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SEPARATION OF ALKYLPHENOLS BY GAS CHROMATOGRAPHY

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อังค์วรา เพชราวุฒิไกร: การแยกแอลคิลฟีนอลด้วยแก๊สโครมาโทกราฟี. (SEPARATION OF ALKYLPHENOLS BY GAS CHROMATOGRAPHY) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ.ดร.อรุณศิริ ชิตางกูร, 59 หน้า.

ศึกษาการแยกสารผสมของแอลคิลฟีนอล 22 ชนิดในการวิเคราะห์ครั้งเดียวด้วยแคพิลลารีแก๊สโครมาโทกราฟี โดยใช้เฟสคงที่พอลิไซลอกเซน (OV-1701), เฮกซะคิส(2,3-ได-*โอ*-เมทิล-6-*โอ*-*เทอร์ต*-บิวทิลไดเมทิลไซลิล)-แอลฟา-ไซโคลเดกซ์ทริน (ASiMe), เฮปตะคิส(2,3-ได-*โอ*-เมทิล-6-*โอ*-*เทอร์ต*-บิวทิลไดเมทิลไซลิล)-บีตา-ไซโคลเดกซ์ทริน (BSiMe) และออกตะคิส(2,3-ได-*โอ*-เมทิล-6-*โอ*-*เทอร์ต*-บิวทิลไดเมทิลไซลิล)-แกมมา-ไซโคลเดกซ์ทริน (GSiMe) พบว่า คอลัมน์ OV-1701 ไม่สามารถแยก 2,4-ไดเมทิลฟีนอลออกจาก 2,5-ไดเมทิลฟีนอลได้ เมื่อวิเคราะห์ด้วยคอลัมน์ที่มีอนุพันธ์ไซโคลเดกซ์ทริน พบว่า คอลัมน์ BSiMe ให้ผลการวิเคราะห์ภายในครั้งเดียวดีที่สุด โดยใช้อุณหภูมิคอลัมน์คงที่ 120 ºC เป็นเวลา 11 นาที จากนั้นเพิ่มอุณหภูมิจาก 120–180 ºC ด้วยอัตรา 25 ºC/นาที สามารถแยกสารผสมทุกชนิดได้ในเวลา 13 นาที นอกจากนี้พบว่าโครมาโทแกรมที่ได้ให้พีกที่ค่อนข้างสมมาตรแม้ไม่ได้เปลี่ยนสารให้อยู่ในรูปอนุพันธ์ก่อนการวิเคราะห์ และยังได้คำนวณค่าทางเทอร์โมไดนามิกส์เพื่ออธิบายถึงแรงกระทำระหว่างสารกับเฟสคงที่ พบว่าแอลคิลฟีนอลเกิดแรงกระทำกับคอลัมน์ที่มีอนุพันธ์ไซโคลเดกซ์ทรินมีลำดับเป็น GSiMe < ASiMe < BSiMe ตามลำดับ และแข็งแรงกว่าคอลัมน์ OV-1701

สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต .....

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The single-run separation of the mixture of twenty-two C_0–C_3 alkylphenols was investigated by capillary gas chromatography using polysiloxane (OV-1701) and three derivatized cyclodextrins as stationary phases. These derivatized cyclodextrins were hexakis(2,3-di-*O*-methyl-6-*O*-*tert*-butyldimethylsilyl)-α-cyclodextrin (ASiMe), heptakis(2,3-di-*O*-methyl-6-*O*-*tert*-butyldimethylsilyl)-β-cyclodextrin (BSiMe) and octakis(2,3-di-*O*-methyl-6-*O*-*tert*-butyldimethylsilyl)-γ-cyclodextrin (GSiMe). The result showed that the separation of 2,4-dimethylphenol from 2,5-dimethylphenol was not achieved on OV-1701 column. When derivatized cyclodextrins were used as stationary phases, the best single-run separation was achieved on BSiMe column using a column temperature of 120 ºC for 11 min and then programmed from 120–180 ºC at 25 ºC/min. The mixture could be separated in 13 minutes. In addition, chromatograms showed acceptable peak shapes without any prior derivatization. Thermodynamic parameters described the interaction between analytes and the stationary phases were also determined. The interactions of analytes on column that contains cyclodextrin derivatives were in the order of GSiMe < ASiMe < BSiMe, respectively, and were stronger than on OV-1701 column.

Field of Study Petrochemistry and Polymer Science Student's Signature .....
Academic Year 2011 Advisor's Signature .....

