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Preparation of Water-Compatible Molecularly Imprinted Polymers for Caffeine with a Novel Ionic Liquid as a Functional Monomer

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ABSTRACT: Water-compatible molecularly imprinted polymers (MIPs) for caffeine were synthesized in aqueous medium with a new functional monomer, 1-(α-methyl acrylate)-3-methylimidazolium bromide (1-MA-3MI-Br), which had π–π and hydrogen-bonding interactions. Caffeine-imprinted polymers were prepared in suspension polymerization with 1-MA-3MI-Br and methacrylic acid (MAA), which only had hydrogen bonding, as a functional monomer. For the specific binding characteristics of the new functional monomer 1-MA-3MI-Br, the adsorption capacity and relative separation factor (β) of MIPs for caffeine were significantly enhanced. The maximum adsorption capacities of 1-MA-3MI-Br–MIP and MAA–MIP imprinted microspheres for caffeine were 53.80 and 28.90 μmol/g, respectively. Moreover, the relative separation factors were measured by comparison of the separation characteristics under competitive adsorption conditions. The results showed that the β of MAA–MIP for caffeine relative to theophylline was only 1.65; this showed a very poor recognition selectivity for caffeine, but β of 1-MA-3MI-Br–MIP for caffeine with respect to theophylline was remarkably enhanced to 3.19; this showed an excellent recognition selectivity and binding affinity toward caffeine molecules in an aqueous environment. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: molecular imprinting; monomers; separation of polymers

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INTRODUCTION

Molecular imprinting technology, which was first introduced by Wulff and Sarhan[1] and Arshady and Mosbach,[2] is a powerful tool for the creation of molecular recognition materials having excellent molecular recognition abilities. Molecularly imprinted polymers (MIPs) are synthesized by the copolymerization of one or more functional monomer–template complexes with a crosslinker. Upon removal of the template molecules, binding sites are produced that are complementary to the template in shape, size, and position of the functional groups. Because MIPs have a predetermined selectivity, recognition, and feasibility, they have attracted considerable interest from scientists and engineers that are involved in the development of separation materials,[3–14] solid-phase extraction adsorbents,[15–20] membranes,[21,22] bionic sensors,[23] catalysis,[24] drug delivery,[25,26] and artificial antibodies.[27] However, current technology often generates MIPs for the recognition of target compounds in aprotic and low-polar organic solvents rather than in aqueous environments.[28] The presence of polar solvents, especially water, may disturb the formation of prepolymerization complexes during the imprinting procedure, and the interactions between the monomers and the template are disrupted easily.[29] As a result, the applications of MIPs for aqueous samples (most common in biological and environment analysis) are limited. The development of water-compatible MIPs for the recognition of a target compound in aqueous environments is, therefore, very important.

Several water-compatible MIPs have been reported recently in the literature. Urraca and coworkers[3,30] prepared penicillin–MIPs in aqueous media and used them for the extraction of penicillin G and its derivatives from aqueous samples. Water-compatible MIPs were used as SPE sorbents for the selective extraction of nine quinolones in urine,[15] melamine from aqueous samples,[17] sildenafil from plasma samples,[18] cholesterol in aqueous media,[31] and fluoroquinolone antibiotics in biological samples.[32] These water-compatible MIPs were synthesized with

novel hydrophilic monomers or/and crosslinkers in aqueous or aprotic organic media. Only a few types of hydrophilic functional monomer are known to date, such as methacrylamidoantipyrine,[7] bisacryloyl β-cyclodextrin,[8] 2-acrylamido-2-methyl-1-propane sulfonic acid,[22] 2-hydroxyethyl methacrylate,[28] and *N,N,*N-trimethylaminoethyml ethacrylate.[33] To obtain better recognition ability in aqueous environments, there is an urgent need to develop a new type of hydrophilic monomer.

In addition, caffeine (1,3,7-trimethylxanthine) is an alkaloid found naturally in foods such as coffee, tea, kola nuts, and cacao beans. Caffeine is an important raw material in medicine and food additives because of its physiological effects, including gastric acid secretion, diuresis, and stimulation of the central nervous and cardiovascular systems.[34] Therefore, attempts are being made to develop caffeine-selective adsorbents that are water-compatible, biocompatible, and clinically efficient. Zougagh et al.[35] and Farrington et al.[36] synthesized caffeine MIPs with methacrylic acid (MAA) as the monomer in chloroform or acetonitrile. However, the caffeine MIPs had a low-level recognition ability in aqueous media. To the best of our knowledge, water-compatible caffeine MIPs prepared in aqueous media have not been reported.

