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Enantioseparation of selected chiral sulfoxides using polysaccharide-type chiral stationary phases and polar organic, polar aqueous–organic and normal-phase eluents

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Abstract

HPLC enantioseparation of selected chiral sulfoxides was studied using cellulose and amylose phenylcarbamate derivatives as chiral stationary phases (CSPs). The contributions of various functional groups of a chiral analyte as well as the polysaccharide derivatives in the analyte retention and chiral recognition were evaluated. A very high enantioseparation factor exceeding 110 was observed in the enantioseparation of 2-(benzylsulfinyl)benzamide (BSBA) on cellulose tris(3,5-dichlorophenylcarbamate) (CDCPC) CSP by using 2-propanol as a mobile phase. The enantiomer elution order was opposite on cellulose and amylose phenylcarbamates. For the polysaccharide-type CSPs, pure alcohols such as methanol, ethanol and 2-propanol represent a valuable alternative to more common alcohol–hydrocarbon and reversed-phase eluents.

Keywords: Enantiomer separation; Chiral stationary phases, LC; Sulfoxides

1. Introduction

The phenylcarbamates and esters of polysaccharides such as cellulose and amylose exhibit the most universal chiral recognition ability among chiral stationary phases (CSPs) available for enantioseparations in high-performance liquid chromatography (HPLC) [1]. These materials not only effectively recognise enantiomers of a wide variety of chiral analytes but also may be used in combination with various mobile phases such as normal-phase alcohol–hydrocarbon mixtures, reversed-phase buffered and unbuffered aqueous–organic mobile phases [1] and pure polar organic solvents [2–6].

The effective chiral recognition with the polysaccharide-type CSPs in various mobile phases is an important advantage for practical problems to be solved because almost any kind of chiral analytes can be resolved using these materials. On the other hand, the universality means that these CSPs provide

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multiple alternative chiral recognition sites which make difficult the understanding of chiral recognition mechanisms. Although significant advancements have been made for a better understanding of chiral recognition mechanisms of the polysaccharide derivatives [1,7,8], this field still remains challenging.

The polysaccharide derivatives have been successfully used for enantioseparation of chiral analytes of different groups. Among them are chiral sulfoxides containing a sulfur atom as a centre of chirality [9–28].

In this work the contributions of various functional groups of the chiral analytes as well as those of the polysaccharide derivatives to binding affinity and chiral recognition of the enantiomers of selected chiral sulfoxides were studied. The preliminary results of the very high chiral recognition of sulfoxides on the polysaccharide derivatives have recently been reported [6].

2. Experimental

2.1. Chemicals and reagents

Methyl phenyl sulfoxide (MPS) and methyl *p*-tolyl sulfoxide (MTS) were from Aldrich (Milwaukee, WI, USA). 3-(Phenylsulfinyl)propionamide (PSPA), 2-(benzylsulfinyl)benzoic acid benzyl ester (BSBABE) and 2-(benzylsulfinyl)benzamide (BSBA) were provided by Bristol Myers Company (Syracuse, NY, USA).

HPLC columns for enantioseparations were either commercially available from Daicel Chemical Industries (Tokyo, Japan) or home-made as described previously [5,6,29,30]. Microcrystalline cellulose (Avicel) was from Merck (Darmstadt, Germany) and amylose (MAS-50) with average molecular mass 54 000 was a gift from Daicel Chemical Industries (Tokyo, Japan). Other chemicals such as 3,5-dichlorophenyl isocyanate, pyridine, tetrahydrofuran, methanol, ethanol, 2-propanol and *n*-hexane were from Tokyo Kasei (Tokyo, Japan).

2.2. Equipments

Chromatographic separations were performed in common size columns (25×0.46 cm) using a Jasco PU 980 Intelligent HPLC pump in combination with a Jasco DG-980 50 in-line degasser (Jasco, Japan), a Rheodyne 7125 injector with a 20-μl loop (Rheodyne, Cotati, CA, USA) and a Jasco UV-970 Intelligent UV–Vis detector which was connected on-line with Jasco OR-990 polarimetric detector. The samples were dissolved in methanol in a concentration 0.1 mg/ml.

IR spectra of polysaccharide phenylcarbamates were taken using Jasco FT-IR Fourier transform infrared spectrometer with Jasco/PTL-396 data processor. The samples were prepared by mixing with potassium bromide and pressing as thin films.

3. Results and discussion

3.1. Effect of the structure of a chiral analyte on retention and enantioseparation

The structure of chiral analytes and polysaccharide derivatives studied in this work are shown in Figs. 1 and 2, respectively.

