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Molecularly imprinted adsorbents for positional isomer separation

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Abstract

2,4-Dihydroxybenzophenone (2,4-DHB) imprinted polymers were synthesized by surface imprinting technique, using allyl alcohol as the functional monomer. The polymers showed a very high selectivity for 2,4-DHB when compared with various positional isomers such as 2-HB, 2,2′-DHB, 4,4′-DHIB and 4,4′-DMB. Solvents were found to affect the selectivity as well as sorption capacity in the case of surface imprinted polymers. The selectivities decreased drastically when the imprint cavity was blocked. This validated the importance of the cavity and the rebinding interactions in governing the selectivity in the case of MIPs. The surface imprinted polymers also showed a high selectivity under non-equilibrium conditions thereby making them suitable adsorbents for industrial separations.

Keywords: Isomer separation; Molecular imprinting; Selective adsorbents; Adsorbents; Hydroxybenzophenone

1. Introduction

Molecular imprinting has attracted wide attention for the synthesis of size and shape selective polymeric hosts, which can be used as sensors [1], catalysts [2] or stationary phases for racemic resolution [3]. Especially their use as a chiral stationary phase for racemic resolution of drug molecules is very attractive, since a large number of chiral drugs have to be resolved to comply with the regulations. Though the MIPs have a high selectivity for the template molecule, their large scale application in this area is limited by low sorption capacity. An application of MIPs, wherein their low sorption capacity need not deter their use on large scale, is in the removal of trace impurities from bulk organic streams. Recently we illustrated this in the separation of phenol from anisole [4].

In addition to the resolution of optical isomers, MIPs can also be used for the separation of positional isomers, which differ from one another only in the position of the functional groups. Many organic reactions involving aromatic nuclei lead to such mixtures, (e.g. alkylation of toluene invariably leads to a mixture of *o*, *m* and *p*-xylenes which needs to be separated to obtain *p*-xylene) which need to be separated either for value addition, by isolating one of the expensive isomers or for removal of small amounts of isomeric impurities. Molecularly imprinted polymers can find a potential application in this untapped area.

Molecularly imprinted polymers (MIPs) are prepared by polymerization of the functional monomers along with a large excess of crosslinker, around a template molecule to form a three-dimensional network [5,6]. The template is leached out from the polymer leaving behind its impression in the form of a cavity with appropriately oriented functional

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groups. The cavity can then form a selective host–guest relationship with the template. The organization of the functional monomers around the template can be carried out with the help of covalent linkages or non-covalent interactions such as hydrophobic interactions [7], metal ion coordination [8], electrostatic interactions [9], etc., and the rebinding interactions are almost always non-covalent.

Traditionally MIPs have been prepared for bulky substrates such as drug molecules [10], steroids [11], carbohydrates [12] etc. having multiple sites for rebinding [13]. These are normally prepared by precipitation polymerization [14], followed by mechanical grinding and sieving to the desired particle size. MIPs can also be prepared by surface imprinting on a preformed support polymer [15]. Both these methods have specific advantages as well as limitations and the choice of the imprinting technique to enhance separation efficacy, depends on the structure of the template molecule [16].

In this communication we report the use of surface imprinted polymers for the separation of positional isomers of hydroxybenzophenone, using 2,4-dihydroxybenzophenone (2,4-DHB) as the template. The selectivity and capacity of these polymers under equilibrium as well as non-equilibrium conditions is reported. The role of the imprint cavity and the rebinding interactions on the selectivity was validated.

2. Experimental

2.1. Reagents and chemicals

2,4-Dihydroxybenzophenone (2,4-DHB), 2-hydroxybenzophenone (2-HB), 4,4′-dihydroxybenzophenone (4,4′-DHB), 2,2′-dihydroxybenzophenone (2,2′-DHB). Bisphenol-A (BPA), 4,4′-dimethoxybenzophenone (4,4′-DMB), (see Fig. 1 for the chemical structures) allyl chloroformate, glycidyl methacrylate (GMA), ethylene glycol dimethacrylate (EGDMA) and polyvinylpyrrolidone (PVP, M_r 360 000) were obtained from Aldrich Chemical Co. and were used as such. All other chemicals and solvents were obtained from local sources and were of highest purity available. Methanol for HPLC was obtained from M/s Qualigens (Ind.) and water for HPLC was purified by filtering it through a Milli-Q water purification system.

2.2. Synthesis of allyl-2,4-DHB carbonate (All24DHBC)

2.14 g of 2,4-DHB and 2.22 g of triethyl amine (TEA) were dissolved in about 50 ml of dry and distilled tetrahydrofuran (THF) and cooled to 0–5°C. To this, a solution of 2.65 g allyl chloroformate, in 25 ml THF was added slowly under stirring. During the addition (45–60 min) the temperature was held constant. After addition the suspension was allowed to warm to room temperature and stirring was continued for another 24 h. The suspension was filtered to remove the TEA salt and the crude monomer was obtained after evaporation of the solvent. The crude product was dissolved in ethyl acetate, washed with chilled brine, dried over anhydrous Na_2SO_4 and the solvent was evaporated to obtain the monomer as a yellow oily liquid (yield 70%).

I.R. (neat): 1764.7 cm^{-1} (C=O, carbonate), 1666.4 cm^{-1} (C=O, aryl ketone).

^{1}H NMR ($CDCl_3$): δ (ppm) 7–8 (M, aromatic, 8 H), 5.9 (M, =CH, 2 H), 5.3 (M, $=CH_2$, 4 H), 4.6 and 4.8 (dd, $-CH_2$, 4 H).

