ELSEVIER

Analytica Chimica Acta 384 (1999) 51–62

ANALYTICA CHIMICA ACTA

Metallomesogens as stationary phases for the separation of phenols by gas chromatography

Chuen-Ying Liu*, Cho-Chun Hu, Jien-Lian Chen, Kung-Tien Liu

Department of Chemistry, National Taiwan University, Taipei, Taiwan

Received 11 June 1998; accepted 24 November 1998

Abstract

Metal complexes of 4-decanoxydithiobenzoate (DDTBA) and 4-(dec-9′-en-1′-oxy)dithiobenzoate siloxane polymer (P-DODTBA) were prepared and used as stationary phases in ligand-exchange gas chromatography for the separation of phenols. A better separation of phenols was achieved in the liquid crystalline state than in the solid state. Van't Hoff plots as a function of temperature indicated that phase transitions were occurring. From specific retention volumes measured at various temperatures in each of the DDTBA-Zn and DDTBA-Ni fluid phases, the thermodynamic behavior of phenols is discussed. The DDTBA-Zn phase showed a higher solute–solvent interaction than DDTBA-Ni. Moreover, DDTBA-Ni phase was more appropriate for the separation of lower volatile phenols. A similar property was exhibited by the metal complexes of P-DODTBA. A spiral glass column (2.1 m×3.2 mm i.d.) was prepared from 5% DDTBA-metal complex deposited on Chromosorb. By dynamic coating, wall-coated P-DODTBA-metal complex capillary columns (12 m×0.25 mm i.d.) were also prepared as stationary phases for the separation of phenols. Factors affecting the retention and the sample selectivity on both the packed column and the capillary column were examined. The calibration graphs for phenol determination were linear over the range of 64–1600 μg ml^{-1} (packed column) and 16–400 μg ml^{-1} (capillary column). The 2σ mass detection limits of most phenols are less than 30 ng for packed column and 4 ng for capillary column. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Metallomesogens; Metallomesogenic siloxane polymer; Ligand-exchange gas chromatography; Stationary phases; Packed column; Capillary column; Phenols

1. Introduction

In recent years, research on liquid crystals has been developing very rapidly both as regards the synthesis of new substances and the knowledge of their properties and applications, as indicated in general monographs and reviews [1] and in those devoted to chromatographic applications [2]. Metallomesogens are metal-containing liquid crystals. The interesting properties derived from the presence of metal atoms in ordered fluid phases have given rise to expectations of new applications of liquid crystals based on metallomesogens. Many metallomesogenic structures have also been introduced into polymeric systems. Metallomesogenic polymers can combine the promising properties of metallomesogens (physical properties of metal entities and molecular ordering of liquid crystals) with the advantageous properties of polymers [3]. In a search of the literature, there are only a few

*Corresponding author.

0003-2670/99/$ – see front matter © 1999 Elsevier Science B.V. All rights reserved.
PII: S0003-2670(98)00857-5

reports on the use of metallomesogens for chromatographic applications [4–9].

Among the variety of separation methods, ligand-exchange chromatography (LEC) is one of the most powerful techniques for resolving complex-forming substances [10,11]. In a search of new stationary phases with ligand-exchange behavior, the desire to combine the properties of liquid crystals with those of metal complexes has led in our laboratory to the preparation and application of low molecular weight metallomesogens and metallomesogenic polymers [8,9]. A new packed column from 4-decanoxydithiobenzoic acid metal complexes [8] and a novel capillary column with wall-coated siloxane polymer of 4-(dec-9′-en-1′-oxy)dithiobenzoate metal complexes [9] have been used successfully for the separation of dialkyl sulfides and polycyclic aromatic hydrocarbons.

The determination of phenols is necessary because of their toxicity and their widespread use in industry. Nowadays, the most widely used analytical technique for the determination of phenols is gas chromatography (GC), because of its high sensitivity and resolving power. GC of underivatized phenols using capillary columns with conventional phases is difficult, and in particular nitrophenols tend to tail, even when using highly deactivated columns [12]. To avoid this disadvantage, phenols are derivatized to give less polar compounds with better chromatographic characteristics.

Improved selectivity for the separation of phenols can be achieved using ligand-exchange liquid chromatography. The complexation between phenols and iron(III) coordinated to iminodiacetate chelating resin, Chelex-100, was first demonstrated by Petronio et al. [13]. In later papers, Petronio et al. [14] showed that different substituted phenols could be stripped in succession from the iron-loaded resin by using eluents of increasing pH. In 1984, Petronio et al. further claimed that modified Amberlite CG 4B in the iron(II) form can be used for the quantitative separation of phenolic compounds, a separation that is not possible with the Chelex-iron(II) resin. Shahwan and Jezorek [15] employed iron(III)-loaded 8-quinolinol silica gel as the stationary phase for the separation of phenols by liquid chromatography.

Since metallomesogens are promising as stationary phases for ligand-exchange gas chromatography (LEGC), the aim of this paper is to extend the wider applicability of the dithiolene metal complexes either coated on Chromosorb as a packed column or on the capillary wall for the gas chromatographic separation of phenols which are environmentally important pollutants.

2. Experimental

2.1. Apparatus

All GC analyses were performed on a Shimadzu (Kyoto, Japan) Model GC-9A gas chromatograph equipped with a flame ionization detector. Both packed column and capillary column systems were examined. A Shimadzu data processor (C-R2A) was used for the determination of retention times. Ammonia-equilibrated nitrogen (10:90, v/v) and pure nitrogen were used as the mobile phases.

2.2. Reagents and chemicals

Most chemicals were of analytical reagent grade from Merck (Darmstadt, Germany). All liquid reagents and solvents used in moisture-sensitive reactions were distilled and collected over type 4 Å molecular sieves. The solid materials used in moisture-sensitive reactions were dried at 110°C for 24 h prior to use. Poly(methylhydrosiloxane) (PS 122, MW= 4500–5000) was purchased from Petrach Systems (Bristol, PA). This reagent was used without further purification.