Among the chiral analytes studied, the retention time of MPS was shortest on the CDCPC column (Fig. 3a and Table 1). This result is in agreement with the expectations because other analytes contain an additional hydrogen bonding or hydrophobic sites for their interaction with the CSP. The enantiomers of MPS were stereoselectively recognised by CDCPC (this was confirmed by on-line polarimetric detection) but no enantioseparation was observed in methanol as an eluent. However, PSPA containing a propionamide moiety instead of the methyl group compared to MPS was almost baseline resolved to the enantiomers on the CDCPC column (Fig. 3b). It seems interesting to note that the enantioseparation of PSPA was improved compared to MPS not on the expense of longer retention on the CSP. The first eluted enantiomer of PSPA was just less retained on the CDCPC material and the second enantiomer eluted in a similar time to both enantiomers of MPS. This is an indication for the important role of intermolecular hydrogen bonding between the analyte and the CSP for chiral recognition in this case. The chiral sulfoxide containing an additional hydrophobic interaction site, in particular, BSBABE was significantly longer retained on this CSP but the

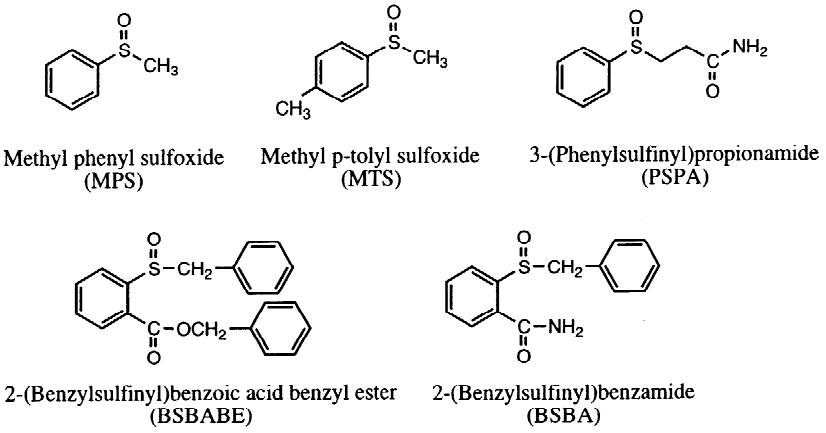

Fig. 1. Structures of chiral sulfoxides.

enantioseparation factor was not much higher compared to the above mentioned amide derivative (PSPA) (Fig. 3c). In contrast to this observation, the first enantiomer of BSBA, the analyte combining amide and benzyl substituents, was even less retained but the second enantiomer was much longer retained compared to the enantiomers of PSPA. This means that the enantioseparation factor was much higher for BSBA compared to all other analytes (Fig. 3d). Taking into account the chemical structures of BSBABE and BSBA one may assume much intensive hydrogen-bonding interactions in the BSBA–CDCPC pair compared to BSBA–CDCPC pair. This seems to be the most likely reason for the much higher enantioseparation factor observed for enantiomers of BSBA in methanol ($\alpha=10.0$) compared to the enantioseparation factor in the case of BSBABE ($\alpha=1.43$). This may lead to an increase of the enantioseparation factor. Taking into account the structure of PSPA and BSBA, it becomes clear that the introduction of the hydrophobic interaction site in the presence of amide group increases the retention time of the second enantiomer enantioselectively whereas in the absence of amide group (compare the structures of BSBABE and BSBA) the introduction of the additional hydrophobic interaction site in the structure of analyte leads to an increase of the retention time of both enantiomers mainly nonenantioselectively.

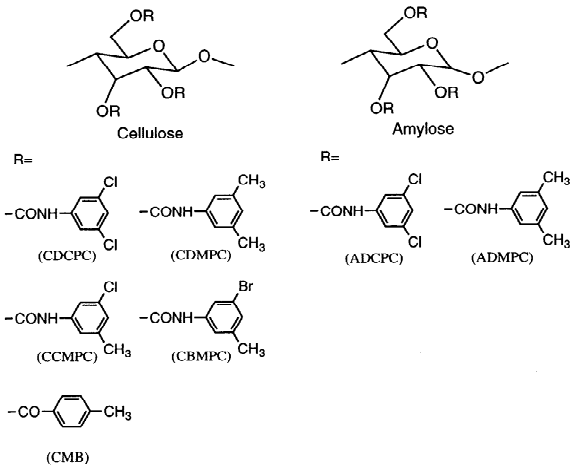

Fig. 2. Structures of polysaccharide derivatives.