A new approach was taken from regions containing both hydrophobic interactions and hydrogen bonding. By considering this concept, we first synthesized a 1-(α-methyl acrylate)-3-methylimidazolium bromide (1-MA-3MI-Br) ionic liquid monomer with a π–π electron-poor imidazolium ring using α-(bromomethyl) acrylic acid and methylimidazole. Caffeine, which has electron-rich imidazolium, was chosen as the template molecule, and a novel MIP was synthesized. In addition, another MIP was synthesized with MAA and only had hydrogen-bonding interaction with caffeine molecules, as a functional monomer, and this MIP was used to compare the effects of selectivity with 1-MA-3MI-Br–MIP.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) 124 (PVA124) and trimethylolpropane trimethacrylate (TRIM) were obtained from Chinese Qianjin Chemistry Reagent Factory (Tianjin, China). MAA, 2,2-azobisisobutyronitrile (AIBN), and methylimidazole were purchased from Beijing Chemical Reagent Factory (Beijing, China). Caffeine, theophylline, diethyl bis(hydroxymethyl)malonate, and hydrobromic acid were supplied by Pure Crystal Shanghai Reagent Co., Ltd. (Shanghai, China).

Other chemical reagents, including methanol and toluene, were analytical grade. Double-distilled water was provided by local suppliers.

Instrumentation

Liquid chromatographic experiments were carried out with an HP1100 HPLC system, Palo Alto, CA, USA (Agilent), which consisted of an high performance liquid chromatograph (HPLC) pump operating at a flow rate of 1.0 mL/min and diode array detector (DAD) monitoring the effluent at 271 nm for caffeine and theophylline. The analytical column was a 250 mm × 4.6 mm, 5 μm C_{18} column (Agilent). The mobile phase was a methanol: 50 m*M* ammonium acetate buffer solution (20 : 80 v/v).

The instruments used in this study were as follows: a Unic-2602 UV spectrophotometer (Unic Co., Shanghai, China), a Perkin Elmer 1700 infrared spectrometer (PerkinElmer Co.), an F-Sorb 3400 automatic surface area and porosimetry instrument (Gold APP Instruments, Beijing, China), a PHS-2 acidometer (The Second Analytical Instrument Factory, Shanghai, China), a TG16-WS high-speed centrifuge with desk type (Changsha Xiangyi Centrifuge Factory, Province Jiangsu, China), and a THZ-92C constant-temperature shaker equipped with a gas bath (Boxun Medical Treatment Equipment Factory, Shanghai, China).

Synthesis and Characterization of α-(Bromomethyl) Acrylic Acid

A 500-mL, three-necked, round-bottom flask was equipped with a magnetic stirrer, fraction collector, cold-finger condenser, and two thermometers. Amounts of 55.0 g (0.25 mol) of diethyl bis(hydroxymethyl)malonate and 160 mL (1.25 mol) of 43.5% hydrobromic acid were placed into the flask. Then, the mixture was heated, and the temperature of the liquid was maintained between 85 and 90°C. During the reaction, a mixture of ethyl bromide and water was distilled for1.5–2 h. The residue was then boiled for 10 h, with the temperature maintained between 85 and 90°C. At the end of this period, the mixture was concentrated on a rotary evaporator at 65–70°C (10–15 mm). About 80 mL of water was removed. The residue was cooled in the refrigerator overnight. Crystals of α-(bromomethyl) acrylic acid were filtered in the cold. After drying, 15.40 g (36.25%) of α-(bromomethyl) acrylic acid was obtained, and the melting point was 73–75°C. Moreover, some IR peak characteristics of the product were as follows:

IR (KBr, cm^{-1}): 3438–2578 (COOH), 1704 (C=O), 1671 (C=C). ^{1}H-NMR (D_2O, δ): 4.08 (s,2H,CH_2Br), 5.96 (s,1H,=CH), 6.19 (s,1H,=CH).