2.3. Synthesis of GMA–EDGMA macroporous support polymer (GE90)

Macroporous GMA–EGDMA support polymer (GE90) was prepared by a modified suspension polymerization process given by Svec et al. [17]. In a typical procedure, a mixture of 2.72 g of GMA, 24.48 g of EGDMA, 36.76 g of cyclohexanol, 4.08 g of dodecanol and 0.272 g azobis isobutyronitrile (AIBN) was degassed by a passage of nitrogen. This was added slowly under stirring to a degassed solution of 3.0 g PVP and 0.3 g of sodium lauryl sulfate in 300 ml water. The suspension was heated to 70°C and stirring continued at 500 rpm for 2 h. The temperature was then raised to 80°C and stirring was continued for further 6 h. After the polymerization (8 h) heating was stopped and the suspension was stirred further for 2 h. The suspension was decanted, washed with water and methanol and then dried in a vacuum oven at 50°C. The microspheres

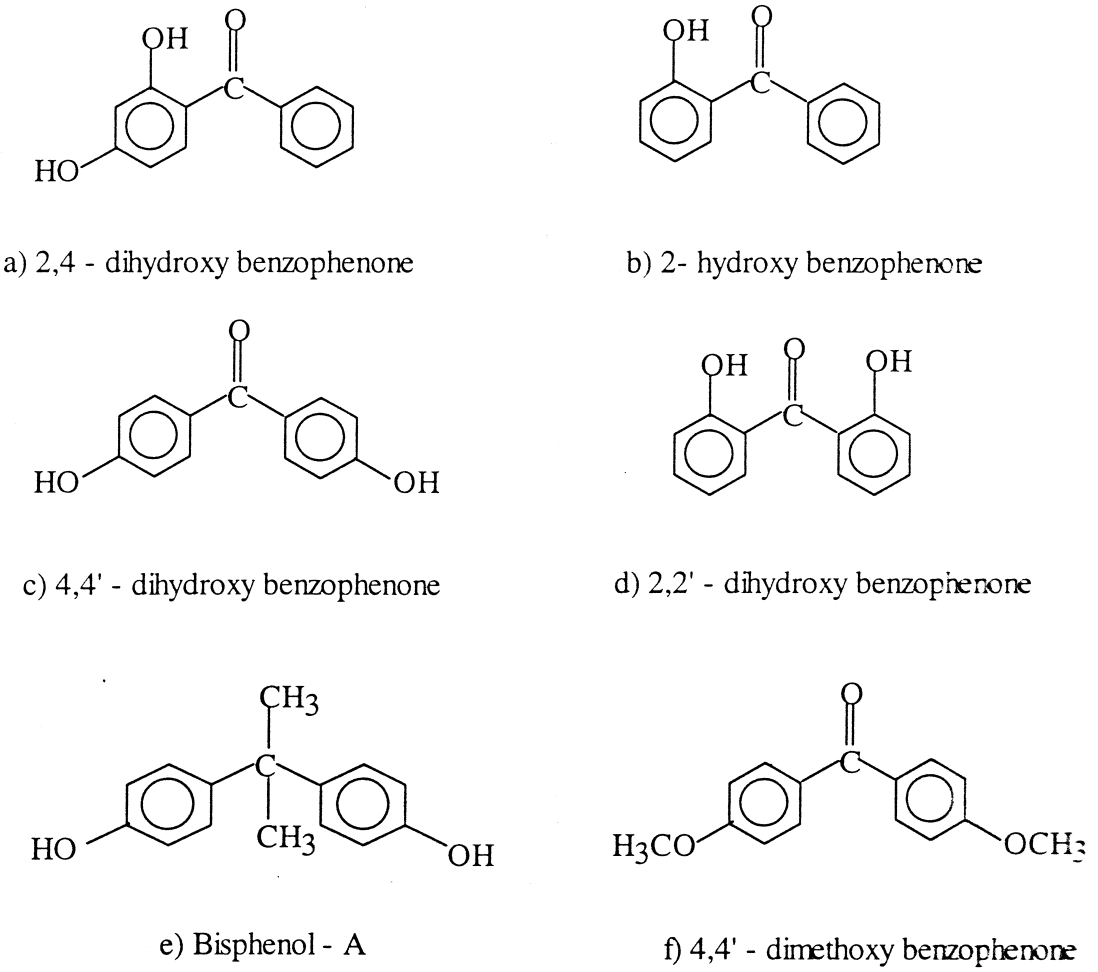


Fig. 1. Chemical structures of 2,4-DHB isomers.

were then sieved and the microspheres in the range 37 to 75 μ diameter were chosen for the adsorption studies.

2.4. Synthesis of surface imprinted polymers

In a typical procedure, 1.0 g of the support polymer, GE90 was suspended in about 50 ml benzene and 0.2 g All24DHBC was added to the suspension along with 1.0 ml EGDMA and 25 mg AIBN. The monomer mixture was then allowed to sorb over the macroporous support polymer for 18–24 h, after which polymerization of the template monomer, sorbed on the support polymer was carried out at 75°C for 24 h. After polymerization, the polymer was washed free of unreacted monomers using methanol.