The same general trend was observed when ethanol and 2-propanol were used as eluents. The hydrophobic interactions might be less favoured in higher alcohols. The opposite applies to the hydrogen-bonding. Thus, the contribution of the hydrogen-bonding in the analyte–CSP interactions can be increased on the expense of hydrophobic interactions with an increase in molecular mass of alcohol type mobile phase. According to the above mentioned hypothesis, this may allow an increase of enantioseparation factor. This trend was actually observed for the all analytes (Table 1) and one of the highest

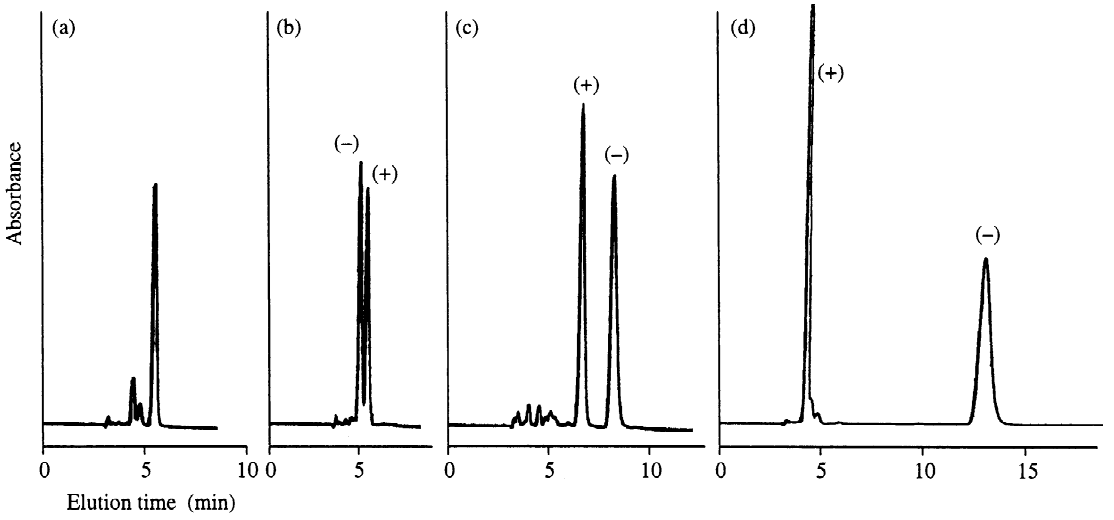

Fig. 3. Enantioseparation of MPS (a), PSPA (b), BSBABE (c) and BSBA (d) on CDCPC column. Mobile phase: methanol (1 ml/min).

enantioseparation factor (α>110) ever observed in chromatographic enantioseparations using any kind of CSPs could be achieved when BSBA was resolved on CDCPC using 2-propanol as a mobile phase [6,28].

Table 1
Capacity (k') and enantioseparation (α) factors of chiral sulfoxides on cellulose tris(3,5-dichlorophenylcarbamate) (CDCPC) in different alcohols

Chiral analyte	Mobile phase	k'_1	k'_2	α
MPS	Methanol[a]	0.50 (−)	–	~1
MTS		0.75 (−)	–	~1
PSPA		0.39 (−)	0.52	1.32
BSBABE		1.06 (+)	1.52	1.43
BSBA		0.31 (+)	3.10	10.0
MPS	Ethanol[a]	0.77 (+)	0.90	1.17
MTS		1.00 (+)	–	~1
PSPA		0.70 (−)	1.10	1.26
BSBABE		0.90 (+)	1.35	1.50
BSBA		0.41 (+)	5.72	13.9
MPS	2-Propanol[b]	1.71 (+)	2.00	1.17
MTS		2.60 (+)	–	~1
PSPA		2.81 (−)	8.19	2.92
BSBABE		3.14 (+)	9.17	2.92
BSBA		0.99 (+)	109.8	110.9

[a] Flow rate: 1.0 ml/min.
[b] Flow rate: 0.5 ml/min.

3.2. Effect of the structure of polysaccharide derivatives on the retention and enantioseparation factor

As shown in several previous studies, in the polysaccharide phenylcarbamates the part of N–H and C=O groups are involved in intramolecular hydrogen-bonding and thus responsible for the higher order structure of these materials. When a polysaccharide derivative is used as the CSP in HPLC, the amount of the carbamate fragments involved in the intramolecular hydrogen bonds may affect peak efficiency (N). The remaining free N–H and C=O groups are involved in analyte–CSP interactions and thus responsible for the analyte retention (k') and enantioseparation factor (α) [1,7,29–33].

