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Liquid chromatographic resolution of racemic amines and amino alcohols on a chiral stationary phase derived from crown ether

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Abstract

A chiral stationary phase (CSP) prepared by bonding (+)-(18-crown-6)-2,3,11,12-tetracarboxylic acid to silica gel was successfully employed in resolving various racemic amines and amino alcohols including therapeutically active compounds such as amphetamine, phenylethanolamine, octopamine and norepinephrine. Related compounds such as α-amino carbonyl compounds were also resolved on the CSP. In order to see the effect of organic and acidic modifiers in the mobile phase and the temperature of the column on the enantioselectivity exerted by the CSP, four racemic compounds which resolved well on the CSP were selected and their resolutions were investigated with the variation of organic and acidic modifiers in the mobile phase and the temperature of the column. From the results, the chromatographic factors such as capacity factors (k'), separation factors (α) and resolution factors (R_s) were expected to be controlled to some extent by varying organic and acidic modifiers in the mobile phase and the temperature of the column. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Chiral stationary phases, LC; Enantiomer separation; Amines; Amino alcohols

1. Introduction

Liquid chromatographic resolution of enantiomers on chiral stationary phases (CSPs) is now understood as one of the most accurate and convenient means of determining enantiomeric composition of chiral compounds [1,2]. In addition, this technique provides the preparative means of obtaining enantiomerically pure compounds [2,3]. Owing to their potential utility, the development of effective CSPs has been challenged by a great many workers [1].

In recent years, we were interested in the liquid chromatographic resolution of racemic compounds containing a primary amino group and devoted our efforts to the development of crown ether-based CSPs, which are known to resolve racemic primary amino compounds without derivatization [4,5]. In the course of this work, we planned to utilize commercially available (+)-(18-crown-6)-2,3,11,12-tetracarboxylic acid 1 (Fig. 1) as a chiral selector in high-performance liquid chromatography. (+)-(18-Crown-6)-2,3,11,12-tetracarboxylic acid 1 has been widely used as a chiral selector in resolving various racemic compounds containing a primary amino group by capillary electrophoresis [6–15]. However, the use of (+)-(18-crown-6)-2,3,11,12-tetracarboxylic acid 1 bound to silica gel as a CSP in high-performance liquid chromatography is quite rare. Recently, a CSP based on (+)-(18-crown-6)-

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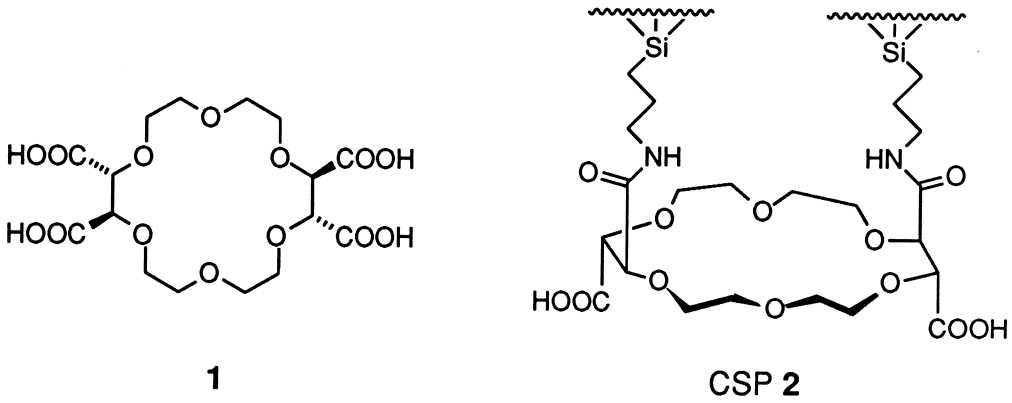

1 CSP 2

Fig. 1. The structure of (+)-(18-crown-6)-2,3,11,12-tetracarboxylic acid 1 and CSP 2.