Twelve representative phenols studied were: 2-chlorophenol, phenol, *o*-cresol, *p*-cresol, *m*-cresol, 2,4-dimethylphenol, 2,4-dichlorophenol, 2-nitrophenol, 2,4,6-trimethylphenol, 4-bromophenol, 3-methyl-4-chlorophenol and 2,4,6-trichlorophenol. These compounds were supplied by Tokyo Chemical Industry (Japan). A stock solution of each compound (0.2 g) was prepared in ethyl acetate (25 ml) and stored at 4°C. Working solutions were prepared daily or weekly by diluting these solutions with ethyl acetate.

2.3. Synthesis of low molecular weight metallomesogens and the metallomesogenic polymer

The detailed procedures for the preparation of *p*-decanoxydithiobenzoates and their siloxane polymer metal complexes were as already reported [8,9].

2.4. Column preparation

2.4.1. Packed column

The *p*-decanoxydithiobenzoate nickel and zinc complexes dissolved in toluene were mixed with Chromosorb W AW-DMCS (80–100 mesh) (5%, w/w) and stirred for 1 h at 60°C. Excess solvent was removed under reduced pressure. Then the glass column (2.1 m×3.2 mm i.d.) was filled with the metallomesogens deposited on Chromosorb by suction at the column end and under ultrasonic stirring. The packed column was then conditioned for 8 h at 150°C.

2.4.2. Capillary column

A fused-silica capillary column with an external coating of polyimide (J & W, Folsom, CA or Ohio Valley Specialty Chemicals, Marietta, OH) was chemically coated with the metallomesogenic siloxane polymer as described in the following procedures.

Fused-silica capillaries were first rinsed with methanol and dichloromethane (5 ml for each) sequentially. Then the capillaries were conditioned at 250°C with a gentle flow of nitrogen for about 4 h, and were then ready to be coated using a static procedure. The apparatus for the coating procedure is that proposed by Grob and Grob [16] with some modification. In order to prepare a capillary column (12 m×0.25 mm i.d.) with film thickness of 0.25 μm, a solution prepared from 0.020 g of linear side-chain liquid crystal polymer in 5 ml of dichloromethane (which also contained benzoyl peroxide, the amount being 5% (w/w) of the linear polymer) was used to fill the capillary. The column was slowly dipped into a water bath at 40°C, followed by removal of the solvent under vacuum for 10 h.

For improving the reproducibility and coating efficiency of the procedure, we considered the possibility of coating fused-silica capillaries by the following method. One end of the fused silica sealed with silicone rubber was immersed in ice water. The other end was connected to a buffer capillary column to which a 0.5 cm diameter empty glass tube was lined up. The latter process was used in order to obtain an almost homogeneous distribution of the deposited material, and as a trap for the vacuum system.

After coating, the columns were placed in the nitrogen-purged oven of a gas chromatograph. The temperature was raised to 200°C at 3°C min^{-1}. After the heat treatment, the interior column wall formed was purged with nitrogen at 200°C for 6 h. During these processes, the cross-linking took place. The column was rinsed with dichloromethane (5 ml) to remove any traces of unreacted material and further purged with nitrogen for about 15 min till a constant stable baseline was obtained.

3. Results and discussion

The coordination unsaturation of the central metal ion in nickel- and zinc-4-decanoxydithiobenzoate complexes has been studied in the previous paper [8], and the phase transitions of the nickel-4-decanoxydithiobenzoate complexes (DDTBA-Ni) were: K 140.2 – SmH 167.5 – SmC 235 – I and those for DDTBA-Zn were: K 131.4 – SmC 160.9 – N 173.2 – I; where K denotes the solid phase, Sm the smectic phase, N the nematic phase, and I the isotropic liquid. While the phase transitions of the nickel-4-(dec-9′-en-1′-oxy)dithiobenzoate complex (DODTBA-Ni) were: K 122.6 – SmH 162.9 – SmC 230 – I and those for DODTBA-Zn were K 123.1 – SmC 140.8 – N 162.9 – I. For examining the ligand-exchange retention behavior and selectivity of phenols on these stationary phases, several types of phenols with different molecular structures were studied: 2-chlorophenol (b.p. 174°C; length to breadth (*L*/*B*) ratio 1.106), phenol (180°C; 1.280), *o*-cresol (191°C; 1.003), *p*-cresol (202°C; 1.625), *m*-cresol (203°C; 1.183), 2,4-dimethylphenol (210°C; 1.271), 2,4-dichlorophenol (210°C; 1.265), 2-nitrophenol (214°C; 1.024), 2,4,6-trimethylphenol (220°C; 1.063), 4-bromophenol (238°C; 1.458), 3-methyl-4-chlorophenol (235°C; 1.110) and 2,4,6-trichlorophenol (246°C; 1.146).

3.1. Optimization of experimental variables

3.1.1. Packed column

The retention times of some typical phenols were measured at various temperatures (Fig. 1). *p*-Cresol and 2,4-dimethylphenol were coeluted at a column temperature of 120°C. With increasing column temperature, the retention of samples was reduced and the peak shape was improved. Additionally, better resolution between *p*-cresol and 2,4-dimethylphenol was found. However, shorter retention times caused poor