Synthesis and Characterization of the 1-MA-3MI-Br Functional Monomer

A 50-mL, three-necked, round-bottom flask was equipped with a magnetic stirrer and a thermometer. Methylimidazole (5.00 g) was placed into the flask, and then, α-(bromomethyl) acrylic acid (10.00 g) was added slowly to the solution with magnetic stirring at 70–75°C for 24 h. At the end of this chemical reaction period, the solution was extracted with ether (3 × 20 mL) for the elimination of excessive methylimidazole. Then, the organic phase was evaporated in a rotary evaporator. The residue was cooled. Finally, 12.66 g of a white and ceraceous solid was obtained. The melting point was found to be 55–57°C, the density was 1.15 g/cm^3, and the yield was 91.8%.

^{1}H-NMR (D_2O, δ): 3.87 (s, 3H, NC*H_3), 5.00 (s,2H,CH_2), 6.04 (s,1H,=CH), 6.47 (s, 1H, =CH), 7.43 (1H, m, CH_3NC*HCHN), 7.45 (1H, m, CH_3NCHC*HN), 8.76 (1H, s, NC*HN). IR (KBr, cm^{-1}): 3400–2578 (COOH), 1576–1451 (imidazole ring of skeleton vibration adsorption bands).

Preparation of the Caffeine MIP Microspheres with Suspension Polymerization

The suspension polymerizations were carried out in a 250-mL, three-necked round-bottom flask equipped with a reflex condenser, a nitrogen inlet, and a stirrer. The flask was immersed in a thermostated water bath at 75°C. The stirring speed was

Table I. Recipes for the Preparation of the Caffeine–MIPs by Suspension Polymerization

MIP	Template (mmol) Caffeine	Monomer (mmol) 1-MA-3MI-Br	Monomer (mmol) MAA	Crosslinker (mmol) TRIM	Initiator (mg) AIBN	α	β
P_1	2	8	0	8	160	1.20	1.35
P_2	0	8	0	8	160	0.89	—
P_3	2	8	0	16	160	1.85	2.17
P_4	0	8	0	16	160	0.85	—
P_5	2	8	0	40	160	2.10	2.33
P_6	0	8	0	40	160	0.90	—
P_7	1	4	0	30	160	2.51	2.49
P_8	0	4	0	30	160	1.01	—
P_9	1	4	0	40	160	2.71	3.08
P_{10}	0	4	0	40	160	0.88	—
P_{11}	1	4	0	60	160	1.48	1.74
P_{12}	0	4	0	60	160	0.85	—
P_{13}	4	4	0	40	160	2.24	2.55
P_{14}	2	4	0	40	160	2.71	3.19
P_{15}	1.33	4	0	40	160	2.45	2.78
P_{16}	1	4	0	40	160	2.21	2.51
P_{17}	0.8	4	0	40	160	2.16	2.45
P_{18}	1	0	4	40	160	1.62	1.65
P_{19}	0	0	4	40	160	0.98	—

maintained at 365 rpm. The polymerization recipes are given in Table I. A typical procedure is as follows. An amount of 4.0 g of PVA124 was dissolved in hot water (ca. 90°C, 120 mL) and then cooled to room temperature. Then, this mixture was transferred into a flask, and stirring was started. AIBN was added to the mixture of caffeine, functional monomer, and TRIM in methanol. The mixture was dissolved by ultrasound for 5 min. The solution was added dropwise to the flask with stirring, and N_2 was passed over the flask simultaneously until the reaction was complete. The reaction lasted for 8 h at 75°C. The generated polymer particles were collected by filtration and were washed with 100 mL of hot water and 50 mL of methanol to remove poly(vinyl alcohol) from the surface of the polymer microspheres. Finally, the obtained polymer particles were washed through Soxhlet extraction with methanol/acetic acid (8 : 2 v/v, for 48 h) and methanol (for 24 h) to remove the template. The nonimprinted microspheres were prepared in the same manner in the absence of template molecules.

Adsorption Experiments

In adsorption isotherm experiments, 50 mg of caffeine MIP microspheres and nonimprinted polymer (NIP) microspheres were introduced into different glass flasks, respectively. Caffeine solutions (25 mL) with initial concentrations of 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50, 0.55, and 0.60 mmol/L were then added to each glass flask. The glass flasks were shaken for 2 h, and the supernatant was analyzed for caffeine content with HPLC. The amount of caffeine adsorbed onto the polymer was determined according to the following formula:

$$Q = (C_0 - C_e)V/m \quad (1)$$

where C_0 and C_e represent the initial and final caffeine solution concentrations (mmol/L), respectively, V is the sample volume (mL), m is the mass of the polymer (g), and Q is the equilibrium binding quality of caffeine in the polymers (mg/g). The tests were carried out in triplicate.