Hydrolysis of the template (2,4-DHB) was carried out by refluxing the polymer with 100 ml 1 *M* NaOH for 6 h and the suspension was filtered. The filtrate was acidified and 2,4-DHB was extracted in ethyl acetate. The ethyl acetate extract was dried over Na_2SO_4 and evaporated to dryness. The amount of the functional monomer loaded in the imprinted polymer can then be calculated from the amount of 2,4-DHB released. This gives an idea about the theoretical sorption capacity of the polymer (Table 2). The polymer was then washed with dilute HCl, water and methanol and dried.

Similarly non-imprinted control polymers were

prepared by using the same amount of the functional monomers and were used to compare the performance of MIPs.

2.4.1. Synthesis of imprinted polymers with a blocked imprint cavity

To elucidate the role of imprint cavity in selectivity, imprint polymers were also prepared, wherein the cavity was blocked with the template molecule. These were prepared exactly as the imprinted polymers, the only difference being that the hydrolysis step for the generation of cavities was not carried out, thus leaving the covalently linked template in the cavity.

2.5. Characterization of polymers

Surface areas and porosity of the polymers were determined by nitrogen adsorption method (Omnisorp CX 100, Coulter). Surface areas and pore volumes for the polymers are listed in Table 1. Scanning electron microscopy (SEM, Stereoscan 440, Leica Labs) was used to check the surface morphology of the polymers (Fig. 2).

2.5.1. Swelling ratios of the polymers (see Table 1)

Swelling ratios of the polymer were measured using two different solvents viz., ethanol and methanol. In a typical experiment, about 50 mg of the polymer was weighed in an eppendorf tube and about 1–1.5 ml of the solvent was added. Entrapped air was removed and the tube was sealed. The tubes were then placed in a constant temperature water bath maintained at 25°C and shaken horizontally for 48 h during which equilibrium was achieved. The tubes were centrifuged at a high speed, the supernatant was drained off and excess solvent was wiped off. The tube was then weighed. From the dry weight of the polymer and the amount of solvent sorbed, the swelling ratio was calculated using the following equation.

$$\text{Swelling ratio} = \frac{\text{wt. of solvent sorbed}}{\text{dry wt. of the polymer}} \quad (1)$$

2.6. Equilibrium sorption capacity

In a typical procedure, 20 mg of the polymer was taken in a screw cap tube and a 10 ml solution of 2,4-DHB was added to it. The concentration of 2,4-DHB was approximately 1.0 mg/ml. The tubes were kept in a water bath maintained at 25°C and shaken horizontally at 180 cpm for 12 h during which the equilibrium was found to be attained. After 12 h the supernatant was analyzed for the concentration of 2,4-DHB using reverse-phase HPLC.

The HPLC system comprised of Waters 510 solvent delivery pump. μ-Bondpak C-18 column (3.9×300 mm), 486 tunable absorbance detector and 746 dual channel integrator. The mobile phase was a mixture of methanol and water (70–30 v/v). The mobile phase flow-rate was 1.0 ml/min and amount injected was 20 μl Using the calibration curve, the concentration of 2,4-DHB in the supernatant was calculated and knowing the inlet concentration, the amount adsorbed was determined. The amount of 2,4-DHB adsorbed gives the equilibrium sorption capacity of the polymers.

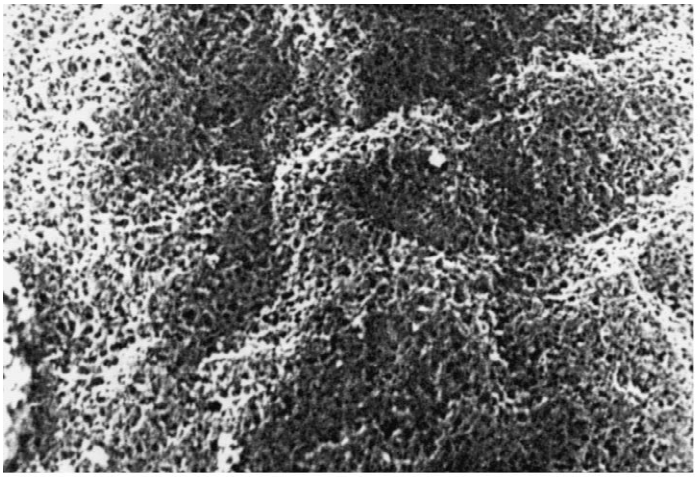
2.7. Selectivity experiments

Selectivity experiments were carried out under equilibrium as well as the non-equilibrium conditions. Competitive selectivity experiments were carried out using four different hydroxybenzophenone isomers as the competing sorbates viz. 2-HB, 4,4′-DHB, 2,2′-DHB, 4,4′-DMB and BPA.

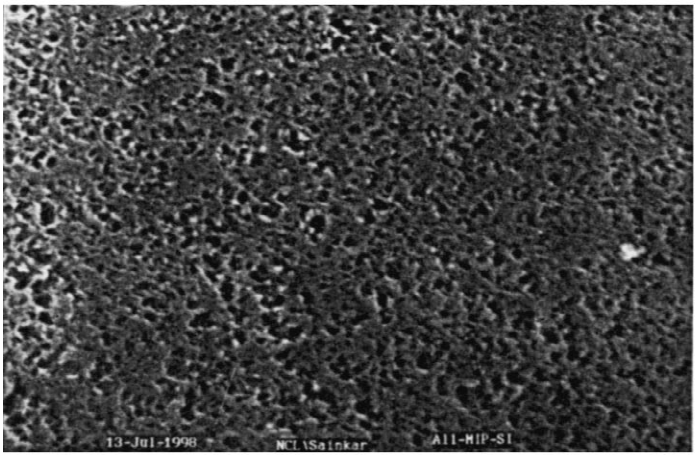
Table 1
Surface areas and swelling ratios of 2,4-DHB imprinted polymers