2,3,11,12-tetracarboxylic acid 1 was reported by Machida et. al. and used for the liquid chromatographic resolution of a limited number of racemates including 1-naphthylethylamine [16]. However, the structure of the CSP developed by Machida et. al. is ambiguous in that the mode of connecting (+)-(18-crown-6)-2,3,11,12-tetracarboxylic acid 1 to silica gel through the reaction with 3-aminopropyl silica gel in the presence of a coupling agent, 2-ethoxy-1-ethoxycarbonyl-1,2-dihydroquinoline (EEDQ) allows structural variety in the linkage. More recently, we also developed a new and structurally well defined CSP (CSP 2, Fig. 1) by bonding (+)-(18-crown-6)-2,3,11,12-tetracarboxylic acid 1 to 3-aminopropyl silica gel via a simple two step procedure [17,18]. CSP 2 thus developed was excellent in resolving racemic quinolone antibacterials [17] and α-amino acids including their derivatives [18]. Especially, the resolution of racemic α-amino acids on CSP 2 was found to be greater than that on the similar CSP reported by Machida et. al. [16]. However, the resolution of racemic amines and amino alcohols on CSP 2 is not tested yet. In this study, we wish to extend the use of CSP 2 to the resolution of racemic amines and amino alcohols including α-amino carbonyl compounds.

2. Experimental

Chromatography was performed with an HPLC system consisting of a Waters model 515 HPLC pump, a Rheodyne model 7125 injector with a 20 μl sample loop, a Younglin M720 Absorbance detector (variable wavelength) and a Youngin D520B computing integrator. The temperature of the column was controlled by using a Julabo F30 Ultratemp 2000 cooling circulator. The chiral column prepared by packing CSP 2 into a 150×4.6 mm I.D. stainless-steel HPLC empty column using a conventional slurry packing method was available from a previous study [17,18] and successfully used to evaluate its performance in this study. The chiral column was found to be equally effective for the chiral separation after the use of more than 1 year under the condition of H_2SO_4 added (up to 20 m*M*) to the mobile phase. Chromatography samples were commercially available or prepared via the general method.

3. Results and discussion

CSP 2 was applied in resolving various amines (3) and amino alcohols (4) including α-amino carbonyl compounds (5), the structures of which are shown in Fig. 2. Some of analytes such as 1-naphthylethylamine (3b) and amino alcohols (4a, b and c) have already been reported to be resolved on the CSP prepared by Machida et al. [16]. However, in this study, we extended the use of CSP 2 to the resolution of even cyclic amines and cyclic amino alcohols.

The chromatographic resolution results on CSP 2 are summarized in Table 1. The chromatographic resolution data shown in Table 1 except for the resolution of four amino alcohols were obtained by