The selectivity adsorption experiments of the caffeine MIP microsphere and NIP microspheres were carried out under equilibrium binding conditions with theophylline as a control substrate. The molecular structures of the two substances are schematically expressed in Figure 1. The concentrations of caffeine and theophylline were determined by HPLC. The recognition selectivity was evaluated by the static distribution coefficient (K_D), the separation factor (α), and the relative separation factor (β). The parameters K_D, α, and β are defined as follows:

$$K_D = Q_e/C_e \quad (2)$$

where Q_e is the binding quality of caffeine at the equilibrium of adsorption.

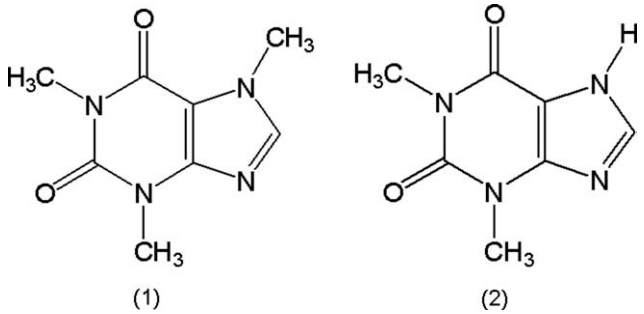

Figure 1. Molecular structure of (1) caffeine and (2) theophylline.

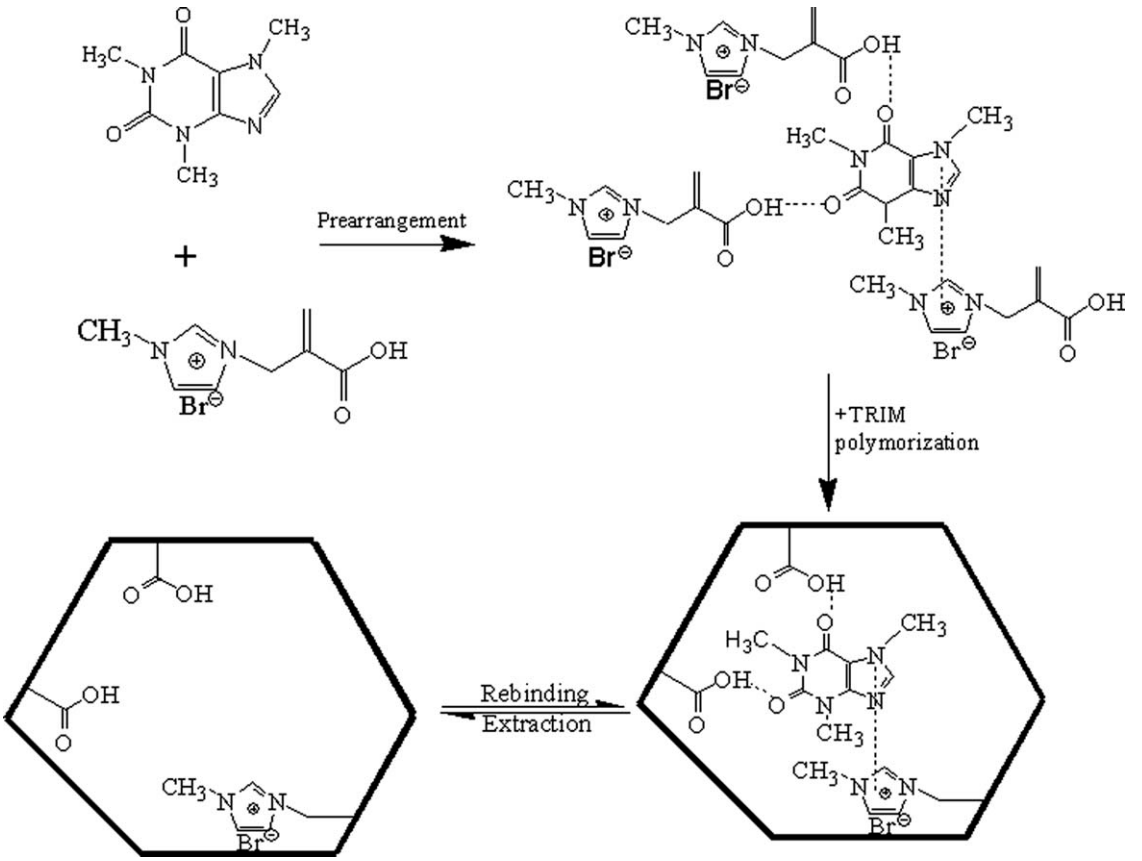

Figure 2. Schematic mechanism of the synthesized MIPs. Step 1: Prearrangement of 1-MA-3MI-Br with caffeine. Step 2: Suspension polymerizations in water. Step 3: Extraction/rebinding of 1-MA-3MI-Br–MIP.