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LIST OF ABBREVIATIONS AND SIGNS

AP	=	alkylphenol
ASiMe	=	hexakis(2,3-di-*O*-methyl-6-*O*-*tert*-butyldimethylsilyl) cyclomaltohexaose in OV-1701
BSiMe	=	heptakis(2,3-di-*O*-methyl-6-*O*-*tert*-butyldimethylsilyl) cyclomaltoheptaose in OV-1701
CD	=	cyclodextrin
DMP	=	dimethylphenol
EP	=	ethylphenol
GC	=	gas chromatography
GSiMe	=	octakis(2,3-di-*O*-methyl-6-*O*-*tert*-butyldimethylsilyl) cyclomaltooctaose in OV-1701
i.d.	=	internal diameter
IPP	=	isopropylphenol
k′	=	retention factor or capacity factor
m	=	meter
MP	=	methylphenol
min	=	minute
mm	=	millimeter
OV-1701	=	poly(14%-cyanopropylphenyl-86%-dimethylsiloxane)
P	=	phenol
PP	=	propylphenol
R	=	universal gas constant (1.987 cal/mol·K)
R^2	=	correlation coefficient
T	=	absolute temperature (K)
TMP	=	trimethylphenol
β	=	phase ratio
ΔH	=	enthalpy change

ΔS	=	entropy change
μm	=	micrometer, 10^{-6} m
°C	=	degree Celsius

CHAPTER I

INTRODUCTION

Nowadays, many petrochemical compounds are widely used in pharmaceutical, agricultural, and petrochemical industries. The environmental problems, such as soil, water and air pollution, increasingly arise due to industrial activities. Especially, the use of phenol and its substituted derivatives are one of the leading causes of environmental pollution.

Phenol and low molecular weight alkylphenols (C_0–C_3 APs) are commonly used in industrial processes, such as production of pesticides, herbicides, drugs, dyes, detergents, wood extractives, textiles and plastic, etc. Thus, the most common phenols contaminated in wastewater are short chain APs because of their relatively good water solubility [1–4].

APs are also found in environment, thus they can cause toxicity and danger to animals and human health. The three primary routes of APs entering into the body are ingestion, skin or eye absorption and inhalation. Ingestion of APs can affect on burning mouth and throat, abdominal pain, headache, dizziness, muscular weakness, weak pulse, lung damage, liver damage, pancreas damage, kidney damage, coma and possible death from circulatory or cardiac failure. If absorbed through the skin, APs can cause severe skin irritation and burns, systemic poisoning and possible death due to effects on heart, blood vessels, lungs and kidneys. Contact with liquid or vapor APs causes severe burns and possible irreversible eye damage. Breathing APs into the body can cause severe irritation of upper respiratory tract with coughing, burns, breathing difficulty and possible coma [5, 6].

Because of their toxicity, a number of APs have been classified as priority pollutants by the US Environmental Protection Agency (EPA) [7–9]. Moreover, the European Union (EU) has classified phenols as priority contaminants and the

80/778/EC directive states a maximum concentration of 0.5 µg/L for total phenols in drinking water [10]. In Thailand, the Ministry of Industry limits the maximum concentration of total phenolic compounds in wastewater not to exceed 1 mg/L [11]. Thus, there is a need for an accurate, sensitive, efficient and fast technique in order to determine the level of each isomer of APs.

APs can be analyzed by gas chromatography (GC), liquid chromatography (LC), high performance liquid chromatography (HPLC) and capillary electrophoresis (CE). Chromatographic instruments could be coupled with several types of detector, such as flame ionization detector (FID), fluorescence detector and mass spectrometry (MS) [12−16]. GC is the most commonly used techniques for the separation of APs because of its high efficiency, sensitivity, and short analysis time. Since the mixture of C_0–C_3 APs contains several structural isomers, the single-run separation of all C_0–C_3 AP isomers has not been reported.

Cyclodextrins and their derivatives have been used as efficient selectors for the separation of enantiomers and isomers in many chromatographic techniques. Previously, heptakis(2,3-di-*O*-methyl-6-*O*-*tert*-butyldimethylsilyl)-β-cyclodextrin (BSiMe) dissolved in polysiloxane has been used as a GC stationary phase for the separation of isomers of cresols and chlorophenols [17, 18]. Complete separations of both groups of isomers were observed without tailing peaks.

Therefore, this research aims to investigate the separation of the mixture of twenty-two C_0–C_3 AP isomers in a single-run by GC-FID using three derivatized cyclodextrins as stationary phases. Thermodynamic parameters attained through van't Hoff equation will be acquired to evaluate the interaction between analytes and stationary phases.