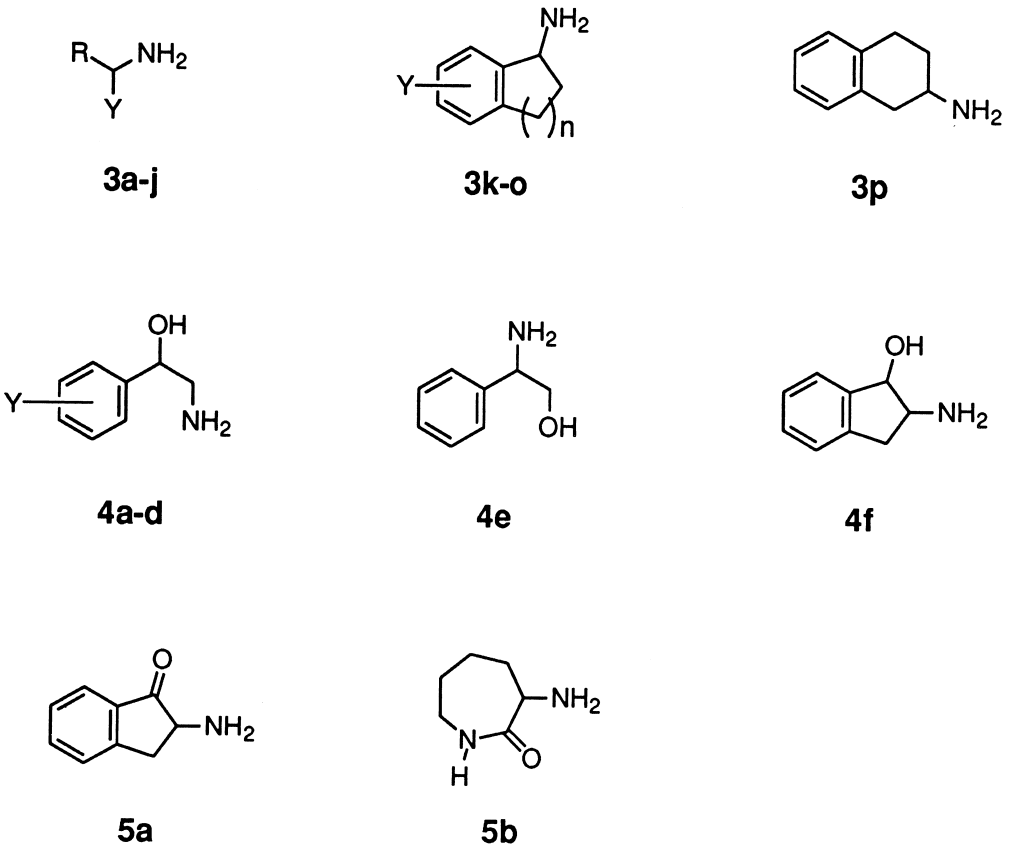

Fig. 2. The structure of racemic amines 3, amino alcohols 4 and α-amino carbonyl compounds 5.

using a mixed solvent of methanol–water (80:20, v/v) containing sulfuric acid (1.0×10^{-2} *M*), which was previously utilized as a successful mobile phase in resolving α-amino acids and their derivatives on CSP 2 [18]. The data for the resolution of four racemic amino alcohols (4a–d) shown in Table 1 were collected by using a mobile phase of 100% water containing sulfuric acid (1.0×10^{-2} *M*). The elution orders were determined by injecting configurationally known samples. As shown in Table 1, all racemic amines and amino alcohols including α-amino carbonyl compounds tested were resolved quite well on CSP 2 except for 1-methyl-3-phenylpropylamine (3j). In particular, it is interesting to note that therapeutically active compounds such as amphetamine (3g), phenylethanolamine (4a), octopamine (4b) and norepinephrine (4c) are resolved quite well on CSP 2. Especially, the resolution of phenylethanolamine (4a), octopamine (4b) and norepinephrine (4c) on CSP 2 was found to be greater than that on the CSP reported by Machida et al. [16].

In order to see the effect of organic and acidic modifiers in the mobile phase and the temperature of the column on the enantioselectivity exerted by CSP 2, four racemic compounds (3e, 3k, 4e and 5b) resolved well on CSP 2 were selected and their resolutions were tested with the variation of organic and acidic modifiers in the mobile phase and the variation of the temperature of the column. First of all, the effect of four organic modifiers (methanol, ethanol, acetonitrile and tetrahydrofuran) on the enantioselectivity exerted by CSP 2 was investigated by changing the content of organic modifiers in the mobile phase at the constant concentration of sulfuric acid (1.0×10^{-2} *M*) and the results are summarized in Table 2. As shown in Table 2, the change of the

Table 1
Resolution of various amines (3), amino alcohols (4) and α-amino carbonyl compounds (5) on CSP 2[a]

Analyte	R	Y	*n*	k_1'[b]	k_2'[c]	α[d]	R_s[e]	Mobile phase	Elution order[f]
3a	CH_3	Phenyl		2.45	2.70	1.10	0.80	A	*S*
3b	CH_3	1-Naphthyl		1.90	2.43	1.28	2.57	A	*R*
3c	CH_3CH_2	1-Naphthyl		2.02	2.93	1.45	1.79	A	*R*
3d	CH_3	6,7-Dimethyl-1-naphthyl		1.38	2.54	1.84	5.23	A	
3e	Isopropyl	6,7-Dimethyl-1-naphthyl		0.25	0.80	3.21	3.85	A	
3f	CH_3	4-Biphenyl		2.86	3.18	1.11	1.05	A	
3g	CH_3	$C_6H_5CH_2$		1.40	1.55	1.11	1.02	A	*R*
3h	CH_3	$2\text{-}CH_3OC_6H_4CH_2$		0.99	1.15	1.16	1.16	A	
3i	CH_3CH_2	$3\text{-OH-4-}CH_3C_6H_4CH_2$		0.46	0.52	1.13	0.73	A	
3j	CH_3	$C_6H_5CH_2CH_2$		1.28	1.28	1.00	0.00	A	
3k		H	1	1.16	1.79	1.55	3.27	A	*S*
3l		H	2	0.51	0.70	1.38	1.09	A	
3m		$4\text{-}OCH_3$	2	0.51	0.70	1.39	1.69	A	
3n		$5\text{-}OCH_3$	2	0.24	0.31	1.27	0.25	A	
3o		3,5-dimethyl	2	0.49	0.82	1.67	1.92	A	
3p				2.49	2.57	1.03	0.28	A	
4a		H		1.10	1.54	1.40	1.52	B	
4b		4-OH		0.92	1.09	1.19	1.41	B	
4c		3-OH, 4-OH		0.90	1.04	1.15	1.00	B	
4d		$3\text{-}OCH_3$, 4-OH		1.25	1.47	1.18	1.23	B	
4e				1.44	1.95	1.35	2.18	A	*R*
4f				1.98	2.33	1.78	0.80	A	*1S,2R*
5a				5.21	18.01	3.46	12.00	A	
5b				1.91	3.14	1.64	4.86	A	