Sr. no.	Polymer code	Surface area m^2/g	Pore volume ml/g	Swelling ratio[a]
1	GE90	398.1	0.674	–
2	All24DHBC-MIP-GE90	134.6	0.344	2.55
3	All-BL-GE90	267.6	0.322	2.33

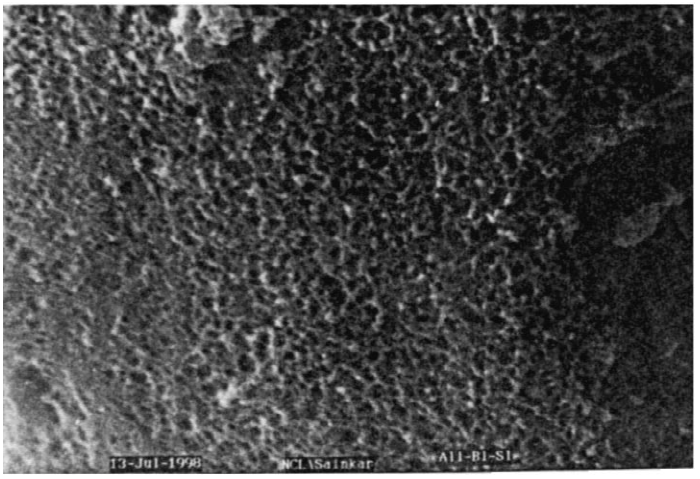
[a] Swelling ratio was determined using ethanol as solvent at 25°C. Swelling ratio = weight of solvent sorbed/dry weight of the polymer.



a) GE90



b)All24DHBC-MIP-GE90



c) All24DHBC-BL-GE90

Fig. 2. Surface morphology of imprinted polymers imprinted for 2,4-DHB based on allyl alcohol.

2.7.1. Selectivity under equilibrium conditions

The procedure for determination of selectivity under equilibrium conditions was the same as that for the determination of sorption capacity. The only difference was that the solution used for selectivity studies contained one or more competing sorbates along with 2,4-DHB. Concentrations of individual sorbates were determined using reverse-phase HPLC as outlined above. All the sorbates were detected by their absorbance at 275 nm. From the amount of individual sorbates adsorbed, the selectivity α was determined as follows.

$$\alpha = \frac{\text{Amount of 2,4-DHB sorbed}}{\text{Amount of competing sorbate sorbed}} \quad (2)$$

Similar experiments were also carried out for non-imprinted polymers and imprinting efficacy β was determined as follows.

$$\beta = \frac{\alpha \text{ for MIP}}{\alpha \text{ for non-imprinted polymer}} \quad (3)$$

Equilibrium selectivity experiments were also carried out for imprinted polymers, wherein the imprint cavity was blocked with the template (2,4-DHB) and α values were determined using Eq. (2).

2.7.2. Selectivity under non-equilibrium conditions

These experiments were carried out in a packed bed adsorber. The detailed procedure is reported by Joshi et al. [4], the only difference being the amount of the adsorbent packed in the column was approximately 0.2 g and the concentration of the individual sorbate was 2.0 mg/ml instead of 5.0 mg/ml as was the case earlier.

The eluate was then analyzed for concentration of individual sorbate using reverse-phase HPLC as outlined above. From the amounts of individual sorbates adsorbed, sorption capacity for 2,4-DHB was determined. Similar selectivity experiments were carried out for non-imprinted polymers as well and α and β were estimated using Eqs. (2) and (3).

3. Results and discussion

The molecular imprinting concept and its applications in catalysis, sensors and chiral separations have been extensively demonstrated. In a prior communication we demonstrated that the molecularly imprinted polymers can be used for selective sorption of trace impurities of phenol from anisole [4]. Often reactions on aromatic nuclei lead to mixtures of isomers and molecularly imprinted polymers can be conveniently used for separation of these isomers. Separations of positional isomers of these kinds have however not been reported so far.

3.1. Choice of system

In this paper we report the separation of hydroxybenzophenone isomers using 2,4-DHB imprinted polymers. The positional isomers; 2-HB, 4,4′-DHB, 2,2′-DHB, 4,4′-DMB were chosen as the competing sorbates. BPA was also chosen as a competing sorbate as it has a similar structure.

Recently, we reported that during separation of phenol from bisphenol-A, bulk imprinted polymers led to high selectivity for phenol, which is a small molecule and has only a single point rebinding interaction. Surface imprinted polymers exhibit high selectivity when used for bulky substrates viz., hydroxybenzophenones [16]. Although most studies on MIPs have used a bulk imprinting technique for synthesis, there are conflicting reports regarding the accessibility of imprint site [14,18,19]. Reinholdsson et al. [20] have reported use of toluene as a porogen in order to obtain a highly porous imprinted matrix by bulk imprinting technique. But our own preliminary work on bulk imprinting using toluene as a porogen resulted in a non-porous matrix. In order to overcome these problems, we synthesized and evaluated surface imprinted polymers with respect to their selectivity and the sorption capacity.

GMA was used as a comonomer for the preparation of the support polymer. Although epoxy group is hydrolyzed during the splitting of the template molecule thereby generating hydroxyl groups which can act as non-specific adsorption sites, it is also easily amenable for chemical modifications which would enhance the hydrophobicity of the support polymer [21]. This would help in attaining higher sorption of the template monomer on the support and thereby enhance the sorption capacity of the imprinted polymers. In the work reported however no attempts were made to modify the support charac-

teristics, since the separation factors were quite satisfactory.

