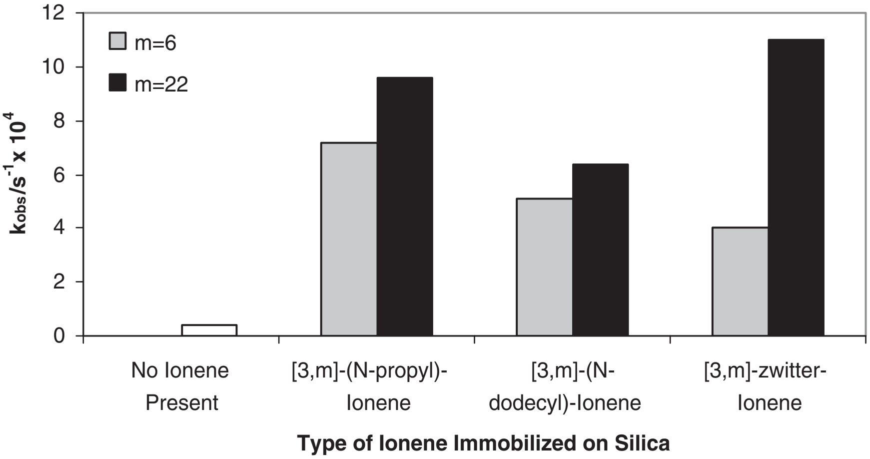


Figure 2.

Comparison of k_{obs} values for the different immobilized ionenes.

Conclusion

The present study describes a new strategy for the covalent attachment of ionene polyelectrolytes to surfaces and demonstrates that the immobilized ionenes retain their capacity to catalyze a bimolecular alkaline hydrolysis reaction. Like the [3,22]-ionene in solution,[2,6] these immobilized ionenes presumably also form micelle-like microdomains that are responsible for the observed catalytic activity.

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[1] V. Soldi, N. M. Erismann, F. H. Quina, *J. Am. Chem. Soc.*, **1988**, *110*, 5137–5143.

[2] A. Renbaum, W. Baumgartner, A. Eisenberg, *Polym. Lett.*, **1968**, *6*, 159–171.

[3] H. Noguchi, A. Rembaum, *Macromolecules*, **1972**, *5*, 253–260.

[4] A. Rembaum, H. Noguchi, *Macromolecules*, **1972**, *5*, 261–269.

[5] V. E. R. Nieves, E. J. Ribaldo, R. Baroud, F. H. Quina, *J. Polym. Sci., Polym. Lett. Ed.*, **1982**, *20*, 433–437.

[6] A. B. Ayres, J. B. Dário, A. T. N. Pires, V. Soldi, *J. Braz. Chem. Soc.*, **1993**, *4*, 93–96.

[7] W. L. Hinze, Jr. Williams, Z. S. Fu, Y. Suzuki, F. H. Quina, *Colloids Surfaces*, **1990**, *48*, 79–94.

[8] W. L. Hinze, B. Moreno, F. H. Quina, Y. Suzuki, H. Wang, *Anal. Chem*, **1994**, *66*, 3449–3457.

[9] W. L. Hinze, L.-W. Feng, B. Moreno, F. H. Quina, Y. Suzuki, H. Wang, *Anal. Sci*, **1995**, *11*, 183–187.

[10] Y. Suzuki, F. H. Quina, A. Berthod, Jr. Williams, M. Culha, I. Ullah Mohammadzai, W. L. Hinze, *Anal. Chem*, **2001**, *73*, 1754–1765.

[11] R. C. Bazito, F. L. Cássio, F. H. Quina, *Macromol. Symp.*, **2005**, *229*, 197–202.

[12] J. K. Landquist, *J. Chem. Soc., Perkin Trans.* 1, **1976**, *4*, 454–456.

[13] H. Chaimovich, J. B. S. Bonilha, M. J. Politi, F. H. Quina, *J. Phys. Chem*, **1979**, *83*, 1851–1854.