The α of caffeine versus theophylline was quantified by the ratio of the two partition coefficients K_{D1} and K_{D2} (for caffeine and theophylline, respectively):

$$\alpha = K_{D2}/K_{D1} \tag{3}$$

The higher value of α was the better selectivity. When α was close to 1.0, the sorbent had no selectivity:

$$\beta = \alpha_M/\alpha_N \tag{4}$$

where α_M and α_N are the distribution coefficients of the MIPs and NIPs, respectively. β demonstrated the difference between the MIPs and NIPs. The higher value of β represented the greater difference. When $\beta = 1.0$, it meant that there was no difference between the MIPs and the control polymer.

RESULTS AND DISCUSSION

Preparation and Characterization of the Caffeine MIP Microspheres

To evaluate the performance of the new functional monomers, caffeine was chosen as the template. Caffeine was chosen because it had a π–π electron-rich imidazolium ring; this allowed for the evaluation of recognition as a diagnostic of polymer performance. Three functional groups, an imidazole ring of caffeine (π donor) and two carbonyls, provided three points for the hydrophobic charge-transfer interactions between the imidazole ring of 1-MA-3MI-Br (π-acceptor) and the imidazole ring of caffeine (π donor) and hydrogen-bonding interactions for the complex before polymerization. The molecular recognition process on the MIPs is shown in Figure 2.

Effect of the Crosslinker Content on the Recognition Selectivity

The content of crosslinkers affected mainly the degree of crosslinking of the polymeric network. For better recognition ability for caffeine in an aqueous environment, the ratio of functional monomers to crosslinkers in the water-compatible MIPs with suspension polymerizations was investigated. The results are shown in Table I. MIPs and NIPs with different crosslinkers were put into contact with caffeine and theophylline aqueous solutions to reach equilibrium; then, α and β were measured. With increasing crosslinker, α and β increased, reached a maximum for a molar ratio of 1 : 10 (1-MA-3MI-Br/TRIM), and then decreased with further increase in the crosslinker amount. The more rigid the polymer structure was, the easier it was to keep the affinity sites with desired three-dimensional structures. Hence α and β increased with the TRIM amount used. When the TRIM content was too high, the number of affinity sites for the caffeine in the polymers became too few; this decreased the binding ability of the MIPs. The equilibrium adsorption amount of caffeine was as high as 53.80 μmol/g of polymer at a molar ratio of 1 : 10 (1-MA-3MI-Br/TRIM). After optimization, a molar ratio of 1 : 10 (1-MA-3MI-Br/TRIM) was used to prepare the water-compatible MIPs.

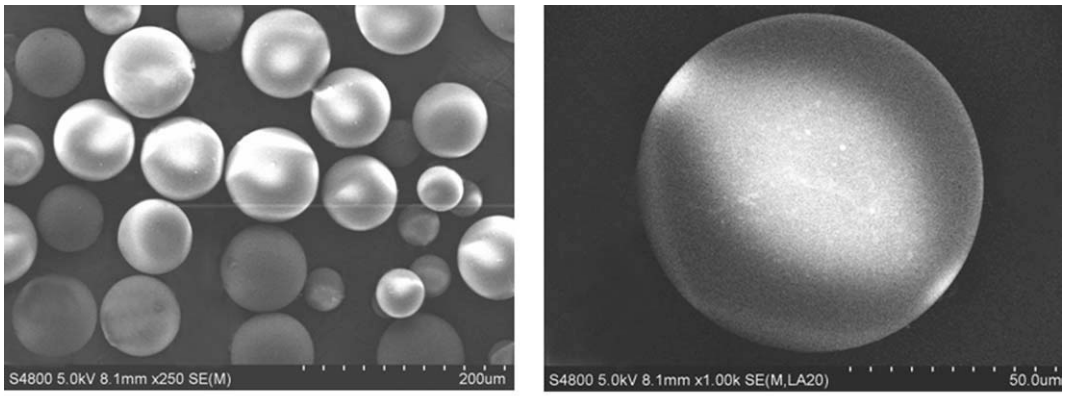

Figure 3. Scanning electron micrographs of 1-MA-3MI-Br–MIPs and magnifications of (A) 250 and (B) 1000×.

