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Enantiomeric Resolution on L-Carnitine Selective Polymers Prepared by Molecular Imprinting

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Abstract: L-carnitine selective polymers were prepared by molecular imprinting using methacrylic acid as the functional monomer. The acid function of the monomer is expected to form hydrogen bond and ionic interactions with the amine function of the target molecule L-carnitine. The imprinted polymers were used as stationary phases in high-performance liquid chromatography (HPLC). It was shown that L-carnitine imprinted polymer exhibited a higher affinity to its template molecule, while the non-imprinted polymer had no affinity to the compounds tested. Racemic carnitine hydrochloride was efficiently resolved on the L-carnitine imprinted polymer, and the separation factor is 1.9.

Keywords: L-carnitine, racemic carnitine hydrochloride, molecular imprinting polymer, HPLC.

Introduction

Molecular imprinting in synthetic polymers is a new and potentially very interesting technique for preparing specialized separation media for chromatography, especially for enantiomeric separations[1-4]. Polymerization is allowed to occur in the presence of a template, the print molecule, which is subsequently removed from the rigid polymer, thereby producing sites within the polymer with affinity for the original print molecule. The resulting molecular imprint polymers (MIPs) can selectively recognize the template molecule used in the imprinting process, even in the presence of compounds with structure and function similar to those of the template. Polymerizable monomers are chosen for specific and definable interactions with the print molecule. Such interaction is subsequently responsible for the recognition of the substrate by the polymer. The interaction can be the non-covalent forces such as ionic and hydrogen bond or the reversible covalent bonds.

In this study, L-carnitine imprinted polymer was prepared using methacrylic acid and ethylene glycol dimethacrylate (EDMA) as the functional monomer and crosslinker respectively[5]. The polymers obtained were analyzed for its ability to separate the enantiomers of racemic carnitine hydrochloride.

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Chromatographic studies

The affinity of the imprinted polymers was evaluated by comparison of the retention times of the samples in HPLC. Methanol was used as the eluent at a flow rate of 0.5 $mL \cdot min^{-1}$. The sample concentration was 1.0 $mmol \cdot L^{-1}$ in methanol, and the injection volume was 20 uL. The samples were injected individually for estimating α values. Acetone was injected as a void marker. The eluent was monitored by UV absorbance at 210 nm. Capacity factors (k) were calculated using the equation, $k = (t-t_0)/t_0$, where t is the retention time of the sample and t_0 is the time to elute the void marker. The separation factor α is calculated from the equation $\alpha = k_2/k_1$, where k_1 and k_2 are the capacity factors of the first and second eluted enantiomers respectively. The results for k values are shown in **Table 1**. Enantiomeric resolution of racemic carnitine hydrochloride was observed, the L-carnitine imprinted polymer showed high affinity for L-carnitine. The results suggest that the carboxylic acid function of the functional monomers was expected to form strong hydrogen bonds with the carboxylic acid function of the print molecules. The methacrylic acid monomers may form electrostatic interactions with the amine functional group of L-carnitine, and the non-covalent forces play an important role in the retention and enantioselectivity.

Table 1 Chromatographic evaluation of imprint polymers M1and M2

samples	t(retention time for a sample, min)		K (capacity factor)		α (separation factor)	
	M1	M2	M1	M2	M1	M2
L-carnitine	18.432	6.057	3.62	0.53	---	---
L-carnitine hydrochloride	23.096	5.984	4.79	0.51	---	---
Racemic carnitine hydrochloride	15.139 25.065	7.665	2.79 5.28	0.94	1.9	---
Acetone	3.990	3.957	---	---	---	---

M1: the L-carnitine imprinted polymer. M2: the reference non-template imprinted polymer.

The results presented in this short communication represent a widening of the scope of molecular imprinting. It may help to show the potential usage of MIPs in chiral separation as the selective adsorption matrices.

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