[a] Mobile phase: (A) 80% CH_3OH in $H_2O+H_2SO_4$ (1×10^{-2} *M*), (B) 100% $H_2O+H_2SO_4$ (1×10^{-2} *M*). Flow rate: 0.5 ml/min. Detection: 210 nm UV. Temperature: 20°C.
[b] Capacity factor for the first eluted enantiomer.
[c] Capacity factor for the second eluted enantiomer.
[d] Separation factor.
[e] Resolution factor.
[f] Absolute configuration of the second eluted enantiomer. For blanks, the elution orders are not determined.

content of each organic modifier in the mobile phase significantly influence the capacity factors (k'), the separation factors (α) and the resolution factors (R_s). In general, the separation factors (α) and the resolution factors (R_s) are improved as the content of organic modifiers in the mobile phase increases. However, the capacity factors (k') behave slightly differently from the separation factors (α) and the resolution factors (R_s) with the variation of the content of organic modifiers in the mobile phase. For example, in the resolution of compound 3e, the capacity factors generally decrease as the content of organic modifiers in the mobile phase increases. However, in the resolution of compounds 3k, 4e and 5b, the capacity factors increase as the content of organic modifiers in the mobile phase increases. These results for the difference in the capacity factors might be supposed to be originated from the different hydrophilicity or lipophilicity of the compounds. Compound 3e contains relatively large hydrophobic groups compared to compounds 3k, 4e and 5b. Consequently, the retention of the enantiomers of compound 3e on the CSP is expected to decrease as the content of organic modifiers in the mobile phase increases because of the increased lipophilic interaction between compound 3e and the organic modifier. However, in resolving relatively more hydrophilic compounds such as 3k, 4e and 5b, the retention of the enantiomers is expected to increase as the content of organic modifiers in the mobile phase increases because of the decreased hydrophilic interaction between compound 3k, 4e

Table 2
Resolution of selected racemic compounds 3e, 3k, 4e and 5b on CSP 2 with the variation of the organic modifier and its content in the aqueous mobile phase at the constant sulfuric acid concentration (1.0×10^{-2} *M*) as an acidic modifier[a]

Organic modifier (%)	3e			3k			4e			5b		
	k_1'[b]	α[c]	R_s[d]	k_1'[b]	α[c]	R_s[d]	k_1'[b]	α[c]	R_s[d]	k_1'[b]	α[c]	R_s[d]
CH_3OH (0%)	7.55	1.10	0.33	0.59	1.25	0.82	0.31	1.19	0.47	0.22	1.00	0.00
CH_3OH (20%)	1.43	1.26	1.45	0.52	1.39	1.17	0.38	1.28	0.79	0.31	1.00	0.00
CH_3OH (40%)	0.49	1.82	2.19	0.60	1.17	1.91	0.52	1.31	1.10	0.41	1.37	0.95
CH_3OH (60%)	0.26	2.50	2.75	0.72	1.51	2.48	0.76	1.32	1.57	0.74	1.51	2.36
CH_3OH (80%)	0.25	3.21	3.85	1.16	1.55	3.27	1.44	1.35	2.18	1.91	1.64	4.86
CH_3CH_2OH (20%)	0.94	1.36	1.72	0.52	1.39	1.18	0.39	1.26	0.61	0.32	1.00	0.00
CH_3CH_2OH (80%)	0.48	2.79	5.22	1.97	1.46	3.07	2.36	1.38	2.90	3.56	1.60	4.35
CH_3CN (20%)	0.52	1.44	1.75	0.42	1.38	1.05	0.27	1.33	0.54	0.23	1.00	0.00
CH_3CN (80%)	0.13	2.16	2.00	0.83	1.47	3.44	0.26	1.37	1.71	1.58	1.25	2.44
THF (20%)	0.38	1.61	1.52	0.38	1.42	1.09	0.28	1.24	0.44	0.24	1.00	0.00
THF (80%)	0.46	1.96	3.32	2.17	1.37	3.56	2.23	1.33	2.66	4.70	1.38	5.70