The substituents on the phenyl moiety significantly affect the extent of the involvement of N–H and C=O groups of polysaccharide phenylcarbamates in intramolecular hydrogen-bonding. The previous studies indicated that with the introduction of alkyl substituents onto the phenyl moiety, the fraction of the carbamate groups involved in intramolecular hydrogen-bonding increases. In opposite to this, with the introduction of halogen substituents the fraction of the free carbamate groups increases (Fig. 4) [1,7,29–33]. Thus, comparison of chiral recognition ability of alkyl- and halogensubstituted phenylcarba-

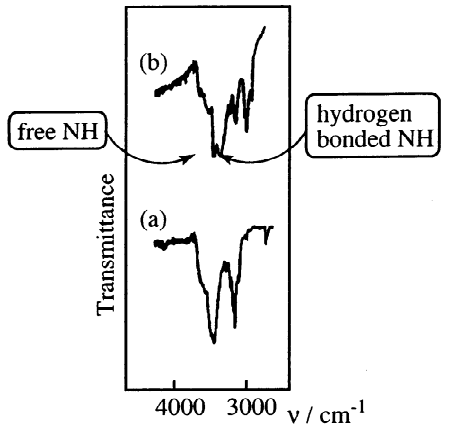

Fig. 4. NH bands in the FTIR spectra of cellulose tris(3,5-dimethylphenylcarbamate) (CDMPC) (a) and cellulose tris(3,5-dichlorophenylcarbamate) (CDCPC) (b).

mates offered good opportunity to examine the above mentioned hypothesis about the role of hydrogen-bonding interactions between the analyte and CSP in enantioseparation factor. For this reason, the chiral recognition abilities of CDCPC and the corresponding cellulose tris(3,5-dimethylphenylcarbamate) (CDMPC) which represents one of the most efficient CSPs for HPLC enantioseparations and is known under the commercial name Chiralcel OD, were compared in methanol, ethanol and 2-propanol as mobile phases. The enantioseparation factor was much higher on a CDCPC column compared to a CDMPC column with the same eluent. Thus, the enantioseparation factor for BSBA in methanol was 10 and 2.0 on the CDCPC and CDMPC columns, respectively. This is in an excellent agreement with the fraction of the free carbamate fragments in these materials. As shown from FT-IR spectra of CDCPC and CDMPC materials (Fig. 4), the former contains much higher fraction of the free carbamate fragments compared to the latter one.

The additional support for the significance of hydrogen-bonding interactions between the chiral sulfoxides and the polysaccharide phenylcarbamates for the enantioseparation factor may be obtained by comparison of CDCPC and CDMPC materials in different mobile phases. The ratio of the enantioseparation factors $\alpha_{CDCPC}/\alpha_{CDMPC}$ increases from methanol as a mobile phase to 2-propanol as follows: methanol < ethanol < 2-propanol. Thus, the ratio $\alpha_{CDCPC}/\alpha_{CDMPC}$ increased from 5.0 in methanol to 42.3 in 2-propanol as the eluent. As mentioned above the hydrogen-bonding will be favored in the same order in these mobile phases. This means that 2-propanol as a mobile phase is more favourable for applying the structural preference (higher amount of free carbamate moieties) which CDCPC offers compared to CDMPC material in these particular separations.

The enantioseparation of the same set of analytes on other selected polysaccharide derivatives were also studied. The ''hybrid''-type CSP of CDCPC and CDMPC, cellulose tris(3-chloro-5-methylphenylcarbamate) (CCMPC) [30] exhibited intermediate enantioselectivity between these two CSPs (Fig. 5a). This result is in agreement with aforementioned ideas because the distribution between the carbamate fragments which are free and those involved in the intramolecular hydrogen-bonding is also intermediate between CDCPC and CDMPC in CCMPC material. High enantioselectivity was observed also on cellulose tris(3-bromo-5-methylphenylcarbamate) (CBMPC) (Fig. 5b). The latter two CSPs represent certain interest because in difference to CDCPC they can be also used in combination with more tradition-