We used the sacrificial monomer approach proposed by Whitcombe et al. [14] for the synthesis of MIPs. Allyl alcohol was linked to the template, 2,4-DHB through a carbonate linkage which, on hydrolysis generated hydroxyl groups which are known to exhibit rebinding of phenolic hydroxyl groups through hydrogen bonding interactions [14]. Though it is known that allyl monomers are difficult to homopolymerize, the copolymerization reactivity ratios with ethyl and methyl methacrylate indicate formation of a copolymer ($r_1 = 0$ and $r_2 = 107.4$ and 78.8, respectively). Allyl amine was recently used for the synthesis of sialic acid imprinted polymers [18]. Thus, allyl monomers can be used for the synthesis of imprinted polymers.

3.2. Equilibrium experiments

Measurement of the absolute selectivity and capacity of the imprinted polymers, under equilibrium conditions is the first step towards the characterization of MIPs. Since diffusional and hydrodynamic influences are eliminated, the data can be used to correlate the structure with the performance of the adsorbents.

3.2.1. Equilibrium sorption capacity

Equilibrium sorption capacity measurements on MIPs give an idea about the efficacy of utilization of the theoretical capacity of the adsorbent. Table 2 lists the sorption capacities for imprinted polymers. Depending on the solvent used, the percentage rebinding efficiency for the imprinted polymers was 40 to 95%.

Fig. 3 shows the plot of pore volume vs. pore radius for the imprinted polymers. It can be clearly seen that the imprinted polymer shows a pore volume maximum in the mesoporous region (pore radius 75 Å). It shows low porosity in the microporous region (pore radius <20 Å). Hence, the accessibility of the imprint site is very high.

Table 2
Equilibrium sorption capacity of the 2,4-DHB imprinted polymer (All24DHBC-MIP-GE90)

Sr. no.	Solvent	Sorption capacity, mg/g
–	Template loading	40–50
1	THF	43.34
2	Ethanol	40.50
3	Methanol	21.50
4	1% acetic acid in methanol	19.05

Equilibrium sorption capacity was determined in various solvents as solvents are known to affect the sorption capacity. The sorption capacity decreases as the solvent polarity increases. With the increase in the solvent polarity the solvent competes, along with the solute, for the sorption sites thereby leading to reduction in sorption capacity.

3.2.2. Equilibrium selectivity

Table 3 summarizes the selectivity data for imprinted polymers. It can be seen that the imprinted polymers exhibit a very high selectivity for the template in all the solvents under study and the selectivity increases with the polarity of the solvent. This increase in selectivity with the increase in the solvent polarity results from the reduction in the non-specific adsorption.

The selectivity of the MIPs for the template increases as the structural difference between the template and the competing sorbate increases. In the series of competing sorbates used in this study, the structural difference between 2,4-DHB and the competing sorbates increases in the following order, 2-HB ~ 2,2′-DHB ~ 4,4′-DHB < BPA < 4,4′-DMB. The difference between 2,4-DHB and 2-HB, 2,2′-DHB and 4,4′-DHB is only the positioning of one of the hydroxyl functional groups. BPA differs from the template in not only the positioning of the functional groups but also in the bridging C atom which is attached to two methyl groups, instead of a carbonyl functionality. 4,4′-DMB differs from the template the most, as it lacks both the functional groups and the positioning of the methyl groups is also different. This trend in selectivity can be seen in the case of surface imprinted polymers when THF was used as the solvent. In other solvents, the high polarity interferes with the solute–sorbate and solute–solvent interactions and hence no distinct trend emerges.

The rebinding interaction in the case of MIPs is hydrogen bonding and hence any factor which affects it can affect the selectivity as well as imprinting efficacy. The intrinsic capacity of the solvent

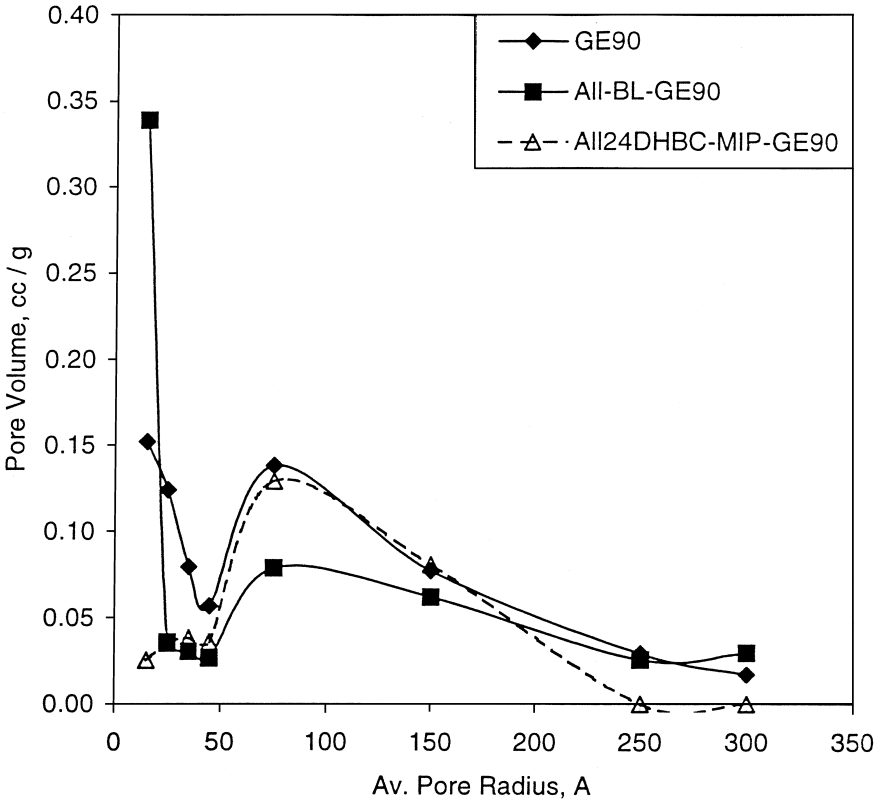


Fig. 3. Pore volume vs. pore radius plot for the imprinted polymers.