Effect of the Template/Functional Monomer Molar Ratio on the Recognition Selectivity

Table I also shows the effect of the template/functional monomer ratio on the recognition selectivity. All β's were higher than 2.4 in the range from 1 : 2 to 1 : 5 when the molar ratio of 1-MA-3MI-Br to TRIM was 1 : 10. The β values indicated that the molecular imprinting procedure produced cavities with an affinity for caffeine in the MIPs. All of the α values being higher than 2.2 showed that the MIPs had a better recognition ability for caffeine than for theophylline; this was attributed to the π–π charge-transfer interaction, although they had very similar structures. α and β increased with the template/functional monomer ratio. α and β reached maximum values when the template/functional monomer ratio was 1 : 2. Then, they decreased with further increases in the molar ratio. Thus, 1 : 2 was chosen as the optimum template/functional monomer ratio for the preparation of the MIPs.

Characterization of 1-MA-3MI-Br–MIPs and 1-MA-3MI-Br–NIP

The morphology of the 1-MA-3MI-Br–MIPs with optimum factors prepared by suspension polymerization was observed by SEM. As shown in Figure 3(a), well-shaped beads with diameter distributions from 40 to 80 μm were achieved. The majority of the beads were spherical, and the surfaces of the beads were porous and rough [Figure 3(b)] and were suitable for rebinding or releasing the target molecules from the MIP beads. The NIP beads prepared with the same recipe had similar morphological structures and size distributions.

It is known that the surface properties of MIPs have much influence on their binding properties. Therefore, the 1-MA-3MI-Br–MIPs/NIPs were characterized by nitrogen adsorption experiments. The surface areas of the 1-MA-3MI-Br–MIPs and NIPs before and after methanol/acetic acid extraction were 3.25, 25.02, and 2.56 m^2/g, respectively. The 1-MA-3MI-Br–MIPs after methanol/acetic acid extraction had larger surface areas. The results show that many imprinting cavities were produced after the caffeine was eluted by a methanol/acetic acid solution. Smaller surface areas in the NIPs suggested that imprinting cavities were not produced. This also verified that caffeine MIPs were prepared successfully.

Adsorption Properties and Mechanism of the MIPs Toward Caffeine

Adsorption Isotherms. The adsorption isotherm experiments for 1-MA-3MI-Br–MIP, 1-MA-3MI-Br–NIP, MAA–MIP, and MAA–NIP were carried out with caffeine concentrations in the range 0.20–0.60 mmol/L (Figure 4). The amount of adsorbed caffeine per unit mass of the polymer increased with the initial concentrations of caffeine and, finally, reached saturation. The maximum adsorption capacities (Q_{max}'s) were observed to be 53.80, 20.10, 28.90, and 18.90 μmol/g for 1-MA-3MI-Br–MIP, 1-MA-3MI-Br–NIP, MAA–MIP, and MAA–NIP, respectively. The value of 1-MA-3MI-Br–MIP increased almost two times compared to that of MAA–MIP; this showed the excellent recognition selectivity and binding affinity toward caffeine molecules in aqueous environments.

The equilibrium adsorption data were fitted according to the Langmuir model, as shown by the following equation:

$$C_e/Q = C_e/Q_{max} + 1/bQ_{max}$$

where b is the Langmuir constant.

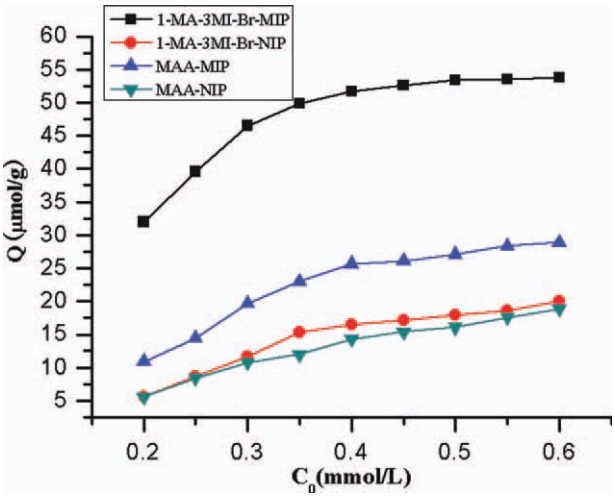

Figure 4. Adsorption isotherms of 1-MA-3MI-Br–MIP for caffeine. Conditions: MIPs microspheres = 50 mg, solution volume = 25 mL, shaking time = 2 h, and temperature = 25°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