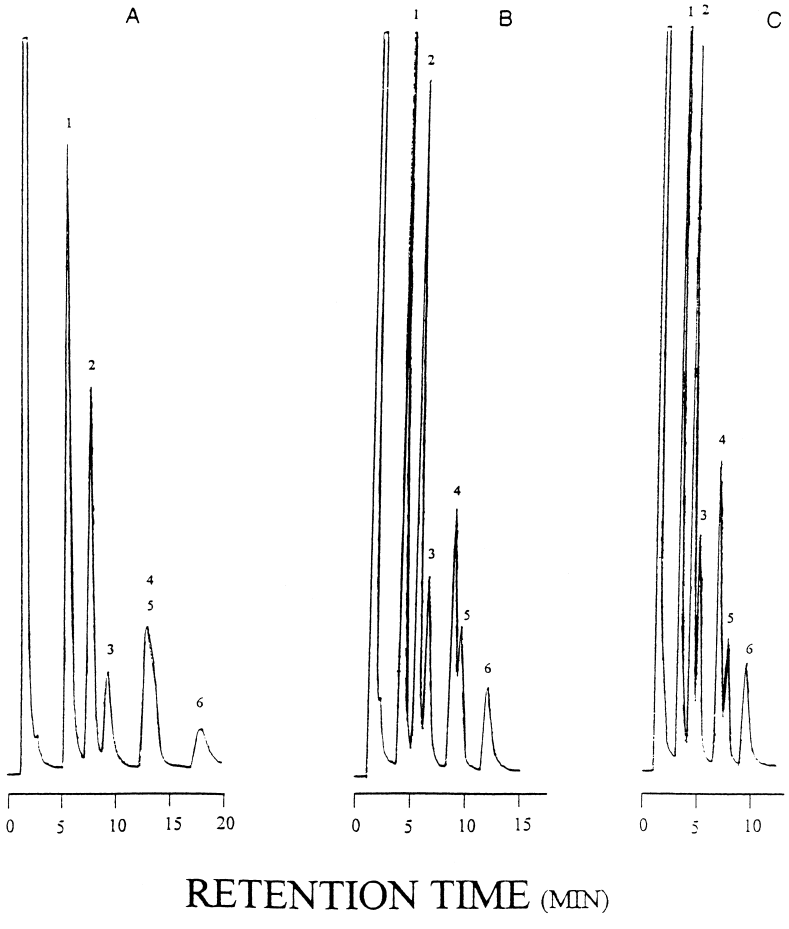

Fig. 1. Chromatogram of the separation of phenols at different temperatures. Stationary phase: 5% DDTBA-Ni coated on Chromosorb, 2.1 m×3.2 mm i.d. glass column; injector temp.: 230°C; mobile phase: nitrogen gas, flow rate: 40 ml min^{-1}; sample volume: 1 μl. Oven temp.: (A) 120°C; (B) 130°C; (C) 140°C. Peak identification: (1) phenol; (2) 2-chlorophenol; (3) *o*-cresol; (4) *p*-cresol; (5) 2,4-dimethylphenol; (6) 2,4-dichlorophenol.

sample selectivity for 2-chlorophenol and *o*-cresol. Fig. 2 shows the separation of phenols at 145°C with both DDTBA-Zn and DDTBA-Ni packed columns. These stationary phases exhibit higher efficiency in the liquid crystal state than in the solid state. The results display a higher column efficiency and better reproducibility for the DDTBA-Ni column in comparison with DDTBA-Zn. Moreover, the utility of DDTBA-Zn in the analysis of high b.p. phenols is diminished by the rather long elution times and the broad bands.

Programmed temperature runs were also carried out with an initial temperature of 140°C at 3°C min^{-1} to the final temperature of 165°C. An improved resolution for 2-chlorophenol and *o*-cresol was obtained (Fig. 3). With extension of the programmed temperature range, more phenols could be separated in a shorter time, but serious baseline drift was observed.

Phase transitions of these stationary phases in GC can be detected from a plot of log k' vs. $1/T$ (Fig. 4). The capacity factor first decreases gradually with an increase of column temperature from 115°C, with a discontinuity at around 140°C, and then decreases markedly. Transition temperatures are clearly indicated by the discontinuities in the curves. The temperature of 140°C corresponds to the phase transition point of DDTBA-Ni. Gas–liquid chromatography has become an established technique for the determination

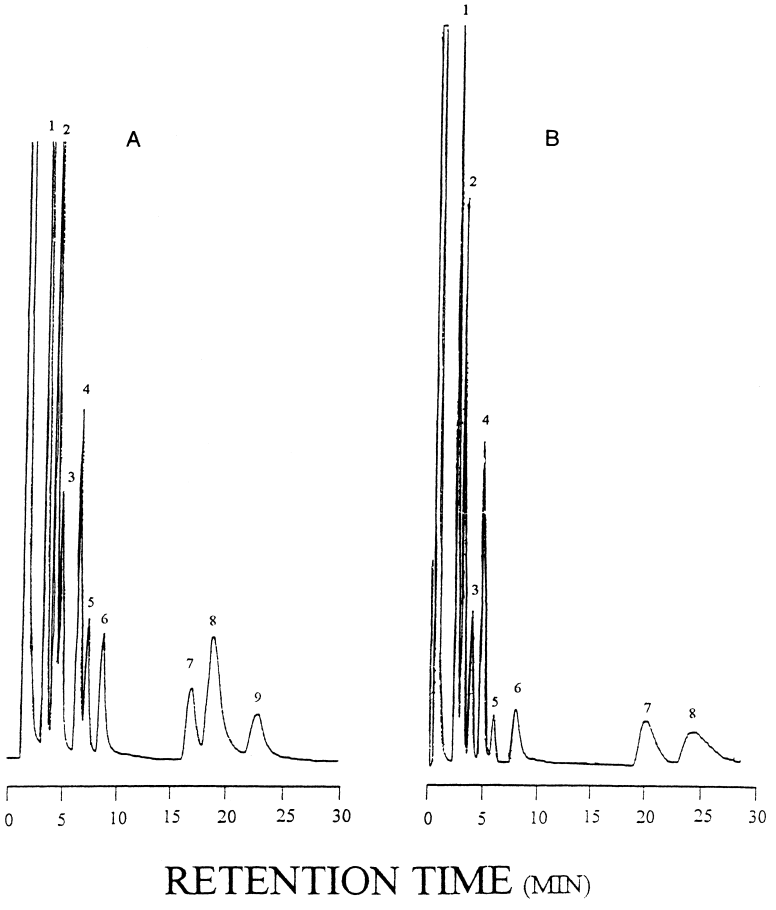

Fig. 2. Chromatogram of the separation of phenols at the liquid crystalline state. Conditions as in Fig. 1, except column temperature=145°C. Stationary phase: (A) 5% DDTBA-Ni coated on Chromosorb; (B) 5% DDTBA-Zn coated on Chromosorb. Peak identification: (A) (1)–(6) as Fig. 1; (7) 3-methyl-4-chlorophenol; (8) 4-bromophenol; (9) 2,4,6-tricholorophenol. (B) (1)–(6) as Fig. 1; (7) 3-methyl-4-chlorophenol; (8) 4-bromophenol.

of reliable thermodynamic data for volatile solutes at "infinite dilution" in non-volatile solvents [17–19]. Specific retention volumes, V_g^o, were obtained at five temperatures in each of the metallomesogenic phases – DDTBA-Ni and DDTBA-Zn. The infinite-dilution solute partial molar enthalpy and entropy of solution were obtained by means of the following equation [20]:

$$\ln(V_g^o) = -\Delta H/RT + \Delta S/R - \ln(M/273.2R),$$

$$V_g^o = V'/W, \qquad V' = (t_r - t_o) \times f,$$

where t_r is the retention time of the sample; t_o the retention time of the non-adsorbed substance; V' the retention volume; f the flow rate of the carrier gas; W the weight of the stationary phase; M the molecular weight of the stationary phase; and V_g^o is the specific retention volume.