molecule to form hydrogen bonds, is reflected in the hydrogen bond donator factor ($\Sigma\alpha H_2^H$) of the solvent. As $\Sigma\alpha H_2^H$ of the solvent increases, the solvent becomes a stronger hydrogen bond donor and can form hydrogen bonds with the solute and sorbate. This can lead to changes in the selectivity behavior of MIPs.

Thus, for a given pair of solute when $\Sigma\alpha_2^H$ of the solvent was plotted against imprinting efficacy, β for the surface imprinted polymer there was an increase in the imprinting efficacy with an increase in the hydrogen bond donator factor (Fig. 4).

As the accessibility of the imprint sites is good in surface imprinted polymers, most of the accessible cavities are filled with the template under equilibrium conditions. On the other hand, solvent competes with the template for the non-specific adsorption sites. With an increase in the hydrogen bond donator

Table 3
Equilibrium selectivity for 2,4-dihydroxybenzophenone from various solvents for MIP, All24DHBC-MIP-GE90

Sr. no.	Solute	Selectivity, α			
		THF	Ethanol	Methanol	1% acetic acid in methanol
1	2-HB	2.45	2.16	1.56	2.79
2	4,4′-DHB	2.40	4.30	1.69	12.38
3	2,2′-DHB	2.64	3.57	1.95	2.02
4	BPA	3.04	1.87	4.86	3.96
5	4,4′-DMB	3.20	1.82	8.16	1.03

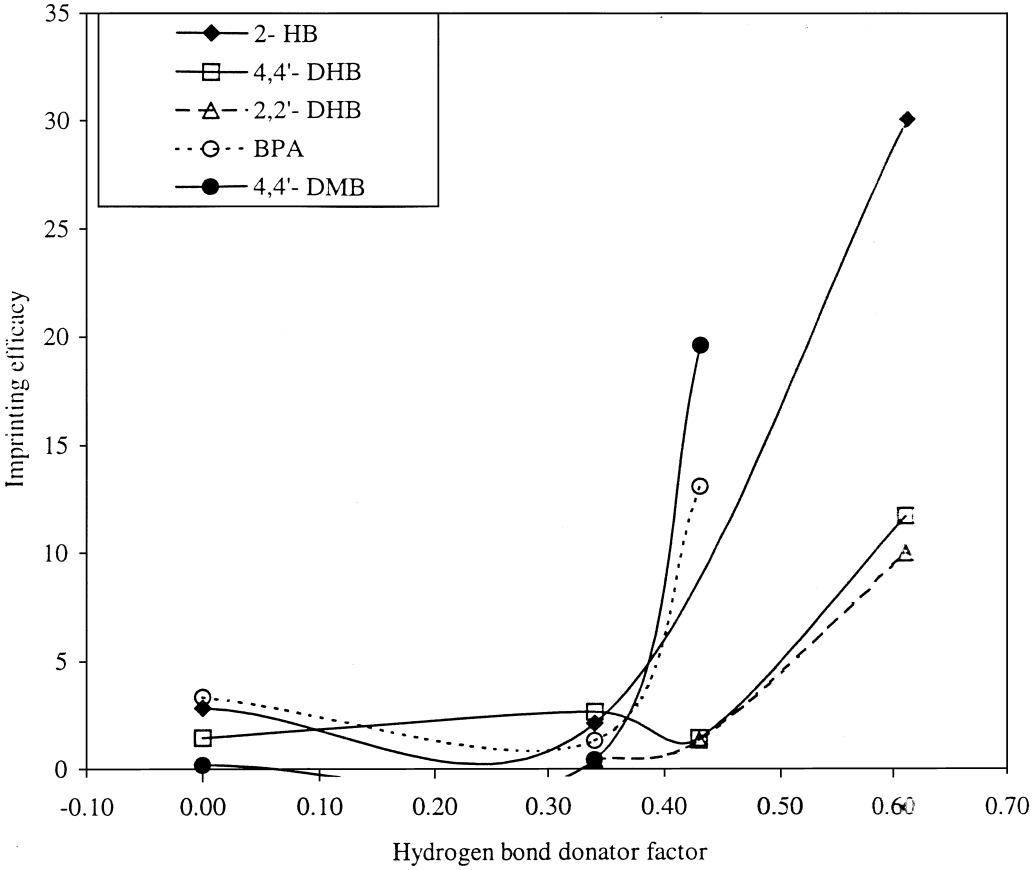


Fig. 4. Plot of imprinting efficacy vs. hydrogen bond donator factor for All24DHBC-MIP-GE90 (equilibrium conditions).

factor of the solvent, the solvent occupies more of the non-specific sorption sites leading to a decrease in the non-specific adsorption. This leads to an increase in the selectivity and a corresponding increase in the imprinting efficacy. This increase in the imprinting efficacy is opposite to that reported by Allender et al. [22]. This could be because in the HPLC separations reported by them, equilibrium was not reached. To verify if this was so we conducted similar selectivity experiments under non-equilibrium, packed bed adsorber conditions and a trend similar to that reported by Allender et al. [22] was observed. The details are discussed in Section 3.3.2.