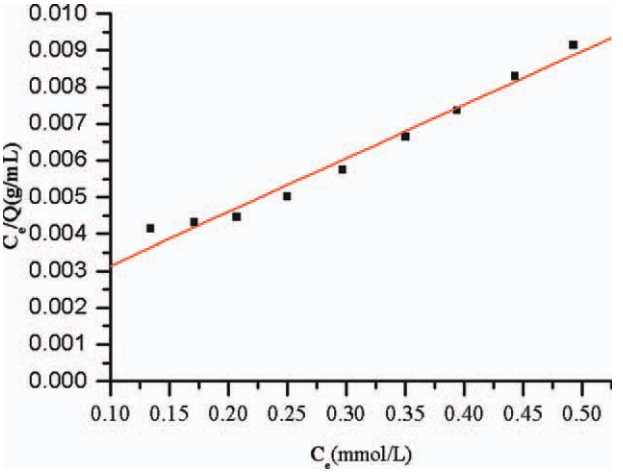

Figure 5. Langmuir plot for the adsorption of caffeine on 1-MA-3MI-Br–MIP. Conditions: MIPs microspheres = 50 mg, solution volume = 25 mL, shaking time = 2 h, and temperature = 25°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The linearized plots of C_e/Q versus C_e were plotted on the basis of the previous equation and are shown in Figure 5. The Langmuir equation fit well for caffeine adsorption on the imprinted microsphere within the experimental concentration range with a Langmuir correlation coefficient of 0.990. The fact that the Langmuir isotherm was in good agreement with the experimental data may have been because of the homogeneous distribution of cavities on the MIP surface. The Q_{max} value was calculated to be 67.88 μmol/g for the Langmuir model. The calculated Q_{max} value was bigger than the measured value. Perhaps this was caused by the incomplete removal of templates in 1-MA-3MI-Br–MIP and competitor adsorption on the MIP surface. A similar observation was described in the literature.[7]

Adsorption kinetics. Figure 6 shows the binding kinetics of the caffeine with the 1-MA-3MI-Br–MIP and 1-MA-3MI-Br–NIP.

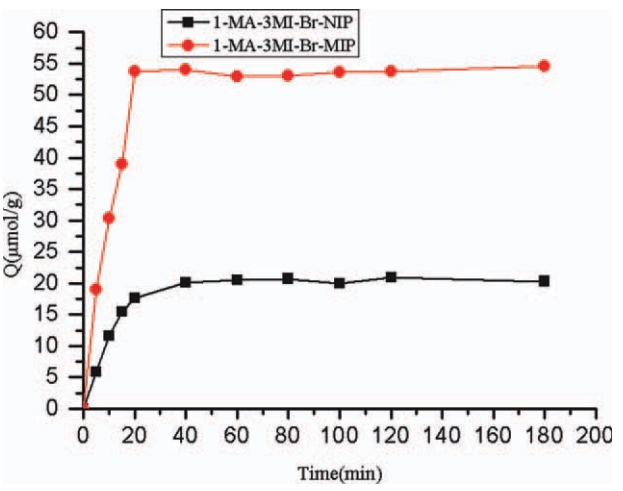

Figure 6. Adsorption kinetic curve of 1-MA-3MI-Br–MIP and 1-MA-3MI-Br–NIP for caffeine. Conditions: MIPs microspheres = 50 mg, solution volume = 25 mL, initial concentration = 0.50 mmol/L, shaking time = 2 h, and temperature = 25°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