A linear least-squares fit of $\ln V_g^o$ vs. the reciprocal of the absolute temperature (Fig. 5) yields ΔH and ΔS as shown in Table 1. By comparing the enthalpy and entropy changes of polycyclic aromatic hydrocarbons (PAHs) [8] with those of phenols, the more effective strength of solute–solvent attractive interactions for phenols was observed, leading to larger ΔH and ΔS values. This is not surprising if one takes into account the different complexation ability between PAHs and phenols toward the central metal ion of the metallo-

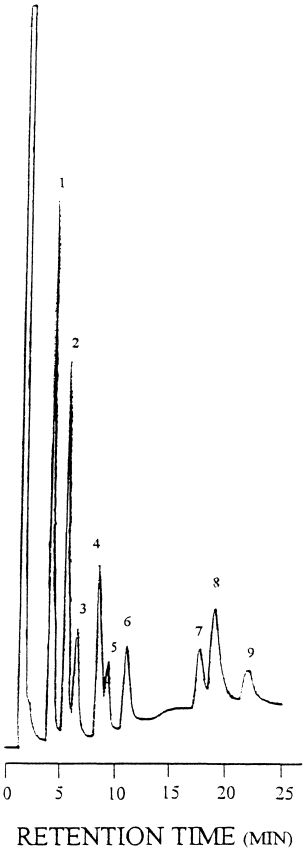

Fig. 3. Separation of phenols with programed temperature. Stationary phase: 5% DDTBA-Ni coated on Chromosorb, 2.1 m×3.2 mm i.d. glass column; oven temp.: 140°C (3 min) to 165°C at 3°C min^{-1}; injector temp.: 250°C; mobile phase: nitrogen gas, flow rate: 40 ml min^{-1}. Peak identification: (1) phenol (t_r=4.52 min); (2) 2-chlorophenol (t_r=5.97 min); (3) *o*-cresol (t_r=6.91 min); (4) *p*-cresol (t_r=9.01 min); (5) 2,4-dimethylphenol (t_r=9.84 min); (6) 2,4-dichlorophenol (t_r=11.53 min); (7) 3-methyl-4-chlorophenol (t_r=15.87 min); (8) 4-bromophenol (t_r=19.44 min); (9) 2,4,6-trichlorophenol (t_r=22.48 min).

mesogens. For phenols, more substituent methyl groups would lead to more electron-rich benzene rings and hence to larger ΔH and ΔS values (Table 2), so the thermodynamic data increase in the order: phenol, *o*-cresol, 2,4-dimethylphenol and 2,4,6-trimethylphenol. Meanwhile the solute–solvent interaction is stronger for the zinc complex than that for the nickel complex. The results are rational since the structure of SmC (zinc complex) is more flexible than that of SmH (nickel complex).

Table 1
Thermodynamic parameters for the dissolution of analytes in the liquid crystal phases of DDTBA-Ni and DDTBA-Zn

Stationary phase	Analyte	$-\Delta H$ (kJ mol^{-1})	$-\Delta S$ (J mol^{-1} K^{-1})
DDTBA-Ni	Phenol	2.49	4.45
	o-Cresol	2.52	4.71
	p-Cresol	2.55	4.98
	2,4-Dimethylphenol	2.58	5.14
	2,4,6-Trimethylphenol	2.61	5.43
	Naphthalene[a]	1.75	3.08
	2-Methylnaphthalene[a]	1.94	3.29
	1-Methylnaphthalene[a]	1.96	3.28
DDTBA-Zn	Phenol	2.57	4.64
	o-Cresol	2.63	4.98
	p-Cresol	2.63	5.19
	2,4-Dimethylphenol	2.76	5.59
	2,4,6-Trimethylphenol	2.82	5.95
	Naphthalene[a]	2.21	3.99
	2-Methylnaphthalene[a]	2.40	4.32
	1-Methylnaphthalene[a]	2.42	4.30

[a]Data from [8].

3.1.2. Capillary column

The results shown above indicate that the thermal stability of the nickel complex is better than that of the zinc complex, hence the optimum condition for the separation of phenols with the capillary column was investigated only with the nickel complex. Fig. 6(A) shows a typical chromatogram using the metallomesogenic siloxane polymer capillary column under 115°C. *m*-Cresol is coeluted with *p*-cresol, and the same situation applies for 2,4,6-trimethylphenol and 2,4-dichlorophenol. Ammonia in nitrogen was used instead of nitrogen as carrier gas. Significant variations in retention time, detector response and peak shape were observed (Fig. 6(B)). Meanwhile, improved selectivity was obtained and more phenols, including 4-bromophenol, 3-methyl-4-chlorophenol and 2,4,6-trichlorophenol, could be separated within a reasonable time. The phenomena indicated that there might be a competitive reaction occurring between phenols and ammonia with the stationary phase. For investigating the column efficiency, isothermal conditions from 100°C to 130°C were studied (Fig. 7). The elution orders are: 2-chlorophenol<phenol< *o*-cresol=2-nitrophenol<*m*-cresol<*p*-cresol<2,4,6-trimethylphenol<2,4-dichlorophenol. Most of them follow the boiling points of these substances, except 2-nitrophenol and the pairs *m*-cresol/*p*-cresol and 2,4-

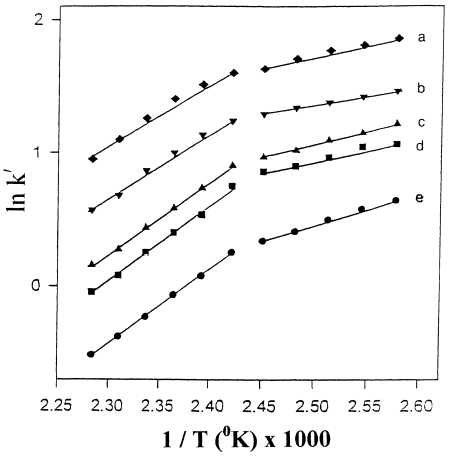

Fig. 4. Van't Hoff plot for phenols. Stationary phase: 5% DDTBA-Ni coated on Chromosorb; 2.1 m×3.2 mm i.d. glass column; mobile phase: nitrogen gas, flow rate: 40 ml min^{-1}; injector temp.: 230°C. Sample: (a) phenol; (b) *o*-cresol; (c) *p*-cresol; (d) 2,4-dimethylphenol; (e) 2,4,6-trimethylphenol.).

dimethylphenol/2,4,6-trimethylphenol/2,4-dichlorophenol. It was also found that 4-bromophenol, 3-methyl-4-chlorophenol and 2,4,6-trichlorophenol strongly adsorbed on the column and no peak was detected during the tested times at 100°C. Increasing the column temperature decreases the retention time significantly, but the lower boiling point substances are non-resolved.