3.2.3. Validating imprinting effect

To prove that the selectivity for template results from the imprinting effect and the rebinding interactions, experiments were carried out on imprinted polymers wherein the imprint cavity was blocked with the template molecule.

The α values are listed in Table 4. The selectivity is drastically reduced when the active sites are blocked. This clearly demonstrates that the selectivity in MIPs is a result of the imprinting effect and rebinding interactions. The decrease in the selectivity as a result of the blockade of the cavity is lowest in the case of 2-HB, the substrate which is structurally closest to the template (see Fig. 1). For the rest of the sorbates there is a substantial decrease in the selectivity.

3.3. Selectivity under non-equilibrium conditions

Many times, in industrial scale adsorptive separations, equilibrium between the sorbate and the adsorbent may not be attained and hence the selec-

Table 4
Equilibrium selectivity for sorption of 2,4-dihydroxybenzophenone from 1% acetic acid in methanol on MIP, All24DHBC-MIP-GE90 (blocked active site)

Sr. No.	Solute	Imprinted polymer (free cavity) α	Imprinted polymer (blocked cavity) α
1	2-HB	2.79	1.47
2	4,4′-DHB	12.38	0.39
3	2,2′-DHB	2.02	0.42
4	BPA	3.96	1.04
5	4,4′-DMB	1.03	1.07

tivity and sorption capacity of surface imprinted polymers were studied under non-equilibrium conditions. These studies were also carried out in various solvents in order to determine the best solvent for the separation under non-equilibrium conditions.

3.3.1. Sorption capacity

Sorption capacity under non-equilibrium conditions varied from 30 to 15 mg/g when solvents were changed from THF to 1% acetic acid in methanol. It is clear from the lower sorption capacity values, that the equilibrium is not achieved even though the accessibility of the imprint site is very high. As the solvent polarity increased from THF to methanol, the sorption capacity decreased. This trend is similar to that observed under equilibrium conditions.

As the imprinted polymers show higher sorption capacity (29.6 mg/g) coupled with a high selectivity in THF (Table 5), a non-polar solvent, it should be the solvent of choice for this separation. In order to enhance the kinetics of the process, highly porous polymers used in perfusion chromatography (for instance, POROS) can be used as support polymers for the preparation of MIPs.

3.3.2. Selectivity under non-equilibrium conditions

Selectivities of the surface imprinted polymers, under non-equilibrium conditions are listed in Table 5. The selectivity values are lower as compared to the values obtained under equilibrium conditions. This is because under the experimental conditions equilibrium is not reached. Under the non-equilibrium conditions, the selectivity is highest in the non-polar solvent THF. As the solvent polarity is increased, the solvent competes for the imprint site and this leads to reduction in sorption capacity as well as selectivity. When the hydrogen bond donator factor of the solvent was plotted against the imprinting efficacy, β decreased with the increase in the hydrogen bond donator factor of the solvent (see Fig. 5). This trend is consistent with the literature reports [22] as well as our own results [23,24].

4. Conclusions

This paper reports the use of molecularly imprinted adsorbents for the separation of positional isomers of 2,4-dihydroxybenzophenone.

Surface imprinted polymers based on allyl alcohol

Table 5
Selectivity for sorption of 2,4-DHB from various solvents for MIP, All24DHBC-MIP-GE90 (non-equilibrium conditions)

Sr. no.	Solute	Selectivity, α			
		THF	Ethanol	Methanol	1% acetic acid in methanol
1	2-HB	1.34	0.99	1.31	1.24
2	4,4′-DHB	1.88	0.81	0.86	1.01
3	2,2′-DHB	2.09	1.17	0.73	1.39
4	BPA	1.69	2.08	1.04	1.66
5	4,4′-DMB	1.69	1.26	0.91	1.25