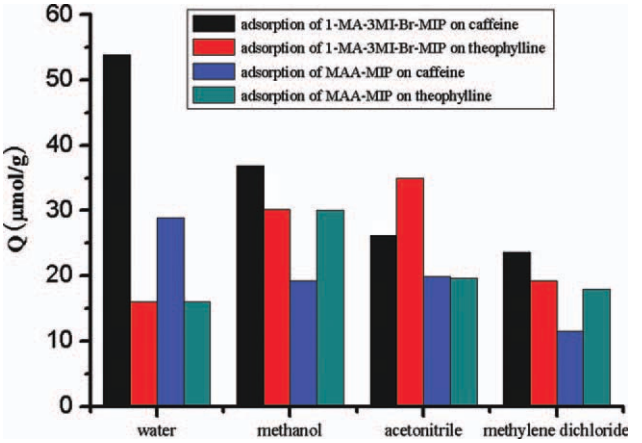

Figure 7. Adsorption of caffeine and theophylline on 1-MA-3MI-Br–MIP and MAA–MIP in different solvents. Conditions: MIPs microspheres = 50 mg, solution volume = 25 mL, shaking time = 2 h, and temperature 25°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As shown, the adsorbed amount of caffeine increased with time during the first 20 min and leveled off as the equilibriums were reached. We assumed that the adsorption equilibrium was fast established because of the smaller diffusion barrier in the two polymers. 1-MA-3MI-Br–MIP possessed bigger adsorption capacities than 1-MA-3MI-Br–NIP. This proved that there were many imprinted cavities in 1-MA-3MI-Br–MIP.

Recognition Selectivity of the MIP Microspheres for Caffeine in Different Solvents

Binding experiments were conducted by immersion of the caffeine MIPs in a different solvent mixture of caffeine and theophylline to investigate the recognition abilities. The results are shown in Figure 7. The following facts were discovered:

1. The adsorption capacity of caffeine with 1-MA-3MI-Br–MIPs in water solvent was the largest among the four solvents. The adsorption capacity of theophylline from water was the smallest among the four solvents. The 1-MA-3MI-Br–MIPs and MAA–MIPs were both synthesized in aqueous environments. The imprinted cavities. whose shape and spatial arrangement of functional groups were complementary to the template, could be not kept well in organic solvent, so the adsorption capacity of caffeine decreased rapidly. The surface area of the MIPs increased in weak polar solvents because of swelling; this led to an increase in the nonspecific adsorption capacity of theophylline. These results demonstrate that the 1-MA-3MI-Br–MIPs had excellent recognition ability for caffeine in water media.
2. The adsorption capacity of caffeine with the 1-MA-3MI-Br–MIPs decreased gradually with the increase of hydrophobicity of the solvent. Perhaps it was caused by the subdued hydrophobic interactions between 1-MA-3MI-Br and caffeine and crumpled imprinting cavities. The adsorption capacity of caffeine with the MAA–MIPs also decreased gradually with increasing hydrophobicity of the solvent because a mass of cavities was destroyed.

3. These adsorption capacities of caffeine with 1-MA-3MI-Br–MIPs in the four solvents were all higher than those of caffeine with MAA–MIPs. The results show that the prepolymerization was disturbed partially during the suspension polymerization procedure when MAA was used as functional monomer because of only hydrogen-bonding interactions for the complex form; thus, the number of imprinted cavities decreased. When 1-MA-3MI-Br was used as a functional monomer because of hydrogen-bonding interactions and charge-transfer interactions for the complex form, the amounts of imprinted cavities increased largely. These results verify that the 1-MA-3MI-Br–MIPs had good water compatibility.

CONCLUSIONS

In this study, caffeine-imprinted microspheres with high performance were prepared with a novel 1-MA-3MI-Br ionic liquid as a functional monomer. The results suggest that the 1-MA-3MI-Br–MIPs had better adsorption capacities compared to the MAA–MIPs. Moreover, the adsorption capacity of caffeine with 1-MA-3MI-Br–MIPs in water was the biggest among the four solvents (water, methanol, acetonitrile, and methylene dichloride). This result verifies that the 1-MA-3MI-Br–MIPs had good compatibility with water. The poor specific binding results of the MAA–MIPs may have caused by the fact that the MAA–MIPs only had hydrogen bonding with caffeine, whereas the 1-MA-3MI-Br–MIPs had both hydrogen bonding and hydrophobic interactions with caffeine. In addition, the Langmuir equation fit the data well for the adsorption of caffeine on the 1-MA-3MI-Br–MIPs within the experimental concentration range with a Langmuir correlation coefficient of 0.990. By employing this novel functional monomer, we obtained various water-compatible MIPs with high performance. Thus, the application range of MIPs can be greatly extended as well.

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