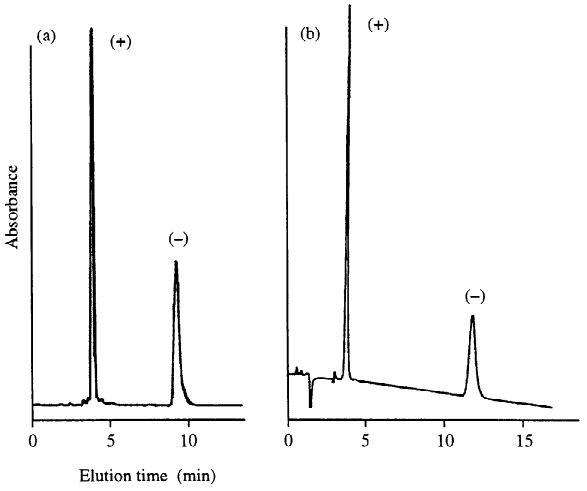

Fig. 5. Enantioseparation of BSBA on cellulose tris(3-chloro-5-methylphenylcarbamate) (CCMPC) (a) and cellulose tris(3-bromo-5-methylphenylcarbamate) (CBMPC) (b) in methanol as a mobile phase. Flow rate: 1 ml/min.

al eluents (*n*-hexane–2-propanol) for polysaccharide-type CSPs (see Section 3.3). Thus, these CSPs offer additional opportunities in order to compare different mobile phases.

The results obtained on the non-carbamate type CSP, cellulose tris(4-methylbenzoate) (CMB, commercial name Chiralcel OJ) were rather multivariate. Thus, from five test compounds only the enantiomers of BSBABE were resolved baseline in methanol as a mobile phase (Fig. 6a). The enantioseparation of this compound was also observed in ethanol (Fig. 6b) but disappeared in 2-propanol (Fig. 6c). This confirms the aforementioned idea about the hydrophobic forces as the major contributor in BSBABE–CSP interactions. CMB apparently does not provide as many hydrogen-bonding interaction sites as cellulose carbamate-type materials do. For this reason, the role of hydrophobic interactions may become more important for achieving enantioseparations. The hydrophobic interactions between the chiral analyte and CMB may be disfavoured with increasing molecular mass of alcohol-type mobile phases. This may be the explanation for decreasing enantioseparation factor of BSBABE on Chiralcel OJ column in the order of the mobile phases: methanol>ethanol>2-propanol. Based on this data, hydrophobic interactions seem to be of certain importance for the analyte–CSP interactions and apparently they are also somewhat enantioselective.

The trend observed for BSBA on CMB material with changing mobile phases was almost opposite to that mentioned above for BSBABE. The enantiomers were not separated in methanol as a mobile phase. However, the enantioseparation was observed in ethanol. Thus, the retention seems to be mainly governed by more strong but at least less stereoselective hydrophobic interaction in methanol as a mobile phase. In opposite to this, less strong but more