[a] Flow rate: 0.5 ml/min. Detection: 210 nm UV. Temperature: 20°C.
[b] Capacity factor for the first eluted enantiomer.
[c] Separation factor.
[d] Resolution factor.

and 5b and the water component of the mobile phase.

The effect of acidic modifiers in the mobile phase on the enantioselectivity exerted by CSP 2 was investigated with three different acids such as sulfuric acid, perchloric acid and trifluoroacetic acid. Previously, it was shown that complexation of the ammonium ion ($R\text{-}NH_3^+$) inside the cavity of crown ether is essential for the chiral recognition of primary amino compounds [12]. Consequently, acidic modifiers in the mobile phase are believed to protonate primary amino groups of the analytes and to enhance the diastereomeric complex formation of the analytes containing a primary amino group inside the cavity of 18-crown-6 ring of CSP 2. The chromatographic results for the resolution of racemic compounds 3e, 3k, 4e and 5b on CSP 2 with three different acids are summarized in Table 3. As shown in Table 3, sulfuric acid in the mobile phase was found to afford, in general, the best resolution results. In particular, the resolution factors, R_s, were very good when sulfuric acid was used as an acidic modifier in the mobile phase. The effect of the concentration of acidic modifiers in the mobile phase on the enantio-

Table 3
Resolution of selected racemic compounds 3e, 3k, 4e and 5b on CSP 2 with the variation of the acidic modifier and its content in the aqueous mobile phase at the constant methanol content (80%) as an organic modifier[a]

Acidic modifier (m*M*)	3e			3k			4e			5b		
	k_1'[b]	α[c]	R_s[d]	k_1'[b]	α[c]	R_s[d]	k_1'[b]	α[c]	R_s[d]	k_1'[b]	α[c]	R_s[d]
H_2SO_4 (1 m*M*)	0.18	3.73	3.60	1.01	1.59	3.09	1.37	1.35	1.97	1.68	1.73	3.91
H_2SO_4 (5 m*M*)	0.19	3.63	3.55	1.02	1.57	2.13	1.35	1.35	2.20	1.68	1.67	3.98
H_2SO_4 (10 m*M*)	0.25	3.21	3.85	1.16	1.55	3.27	1.44	1.35	2.18	1.91	1.64	4.86
H_2SO_4 (20 m*M*)	0.35	2.66	1.76	1.31	1.52	3.45	1.58	1.34	2.78	2.12	1.60	5.03
$HClO_4$ (10 m*M*)	0.20	3.20	2.80	0.97	1.52	3.33	1.13	1.33	2.16	1.60	1.56	3.15
CF_3COOH (10 m*M*)	0.09	4.00	2.23	0.55	1.55	1.87	0.67	1.34	1.60	0.83	1.27	3.24

[a] Flow rate: 0.5 ml/min. Detection: 210 nm UV. Temperature: 20°C.
[b] Capacity factor for the first eluted enantiomer.
[c] Separation factor.
[d] Resolution factor.

selectivity was also investigated with variation of the concentration of sulfuric acid in the mobile phase. The resolution results on CSP 2 with variation of the concentration of sulfuric acid in the mobile phase are included in Table 3. The capacity factors (k'), increase as the concentration of sulfuric acid in the mobile phase increases. However, the separation factors (α), decrease (for compound 3e) or remain almost constant (compounds 3k, 4e and 5b) throughout the change of the concentration of sulfuric acid in the mobile phase as shown in Table 3. The reason for those chromatographic resolution behaviors is not clear yet.