A program with an initial temperature of 100°C for 10 min followed by a 3°C min^{-1} gradient to 170°C final temperature was found to produce more satisfactory resolution of phenols. At the same condition but altering the initial temperature only, an even better resolution for *o*-cresol and 2-nitrophenol was found and more phenols could be separated within 30 min (Fig. 8(A)–(C)), but the pairs *m*-cresol/*p*-cresol and 3-methyl-4-chlorophenol/2,4,6-trichlorophenol were coeluted. Increasing the holding time of the initial temperature, 3-methyl-4-chlorophenol and 2,4,6-trichlorophenol were well resolved but not at the baseline (Fig. 8(D)). The elution orders are 2-chlorophenol<phenol<*o*-cresol<2-nitrophenol<*m*-cresol<*p*-cresol<2,4-dimethylphenol<2,4,6-trimethylphenol<2,4-dichlorophenol<4-bromophenol<3-methyl-4-chlorophenol<2,4,6-trichlorophenol.

3.2. Separation mechanism

3.2.1. Packed column

The elution mainly follows the order of boiling points of the tested substances. Deviations from the elution order were observed only for the pair 2-chlorophenol/phenol (Fig. 2). Phenols are expected to form complexes with the central metal ion of the metallomesogens coated on Chromosorb. Any change in the substituent of phenols had pronounced effects on the retention time. Chlorine is an electron-donating atom,

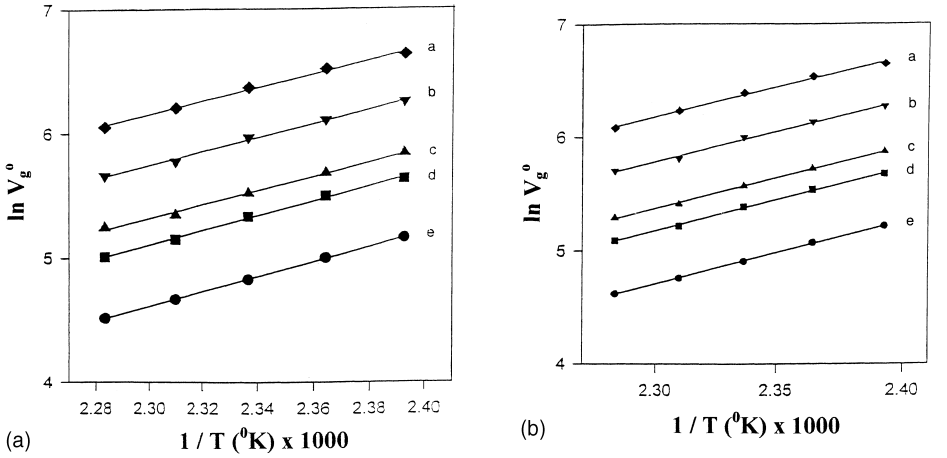

Fig. 5. Temperature dependence of specific retention volume for phenols: (A) stationary phase: 5% DDTBA-Ni coated on Chromosorb; 2.1 m×3.2 mm i.d. glass column; mobile phase: nitrogen gas, flow rate: 40 ml min^{-1}; injector temp.: 230°C. Sample: as Fig. 4. (B) as in (A), except stationary phase: 5% DDTBA-Zn coated on Chromosorb.

Table 2
Optimum conditions for the separation of phenols

	Packed column	Capillary column
Stationary phase	5% DDTBA-Ni on Chromosorb	DDTBA-Ni siloxane polymer
Dimension of column	2.1 m×3.2 mm i.d. glass column	12 m×0.25 mm i.d. fused silica
Injector temperature	250°C	260°C
Column temperature	140°C (3 min) to 165°C at 3°C min^{-1}	110°C (15 min) to 170°C at 3°C min^{-1}
Carrier gas	Nitrogen	10% ammonia in nitrogen (v/v)
Flow rate of carrier gas	40 ml min^{-1}	30 ml min^{-1} (total flow rate) with split ratio of 1/25; 40 ml min^{-1} (make-up gas)
Total weight of Chromosorb	7.248 g	
Total weight of DDTBA-Ni	0.382 g	
Molecular weight of DDTBA-Ni	678.9	