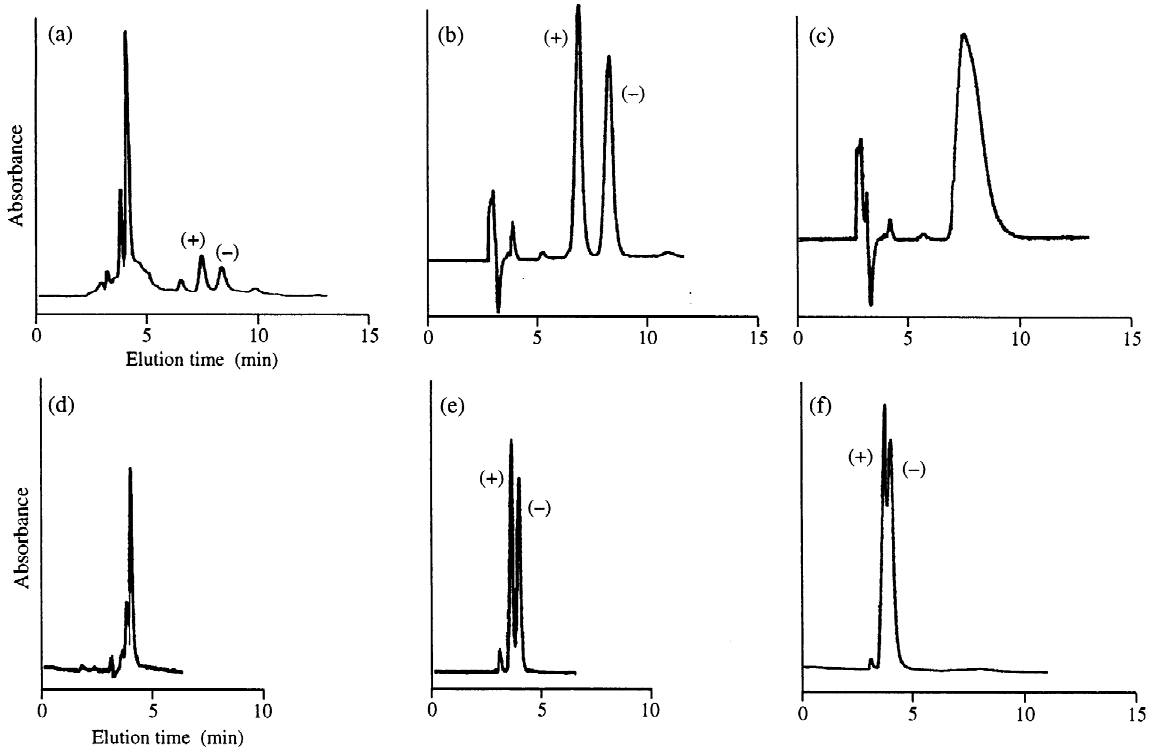

Fig. 6. Enantioseparation of BSBABE (a–c) and BSBA (d–f) on cellulose tris(4-methylbenzoate) (CMB) in methanol (a,d), ethanol (b,e) and 2-propanol (c, f) as a mobile phase. Flow rate: 1 ml/min.

stereoselective hydrogen-bonding interactions seem to be the major contributor to selector–selectand interactions in 2-propanol.

Among the three mobile phases studied on Chiralcel OJ column, methanol and 2-propanol behaved somewhat complimentary regarding the enantioseparation of BSBABE and BSBA (Fig. 6). Thus, the enantiomers of the more hydrophobic analyte (BSBABE) was baseline resolved in methanol (Fig. 6a) and not in 2-propanol (Fig. 6c), whereas the opposite was true for the enantiomers of less hydrophobic analyte BSBA. The enantiomers of this analyte were not resolved in methanol but partially resolved in 2-propanol. Ethanol exhibited the intermediate properties between methanol and 2-propanol and resolved the enantiomers of both analytes.

2-Propanol which was a more favourable mobile phase for polysaccharide phenylcarbamates, was less useful for cellulose ester-type CSP (Chiralcel OJ). This indirectly indicates that the role of hydrophobic interactions can be more important in the chiral recognition of polysaccharide esters compared to polysaccharide phenylcarbamates.

3.3. Comparison between polar organic, aqueous–organic (reversed-phase) and hydrocarbon–alcohol (normal-phase) eluents

As mentioned above, hydrogen bonding may significantly contribute to the interactions of the analytes with the polysaccharide derivatives. For this reason the polysaccharide phenylcarbamates may not always behave themselves as true reversed-phase adsorbents in organic–aqueous eluents. This has actually been observed with increasing water additives to 2-propanol as the eluent on the CDCPC column in the case of the all analytes under this study (Table 2). Thus, with addition of 30% water to 2-propanol (v/v) the capacity factors of BSBA enantiomers decreased from $k'_1 = 0.99$ and $k'_2 = 109.8$ to $k'_1 = 0.47$ and $k'_2 = 13.0$ and the separation factor from $\alpha = 110.9$ to $\alpha = 27.7$. However, this effect is dependent on the mobile phase and the analyte. Thus, when increasing amounts of water were added to the mobile phase consisting of pure methanol, the behaviour of a separation system was typical to that of a reversed-phase system, i.e. the capacity and enantioseparation factors increased with increasing amounts of water additive (Table 2). The most likely explanation for the opposite effect of water additive to the retention in the mobile phases consisting of pure methanol and 2-propanol seems to be following: the hydrogen-bonding is the main contributor to the retention of the analyte in 2-propanol. Water diminishes the hydrogen-bonding interactions and thus leads to a decrease of the capacity and enantioseparation factors.

In the case of methanol, hydrophobic interactions are more favoured compared to hydrogen-bonding. The addition of water intensifies hydrophobic interactions and thus leads to the increase of the capacity and enantioseparation factors (Table 2). Thus, the separation system is governed by hydrophobic interactions and its behaviour is similar to a typical reversed-phase separation system.

As mentioned above, CDCPC is soluble in alcohol–hydrocarbon mixtures and therefore it is not useful in the typical normal-phase eluents. However, cellulose tris(3-bromo-5-methylphenylcarbamate) (CBMPC) is insoluble in polar organic, aqueous–organic and alcohol–hydrocarbon mixtures. Thus, this CSP can be used in three different modes: polar organic, reversed-phase and normal-phase separations.