The effect of the temperature of the column on the enantioselectivity for the resolution of compounds 3e, 3k, 4e and 5b on CSP 2 is summarized in Table 4. As shown in Table 4, all chromatographic factors including capacity factors (k'), separation factors (α) and resolution factors (R_s) are improved as the temperature is lowered. At lower temperature, the formation of the two diastereomeric complexes formed by the two enantiomers of racemic compounds inside the cavity of the crown ether ring of CSP 2 is expected to be more favorable. In particular, the formation of the more stable diastereomeric complex is expected to be much more favorable than that of the less stable diastereomeric complex. As a consequence, it is concluded that the difference in the stability of the two diastereomeric complexes increases as the temperature of column is lowered. The chromatographic resolution behaviors which are dependent on the temperature of the column shown in Table 4 are well consistent with the chromatographic resolution behaviors observed on other CSPs based on crown ethers [4,5,16].

The difference in the stability of the two diastereomeric complexes with the variation of temperature is also illustrated by the plots of the natural logarithm of the capacity factors of the two enantiomers and the natural logarithm of the separation factors against the reciprocal of absolute temperature (known as Van't Hoff plot). All of the four compounds shown in Table 4 were found to show similar trends in their van't Hoff plots and one example for the resolution of amino alcohol 4e is presented in Fig. 3. As shown in Fig. 3(a), the extent of separation between the two lines increases as the temperature decreases, indicating that the difference in the stability of the two diastereomeric complexes increases as the temperature decreases (in other words, as the reciprocal of absolute temperature increases). Consequently, the separation factors increase as the temperature decreases as shown in Fig. 3(b). In addition, from the positive slope of the line shown in Fig. 3(b) corresponding to $-\Delta\Delta H/R$, it is concluded that the value of $\Delta\Delta H$, the differential enthalpy of absorption for the two enantiomers, is quite exothermic and the enantioselectivity is enthalpy controlled [19,20].

In conclusion, CSP 2 prepared by bonding (+)-(18-crown-6)-2,3,11,12-tetracarboxylic acid 1 to silica gel is successfully employed in resolving various racemic amines and amino alcohols including α-amino carbonyl compounds. In particular, the baseline resolution of pharmaceutically important compounds such as amphetamine (3g), phenylethanolamine (4a), octopamine (4b) and norepineph-

Table 4
Resolution of selected racemic compounds 3e, 3k, 4e and 5b on CSP 2 with the variation of the temperature of the column[a]

Temperature (°C)	3e			3k			4e			5b		
	k_1'[b]	α[c]	R_s[d]	k_1'[b]	α[c]	R_s[d]	k_1'[b]	α[c]	R_s[d]	k_1'[b]	α[c]	R_s[d]
30	0.19	2.63	2.61	0.74	1.48	2.43	0.91	1.29	1.80	1.19	1.26	3.45
25	0.23	2.76	3.26	0.99	1.49	3.07	1.14	1.32	1.35	1.46	1.58	3.97
20	0.25	3.21	3.85	1.16	1.55	3.27	1.44	1.35	2.18	1.91	1.64	4.86
10	0.38	3.25	4.80	1.84	1.61	4.36	2.28	1.39	3.39	3.03	1.72	4.88

[a] Mobile phase: 80% CH_3OH in $H_2O+H_2SO_4$ (1×10^{-2} *M*). Flow rate: 0.5 ml/min. Detection: 210 nm UV.
[b] Capacity factor for the first eluted enantiomer.
[c] Separation factor.
[d] Resolution factor.