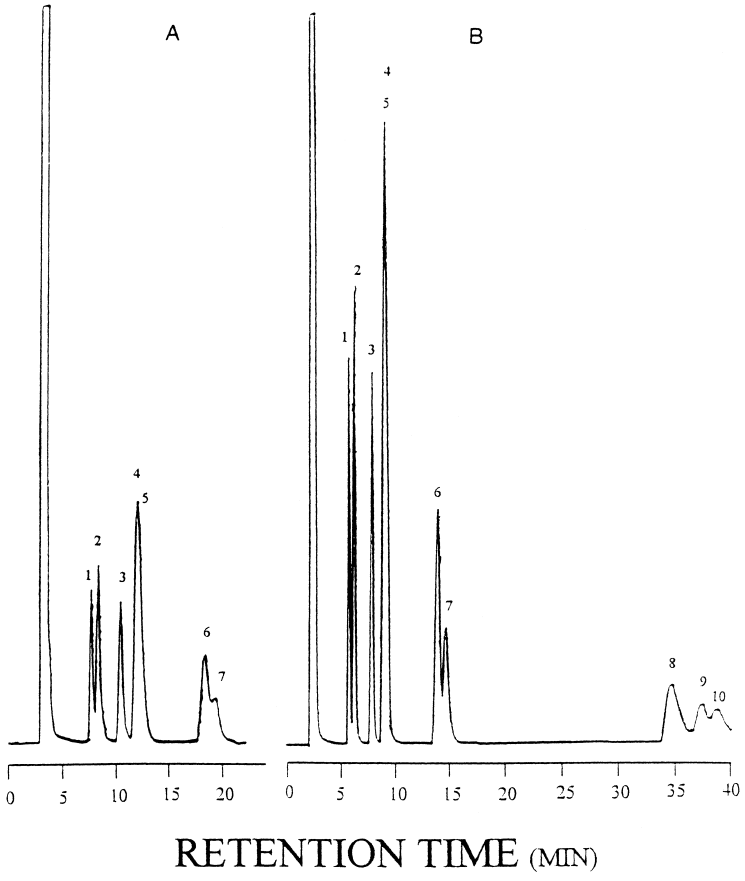

Fig. 6. The separation of phenols using various carrier gases with capillary column. Stationary phase: fused-silica capillary column (12 m×0.25 mm i.d.) coated with metallomesogenic siloxane polymer; injector temp.: 260°C; oven temperature: 115°C; total flow rate: 30 ml min^{-1}; split ratio: 1/30; make-up gas flow rate: 40 ml min^{-1}. Carrier gas: (A) nitrogen gas; (B) 10% ammonia in nitrogen (v/v). Peak identification: (1) 2-chlorophenol; (2) phenol; (3) *o*-cresol; (4) *m*-cresol; (5) *p*-cresol; (6) 2,4,6-trimethylphenol; (7) 2,4-dichlorophenol; (8) 4-bromophenol; (9) 3-methyl-4-chlorophenol; (10) 2,4,6-trichlorophenol.

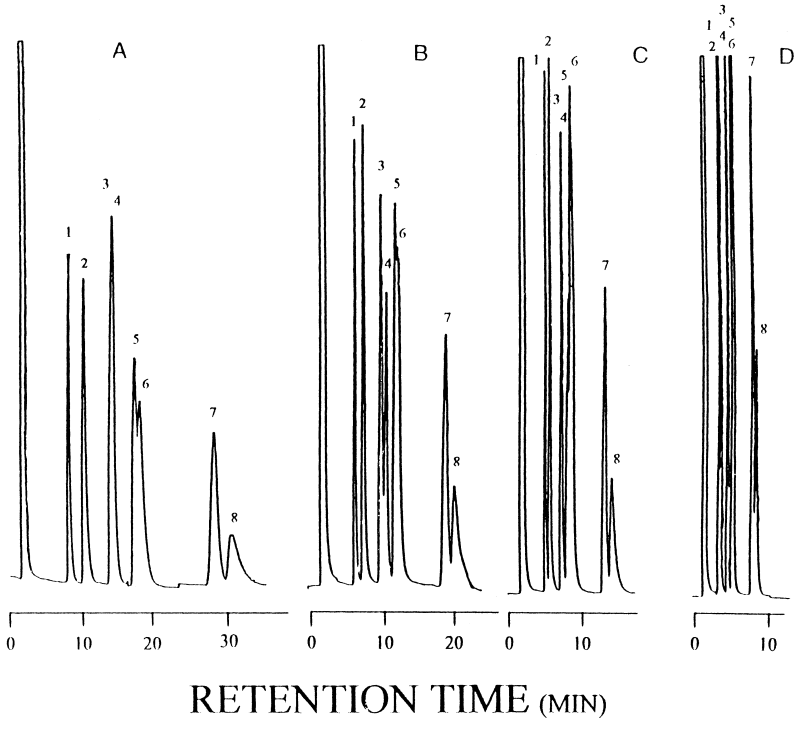

Fig. 7. Separation of phenols at various oven temperatures. Stationary phase: fused-silica capillary column (12 m×0.25 mm i.d.) coated with metallomesogenic siloxane polymer; injector temp.: 260°C; total flow rate: 30 ml min^{-1}; split ratio: 1/25; make-up gas flow rate: 40 ml min^{-1}. Carrier gas: 10% ammonia in nitrogen (v/v). Oven temperature: (A) 100°C; (B) 110°C; (C) 120°C; (D) 130°C. Peak identification: (1) 2-chlorophenol; (2) phenol; (3) *o*-cresol; (4) 2-nitrophenol; (5) *m*-cresol; (6) *p*-cresol; (7) 2,4,6-trimethylphenol; (8) 2,4-dichlorophenol.

2-chlorophenol forms a stronger complex than phenol itself, thus phenol is eluted first. Methyl is an electron releasing group, the effect of the substituent is much greater in the case of *p*-isomer than in the cases of *m*-isomers. Hence the elution order of the positional isomers was *m*-<*p*-. The greater retention could be explained also by the larger *L*/*B* value of the *p*-isomer. 2,4-Dimethylphenol and 2,4-dichlorophenol are similar in b.p. and *L*/*B* ratio. Due to the greater MW and a higher affinity toward the central metal ion, 2,4-dimethylphenol is eluted as expected followed by 2,4-dichlorophenol, and they are well resolved. 3-Methyl-4-chlorophenol and 4-bromophenol were separated successively, and the most retained solute is 2,4,6-trichlorophenol. It can be concluded that the retention behavior seems related mostly to the affinity of metal–ligand interaction. Structural selectivity involving the *L*/*B* ratio seems to be only a minor contribution. In other words, the electron density in the donor group favoring the ligand-exchange reaction would explain the unexpected behavior.