The comparison between polar organic, alcohol–hydrocarbon and alcohol–aqueous eluents was performed for CBMPC column (Table 3). The capacity factors for the enantiomers of all the compounds under this study increased with increasing amount of *n*-hexane in the mobile phase and the second peak of BSBA was not eluted from this column in 24 h with the eluent containing 70% *n*-hexane (v/v). The enantioseparation factors also increased with increasing content of *n*-hexane almost for the all analytes. Thus, although polysaccharide phenylcarbamates may effectively be used in combination with polar organic eluents, the traditional alcohol–hydrocarbon mobile phases may still represent very good alternative especially for the compounds with low capacity and enantioseparation factors.

The same CBMPC column was also used in alcohol–aqueous mobile phases. Retention and separation factors decreased significantly for most of the compounds studied except BSBABE with increasing amounts of water (Table 3). The first enantiomer of BSBABE was slightly longer retained in the aqueous

Table 2
Capacity (k') and enantioseparation (α) factors of chiral sulfoxides on cellulose tris(3,5-dichlorophenylcarbamate) (CDCPC) in polar organic and aqueous–organic solvents

Chiral analyte	Mobile phase	k'_1	k'_2	α
MPS	Methanol[a]	0.50 (−)	–	~1
MTS		0.75 (−)	–	~1
PSPA		0.39 (−)	0.52	1.32
BSBABE		1.06 (+)	1.52	1.43
BSBA		0.31 (+)	3.10	10.0
MPS	MeOH–H_2O[a]	0.74 (+)	0.90	1.17
MTS	(85:15, v/v)	1.25 (−)	–	~1
PSPA		0.45 (−)	–	~1
BSBABE		6.74 (+)	13.4	1.92
BSBA		0.58 (+)	8.23	14.0
MPS	MeOH–H_2O[a]	1.32(+)	–	~1
MTS	(66:34, v/v)	0.93 (+)	–	~1
PSPA		0.83 (−)	1.00	1.2
BSBABE		~45 (+)	–	–
BSBA		2.41 (+)	31.9	13.2
MPS	2-Propanol[b]	1.71 (+)	2.00	1.17
MTS		2.60 (+)	–	~1
PSPA		2.81 (−)	8.19	2.92
BSBABE		3.14 (+)	9.17	2.92
BSBA		0.99 (+)	109.8	110.9
MPS	2-Propanol–H_2O[b]	0.50 (+)	–	~1
MTS	(85:15, v/v)	–	–	–
PSPA		0.36 (−)	0.45	1.19
BSBABE		2.60 (+)	5.60	2.15
BSBA		0.30 (+)	10.3	34.3
MPS	2-Propanol–H_2O[b]	–	–	–
MTS	(70:30, v/v)	–	–	–
PSPA		0.43 (−)	0.60	1.39
BSBABE		0.70 (+)	2.20	3.10
BSBA		0.47 (+)	13.0	27.7

[a] Flow rate: 1.0 ml/min.
[b] Flow rate: 0.5 ml/min.

2-propanol 85:15 (v/v). This result supports again the idea that the hydrophobic interactions are prevailing in BSBABE–CBMPC interactions whereas hydrogen bonding seems to be more important in the interactions between the other analytes and CBMPC.

3.4. Enantiomer elution order

Enantiomer elution order is important issue in analytical as well as in preparative scale LC enantioseparations [34–36]. It is easy to design the enantiomer elution order with some type of CSPs which are available in both configurations. To these belong Pirkle-type CSPs, some ligand exchangers, etc. However, it is difficult to predict and revert the enantiomer elution order with the CSPs which are based on natural materials available commonly in one configuration. To these belong cyclodextrins, macrocyclic antibiotics, peptides, many alkaloids and polysaccharide derivatives.

In the case of the all sulfoxides studied the elution order was the same on the all cellulose based CSPs independent of the substituent. At the same time, for

Table 3
Capacity (k') and enantioseparation (α) factors of chiral sulfoxides on cellulose tris(3-bromo-5-methylphenylcarbamate) (CBMPC) in pure polar organic, alcohol–hydrocarbon and aqueous–organic solvents (flow-rate: 1.0 ml/min)