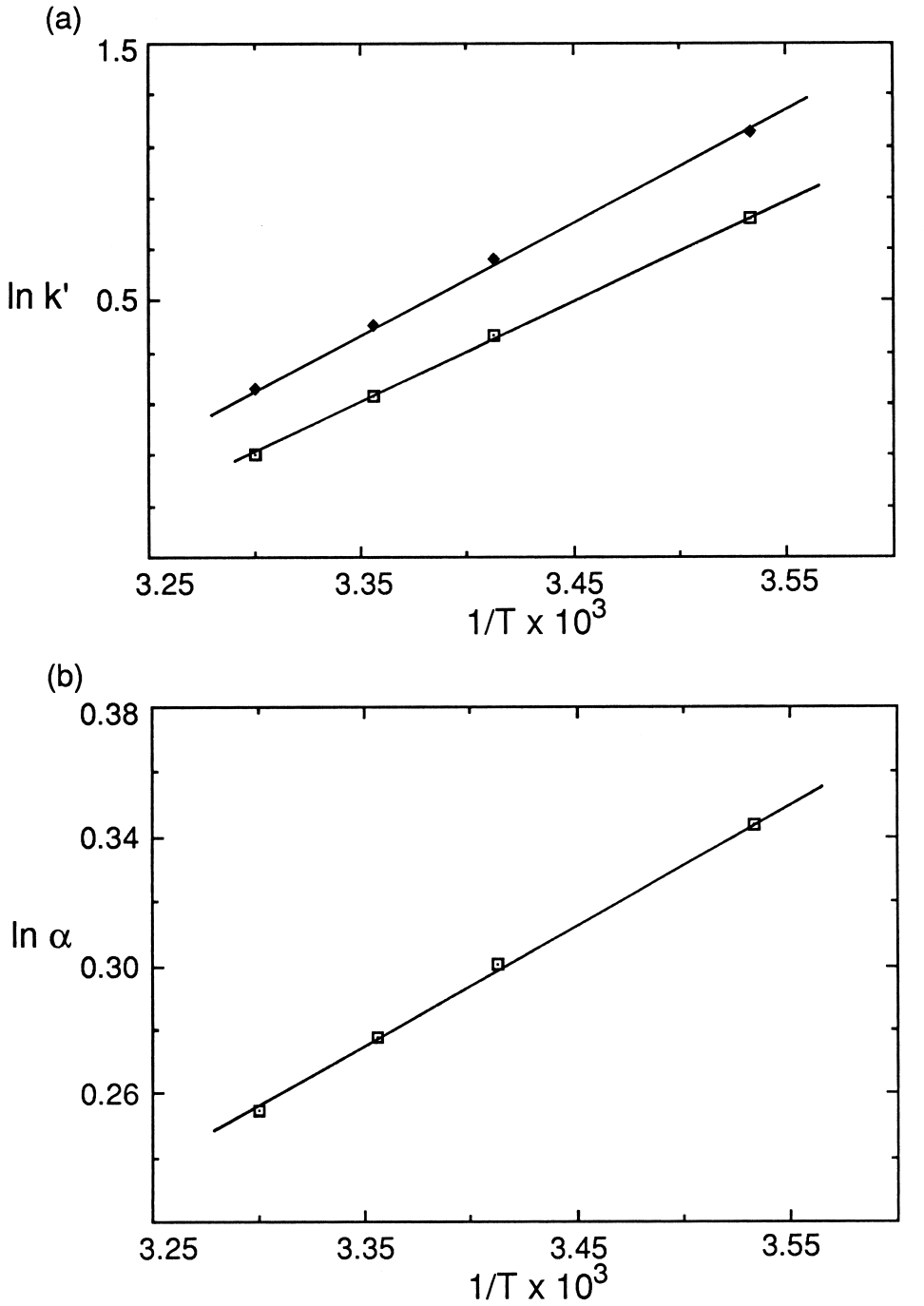

Fig. 3. Van't Hoff plots for the resolution of amino alcohol 4e on CSP 2. (a) Plots of natural logarithm of capacity factors against the reciprocal of absolute temperature. Upper line is for the more retained enantiomer. Lower line is for the less retained enantiomer. (b) A plot of natural logarithm of separation factors against the reciprocal of absolute temperature.

rine (4c) on CSP 2 is noteworthy. The effect of organic and acidic modifiers in the mobile phase and temperature on the enantioselectivity exerted by CSP 2 for the resolution of four selected compounds 3e, 3k, 4e and 5b demonstrates that chromatographic factors such as capacity factors (k'), separation factors (α) and resolution factors (R_s) can be controlled to some extent by varying the organic and acidic modifiers in the mobile phase or varying the temperature of the column. The mechanism of chiral recognition is not clear yet except that the complexation of the primary ammonium group ($R\text{-}NH_3^+$) formed from the primary amino group of racemic analytes under an acidic condition inside the cavity of the 18-crown-6 ring of the CSP is essential for the chiral recognition [12]. The efforts for the elucidation of the mechanism of chiral recognition including the role of the two carboxylic acid groups of CSP 2 are underway in our laboratory. In addition, the efforts to extend the use of CSP 2 to the resolution of pharmaceutically important compounds containing a primary amino group or amino groups are underway in our laboratory and will be reported in the future.

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