3.2.2. Capillary column

The favorable chromatographic behavior of the column as demonstrated above might be attributed to multiple properties derived from its chemical structure, i.e., polysiloxane backbone and mesogenic side chains, as well as ligand-exchange reaction. Deviations from the elution order according to boiling points can be observed for 2-nitrophenol and for the pairs *m*-cresol/*p*-cresol, 2,4-dimethylphenol/2,4,6-trimethylphenol/2,4-dichlorophenol and 4-bromophenol/3-methyl-4-chlorophenol. The sequence of most phenols in Fig. 8 agrees very well with that on the packed column which is mainly based on the mechanism of LEGC, except the pairs 2-chlorophenol/phenol and 4-bromophenol/3-methyl-4-chlorophenol, which are eluted in reverse order. This might be due to the

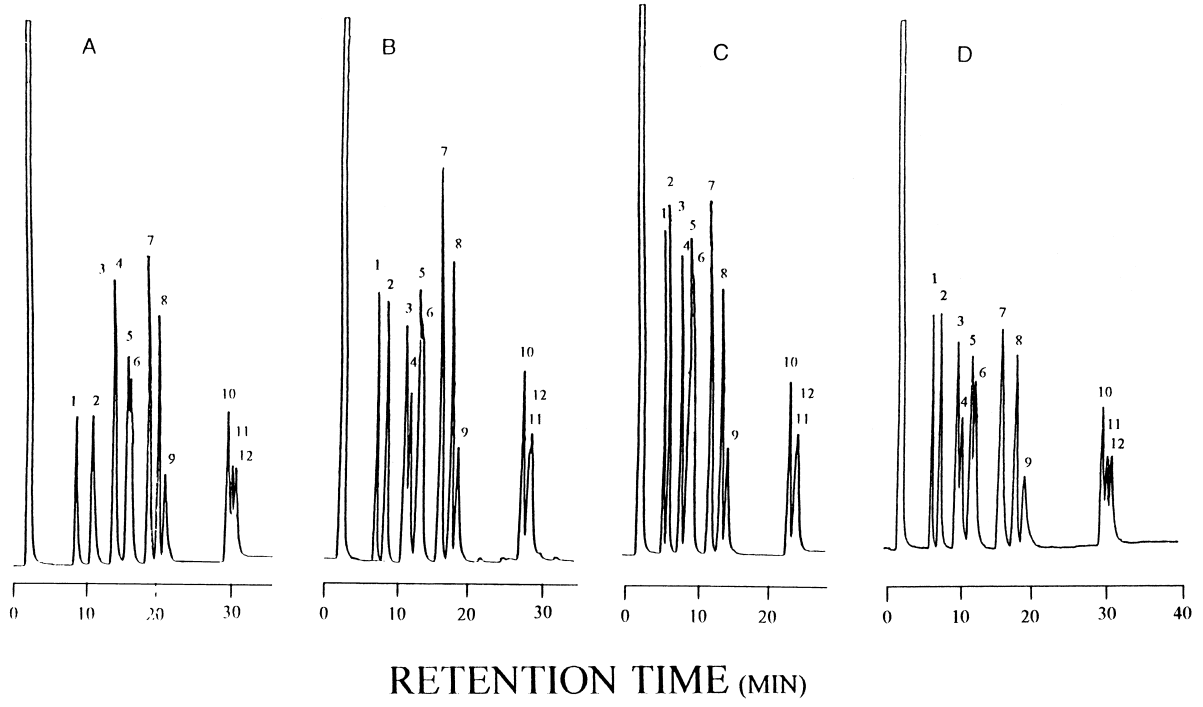

Fig. 8. Separation of phenols under temperature programed conditions. Stationary phase: fused-silica capillary column (12 m×0.25 mm i.d.) coated with metallomesogenic siloxane polymer; injector temp.: 260°C; carrier gas: 10% ammonia in nitrogen (v/v); total flow rate: 30 ml min^{-1}; split ratio: 1/25; make-up gas flow rate: 40 ml min^{-1}. Oven temperature: (A) 100°C (10 min) to 170°C at 3°C min^{-1}; (B) 110°C (10 min) to 170°C at 3°C min^{-1}; (C) 120°C (10 min) to 170°C at 3°C min^{-1}; (D) 110°C (15 min) to 170°C at 3°C min^{-1}. Peak identification: (1) 2-chlorophenol (t_r=6.52 min); (2) phenol (t_r=7.68 min); (3) *o*-cresol (t_r=10.04 min); (4) 2-nitrophenol (t_r=10.67 min); (5) *m*-cresol (t_r=11.92 min); (6) *p*-cresol (t_r=12.56 min); (7) 2,4-dimethylphenol (t_r=15.94 min); (8) 2,4,6-trimethylphenol (t_r=17.92 min); (9) 2,4-dichlorophenol (t_r=19.13 min); (10) 4-bromophenol (t_r=29.35 min); (11) 3-methyl-4-chlorophenol (t_r=30.02 min); (12) 2,4,6-trichlorophenol (t_r=30.07 min).

greater hydrophobic interaction of phenol and 3-methyl-4-chlorophenol with the polysiloxane backbone.

In a ligand-exchange separation mechanism, silica gel bonded with 8-quinolinol and loaded with Fe(III) was tested by Shahwan and Jezorek [15]. They found that the presence of electron-withdrawing substituents in the *ortho*- and *para*-positions of the phenol results in substantially increased retention relative to phenol itself. These substituents decrease the electron density in the aromatic ring, and hence the π–π interactions. However, they also decrease the electron density on the phenolic oxygen permitting stronger hydrogen bonding by the phenolic proton. The substantially greater retention exhibited by these compounds suggests that hydrogen bonding is a major interaction with the stationary phase. The presence of the methyl group results in greater electron density on the aromatic ring and hence π–π interactions, as well as dispersion interactions, are enhanced. In their work, the substituents Cl, CH_3 and NO_2 increased retention compared with phenol. The same phenomena were indicated in our study, although their work was in the liquid system.

3.3. Linear calibration range

The optimum conditions for the separation of phenols are summarized in Table 2. Solution mixtures containing known amounts of phenols were prepared and used for the construction of calibration graphs. Under optimum conditions, the calibration graphs of peak height against the quantity of each analyte were found to be linear over the concentration range stu-