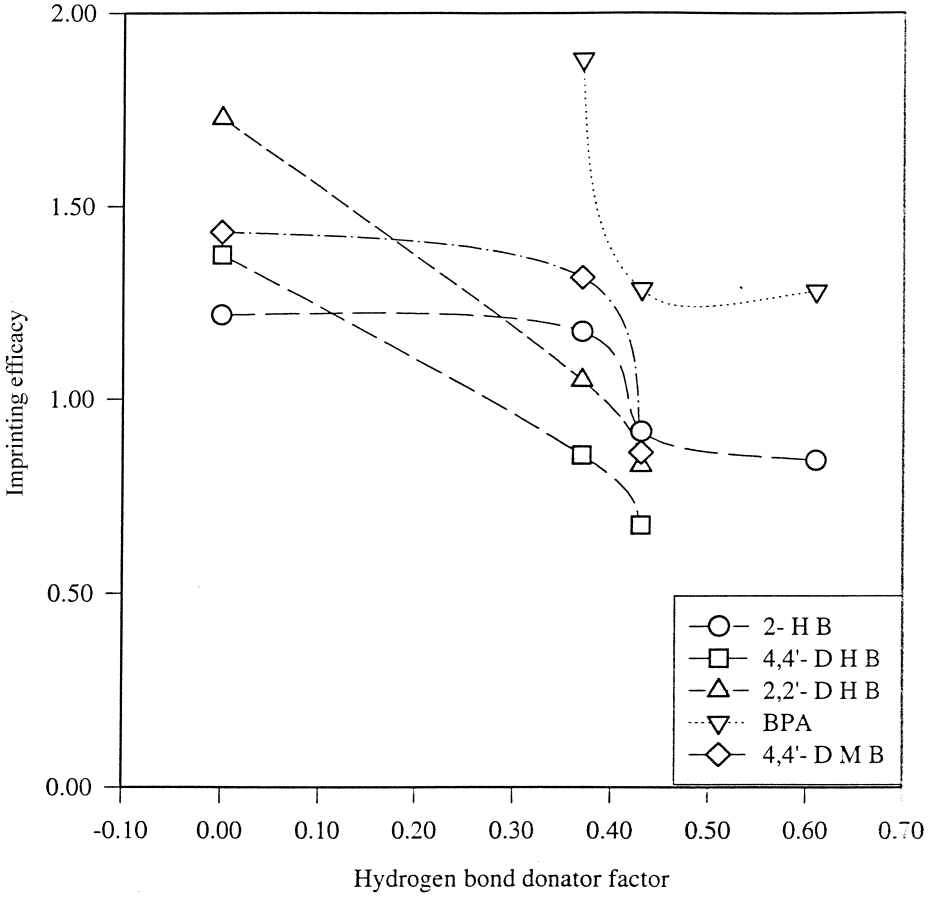


Fig. 5. Plot of imprinting efficacy vs. hydrogen bond donator factor for All24DHBC-MIP-GE90 (non-equilibrium conditions).

were prepared and evaluated in terms of their equilibrium sorption capacity and selectivity. The sorption capacity and capacity utilization was much higher in the case of imprinted polymers (40–95%). Both the sorption capacity and selectivity depend strongly on the solvent used. While the sorption capacity decreased with the increase in the solvent polarity, the imprinting efficacy increased with the solvent polarity.

For imprinted polymers, under non-equilibrium conditions, the sorption capacity and selectivities were lower than those obtained under equilibrium conditions The selectivities were still high enough for the industrial separations. Use of a non-polar solvent such as THF gave a high selectivity coupled with high capacity, although this was limited since equilibrium was not reached. This limitation could be overcome by selecting resins used in perfusion chromatography as support polymers for surface imprinting.

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References

[1] D. Kriz, O. Ramstrom, A. Svensson, K. Mosbach, Anal. Chem. 67 (1995) 2142.
[2] L. Andersson, K. Mosbach, Makromol. Chem., Rapid Commun. 10 (1989) 491.
[3] L. Fischer, R. Muller, B. Ekberg, K. Mosbach, J. Am. Chem. Soc. 113 (1991) 9358.
[4] V.P. Joshi, S.K. Karode, M.G. Kulkarni, R.A. Mashelkar, Chem. Eng. Sci. 53 (1998) 2271.
[5] J. Steinke, D.C. Sherrington, I.R. Dunkin (Eds.), Advances in Polymer Science, Vol. 123, Springer Verlag, Berlin, 1995, p. 82.
[6] G. Wulff, Angew. Chem., Int. Ed. Engl. 34 (1995) 1812.
[7] C. Yu, O. Ramstron, K. Mosbach, Anal. Lett. 30 (1997) 2123.
[8] P. Dhal, F. Arnold, New J. Chem. 20 (1996) 695.
[9] M. Kempe, L. Fischer, K. Mosbach, J. Mol. Recognit. 6 (1993) 25.
[10] Y. Tomioka, Y. Kudo, T. Hiyashi, H. Nakamura, M. Niizeki, T. Hishinuma, M. Mizugaki, Biol. Pharm. Bull. 20 (1997) 397.
[11] K. Sreenivasan, Polym. Int. 42 (1997) 169.
[12] K. Nilsson, K. Sakaguchi, P. Gemeiner, K. Mosbach, J. Chromatogr. A 707 (1995) 199.
[13] B. Sellergren, K. Nilsson, Methods Mol. Cell Biol. 1 (1989) 59.
[14] M. Whitcombe, M. Rodriguez, P. Villar, E. Vulfson, J. Am. Chem. Soc. 117 (1995) 7105.
[15] R.N. Karmalkar, M.G. Kulkami, R.A. Mashelkar, Macromolecules 29 (1996) 1366.
[16] V.P. Joshi, M.G. Kulkami, R.A. Mashelkar, Chem. Eng. Sci. (1998) in press.
[17] F. Svec, J. Hrdil, J. Coupec, J. Kalal, Angew. Makromol. Chem. 48 (1975) 135.
[18] S. Piletsky, E. Piletskaya, T. Panasyuk, A. El'skaya, R. Levi, I. Karube, G. Wuiff, Macromolecules 31 (1998) 2137.
[19] P. Dhal, S. Vidyasankar, F. Arnold, Chem. Mater. 7 (1995) 154.
[20] P. Reinholdsson, T. Hargitai, R. Isaksson, B. Tornell, Angew. Makromol. Chem. 192 (1991) 113.
[21] B.S. Lele, M.G. Kulkarni, R.A. Mashelkar, Polymer 40 (1999) 4063.
[22] C. Allender, C. Heard, K. Brain, Chirality 9 (1997) 238.
[23] V.P. Joshi, M.G. Kulkami, R.A. Mashelkar, Polymer (1998) submitted for publication.
[24] V.P. Joshi, M.G. Kulkarni, R.A. Mashelkar, (1998) in preparation.