Chiral analyte	Mobile phase	k'_1	k'_2	α
MPS	2-Propanol	0.61 (+)	–	~1
MTS		0.76 (+)	0.85	1.11
PSPA		1.37 (−)	3.13	2.29
BSBABE		1.71 (+)	2.56	1.49
BSBA		0.59 (+)	27.6	46.9
MPS	2-Propanol–$H_2$0	–	–	–
MTS	(85:15, v/v)	–	–	–
PSPA		0.22 (−)	0.43	1.93
BSBABE		2.60 (+)	5.33	2.05
BSBA		0.21 (+)	9.18	43.3
MPS	2-Propanol–H_2O	0.72 (−)	–	~1
MTS	(70:30, v/v)	–	–	–
PSPA		0.39 (−)	0.52	1.32
BSBABE		3.86 (+)	8.70	2.25
BSBA		0.27 (+)	6.50	24
MPS	2-Propanol–*n*-hexane	–	–	–
MTS	(88.3:11.7, v/v)	0.85	0.92	1.09
PSPA		1.14	3.14	2.75
BSBABE		1.70	2.42	1.7
BSBA		0.57	32.0	56.0
MPS	2-Propanol–*n*-hexane	0.70	–	–
MTS	(72:29, v/v)	0.87	–	–
PSPA		1.60	4.63	4.63
BSBABE		1.77	2.92	1.65
BSBA		0.69	53.7	77.6
MPS	2-Propanol–*n*-hexane	1.00	–	–
MTS	(44.5:55.5, v/v)	1.05	1.16	1.10
PSPA		2.38	6.60	2.72
BSBABE		1.82	3.44	1.89
BSBA		~1	77.0	~77
MPS	2-Propanol–*n*-hexane	1.21	–	–
MTS	(30:70, v/v)	1.79	2.00	1.12
PSPA		7.19	20.1	2.79
BSBABE		3.2	6.88	2.06
BSBA		1.38	–	–

all analytes the enantiomer elution order on amylose tris(3,5-dichlorophenylcarbamate) (ADCPC) was opposite to that on the cellulose derivatives. Although, the enantioseparation factor was higher on the cellulose derivatives compared to the amylose derivatives, the latter may represent some interest for the reversal of the enantiomer elution order (Fig. 7). This was possible not only for the chiral sulfoxides tested but also for some other compounds studied, for example, chiral antiduretic drugs etozolin and piprozolin, which contain a chiral carbon atom.

The reversal of the enantiomer elution order on polysaccharide type CSPs has been previously described depending on the alcohol modifiers [37–40], water [40,41] and acetic acid [41] content in organic mobile phases or separation temperature [40]. The most likely explanation for these effects seems to be the change of contributions of various intermolecular

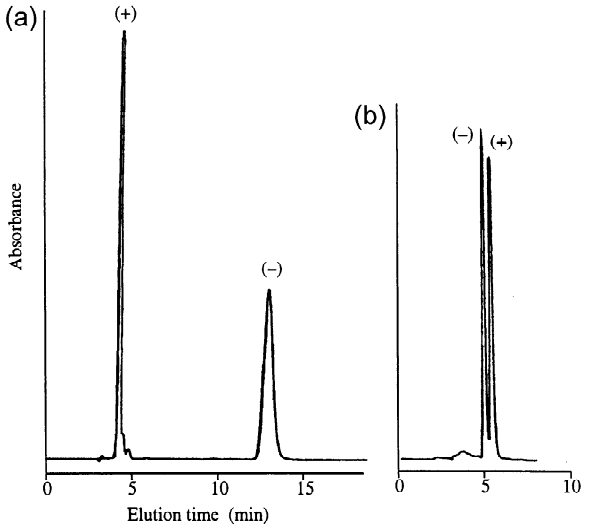

Fig. 7. Enantioseparation of BSBA on cellulose tris(3,5-dichlorophenylcarbamate) (CDCPC) (a) and amylose tris(3,5-dichlorophenylcarbamate) (ADCPC) (b). Mobile phase: methanol (1 ml/min).

forces such as hydrogen bonding, hydrophobic, electrostatic, van der Waal's, $\pi-\pi$, etc. in overall analyte–CSP interactions.

4. Conclusions

The polysaccharide phenylcarbamates exhibited an interesting chiral recognition ability towards chiral sulfoxides in polar organic solvents and very high enantioseparation factors were observed for some compounds. The role of hydrogen-bonding interactions between the CSP and the chiral sulfoxide seems to be of prevailing importance for enantioseparation. The hydrophobic interactions which were commonly stronger and significantly contributed to the retention of sulfoxides on the CSPs, were at least less stereoselective compared to hydrogen-bonding interactions. The enantiomer affinity patterns of the analytes studied were opposite between the derivatives of cellulose and amylose. Some of the polysaccharide derivatives may successfully be used in the three different kinds of eluents: pure polar organic, organic–aqueous and alcohol–hydrocarbon solutions.

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