Table 3
Calibration equations for the determination of phenols

Compound	Regression equation[b]	Correlation coefficient[b]	Linear range (μg ml^{-1})	Detection limit (ng)
With packed column[a]				
Phenol	$y=27.1x-105.6$	0.9998	64–1600	22
2-Chlorophenol	$y=27.4x-168.7$	0.9997	64–1600	22
o-Cresol	$y=25.4x-147.2$	0.9998	64–1600	22
p-Cresol	$y=24.6x-60.2$	0.9997	64–1600	24
2,4-Dichlorophenol	$y=23.3x-121.4$	0.9989	64–1600	24
3-Methyl-4-chlorophenol	$y=20.2x-107.6$	0.9975	64–1600	32
4-Bromophenol	$y=19.9x-257.0$	0.9972	64–1600	32
2,4,6-Trichlorophenol	$y=19.3x-103.1$	0.9974	64–1600	32
With capillary column[c]				
2-Chlorophenol	$y=109.9x-167.3$	0.9974	16–400	4
Phenol	$y=109.9x-171.3$	0.9983	16–400	4
o-Cresol	$y=101.5x-73.4$	0.9985	16–400	4
2-Nitrophenol	$y=87x-143.2$	0.9985	16–400	4
p-Cresol	$y=92.0x-147.4$	0.9948	16–400	4
2,4-Dimethylphenol	$y=90.7x-104.7$	0.9954	16–400	4
2,4,6-Trimethylphenol	$y=59.8x-116.6$	0.9941	16–400	7
2,4-Dichlorophenol	$y=82.6x-84.2$	0.9956	16–400	5
3-Methyl-4-chlorophenol	$y=41.8x-126.3$	0.9922	16–400	10
4-Bromophenol	$y=46.8x-99.4$	0.9921	16–400	10
2,4,6-Trichlorophenol	$y=37.6x-101.2$	0.9918	16–400	10

[a]Stationary phase: 5% DDTBA-Ni coated on Chromosorb, 2.1 m×3.2 mm i.d. glass column; oven temp.: 140°C (3 min) to 165°C at 3°C min^{-1}; injection temp.: 250°C; mobile phase: nitrogen gas, flow rate: 40 ml min^{-1}.
[b]y=Peak height, x=phenol conc. (μg ml^{-1}), number of measurements: 8.
[c]Stationary phase: fused-silica capillary column (12 m×0.25 mm i.d.) coated with metallomesogenic siloxane polymer; injector volume: 1 μl; injector temp.: 260°C; oven temperature: 110°C (15 min) to 170°C at 3°C min^{-1}; carrier gas: 10% ammonia in nitrogen (v/v); total flow rate: 30 ml min^{-1}; split ratio: 1/25; make-up gas flow rate: 40 ml min^{-1}.

died, i.e., 64–1600 μg ml^{-1} (packed column) and 16–400 μg ml^{-1} (capillary column) for an injection volume of 1 μl. The results were summarized in Table 3(A) and (B). The mass detection limits of most phenols, defined as the minimum weight of analyte that can be detected at a known confidence level (95%, i.e., 2σ) [21], are less than 30 ng (packed column) and 4 ng (capillary column).

4. Conclusion

Nowadays, the most widely used analytical technique for the determination of phenols is gas chromatography. However, phenols tend to produce broad peaks (often with tailing) due to their high polarity and low vapor pressure, which increase with aging of the column. Derivatization of phenols prior to analysis is necessary to give less polar compounds with better chromatographic characteristics [22]. In this study, both nickel and zinc complexes of *p*-decanoxydi thiobenzoate could be used as gas chromatography stationary phases for the separation of phenols. However, a slightly different selectivity could be seen for the separation of higher boiling point phenols. The phenomena indicate that nickel complex is superior to the zinc complex. The nickel complex either coated on Chromosorb or its siloxane polymer coated on a capillary column are efficient for the separation of phenols. The procedures are direct and efficient, and derivatization is not necessary. Nitrogen gas can be used as carrier gas, but ammonia in nitrogen improves the peak shape and selectivity. The prepared columns are highly promising for the separation and determination of phenols in environmental samples.

Acknowledgements

We thank the National Science Council of the Republic of China (Taiwan) for financial support.

References

[1] R.A. Weiss, C.K. Ober (Eds.), Liquid-Crystalline Polymers, American Chemical Society, Washington, DC, 1990.
[2] Z. Witkiewicz, J. Chromatogr. 466 (1989) 37.
[3] L. Oriol, J.L. Serrano, Adv. Mater. 7 (1995) 348.
[4] K. Fujimura, M. Kitanaka, H. Takayanagi, T. Ando, Anal. Chem. 54 (1982) 918.
[5] H. Takayanagi, M. Hashizume, K. Fujimura, T. Ando, J. Chromatogr. 350 (1985) 63.
[6] H. Takayanagi, M. Akita, K. Fujimura, T. Ando, J. Chromatogr. 350 (1985) 75.
[7] P. Berdague, F. Perez, J. Courtieu, J.P. Bayle, O. Abdelhadi, S. Guermouche, M.H. Guermouche, J. High Resolut. Chromatogr. 18 (1995) 304.
[8] C.C. Hu, C.Y. Liu, Anal. Chim. Acta 332 (1996) 23.
[9] C.Y. Liu, C.C. Hu, C.L. Yang, J. Chromatogr. A 773 (1997) 199.
[10] V.A. Davankov, J.D. Navratil, H.F. Walton, Ligand Exchange Chromatography, CRC Press, Boca Raton, FL, 1988.
[11] D. Cagniant (Ed.), Complexation Chromatography, Marcel Dekker, New York, 1992.
[12] P. Mubmann, K. Levsen, W. Radeck, Fresenius' J. Anal. Chem. 348 (1994) 654.
[13] B.M. Petronio, A. Lagana, M.V. Russo, Talanta 28 (1981) 215.
[14] B.M. Petronio, A. Lagana, G.D. Andrea, Talanta 31 (1984) 357.
[15] G.J. Shahwan, J.R. Jezorek, J. Chromatogr. 256 (1983) 39.
[16] K. Grob, G. Grob, J. High Resolut. Chromatogr. Chromatogr. Commun. 5 (1982) 119.
[17] J. Rayss, Z. Witkiewicz, A. Waksmundzki, R. Dabrowski, J. Chromatogr. 188 (1980) 107.
[18] S. Ghodbane, G.A. Oweimreen, D.E. Martire, J. Chromatogr. 556 (1991) 317.
[19] E.F. Meyer, J. Chem. Educ. 50 (1973) 191.
[20] G.M. Janini, M.T. Ubeid, J. Chromatogr. 236 (1982) 329.
[21] D.A. Skoog, F.J. Holler, T.A. Nieman, Principles of Instrumental Analysis, 5th ed., Saunders, Philadelphia, 1998, p. 13.
[22] D. Puig, D. Barcelo, Trends Anal. Chem. 15 (1996) 362.