CHAPTER II

THEORY

2.1 C_0–C_3 alkylphenols

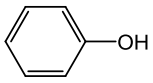
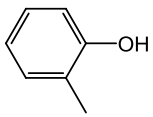
Phenol (P) is the aromatic alcohol which characterized by a hydroxyl group (-OH) attached to a benzene ring.

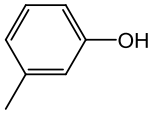
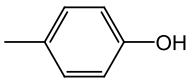
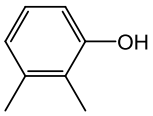
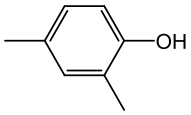
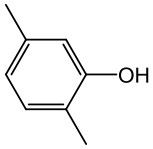
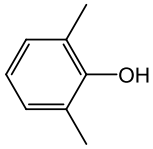
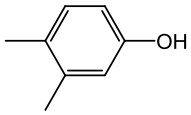
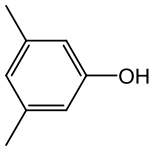
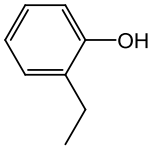
Alkylphenols (APs) are a group of organic compounds obtained by the alkylation of phenols. In this research, APs can be divided into four groups according to the number of carbon atom of alkyl substituted on the phenolic ring:

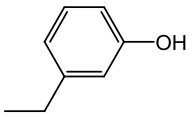
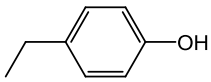
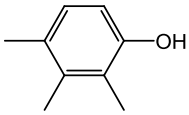
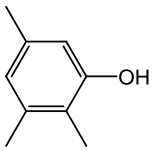
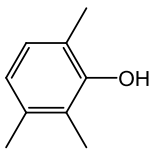
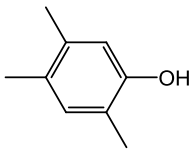
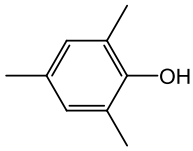
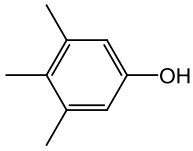
- C_0 AP is an unsubstituted phenol .
- C_1 APs contain three isomers of three methylphenols (MPs).
- C_2 APs contain nine isomers: six dimethylphenols (DMPs) and three ethylphenols (EPs).
- C_3 APs contain twelve isomers: six trimethylphenols (TMPs), three propylphenols (PPs) and three isopropylphenols (IPPs).

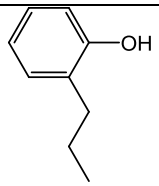
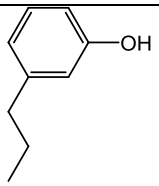
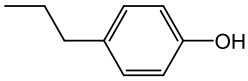
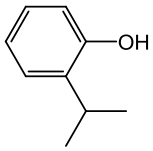
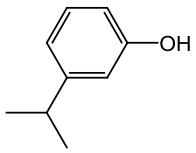
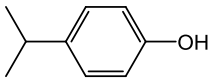
Structure and physical properties of C_0–C_3 APs were shown in Table 2.1 [19, 20].

Table 2.1 Structure and properties of C_0–C_3 APs

compound	abbreviation	structure	MW (g/mol)	mp/bp (°C)
phenol	P		94.11	mp: 40.89 bp: 181.87
2-methylphenol (*o*-cresol)	2-MP		108.14	mp: 31.03 bp: 191.04

compound	abbreviation	structure	MW (g/mol)	mp/bp (°C)
3-methylphenol (*m*-cresol)	3-MP		108.14	mp: 12.24 bp: 202.27
4-methylphenol (*p*-cresol)	4-MP		108.14	mp: 34.77 bp: 201.98
2,3-dimethylphenol	2,3-DMP		122.16	mp: 72.5 bp: 216.9
2,4-dimethylphenol	2,4-DMP		122.16	mp: 24.5 bp: 210.98
2,5-dimethylphenol	2,5-DMP		122.16	mp: 74.8 bp: 211.1
2,6-dimethylphenol	2,6-DMP		122.16	mp: 45.8 bp: 201.07
3,4-dimethylphenol	3,4-DMP		122.16	mp: 65.1 bp: 227
3,5-dimethylphenol	3,5-DMP		122.16	mp: 63.4 bp: 221.74
2-ethylphenol	2-EP		122.16	mp: -18 bp: 204.5

compound	abbreviation	structure	MW (g/mol)	mp/bp (°C)
3-ethylphenol	3-EP		122.16	mp: -4 bp: 218.4
4-ethylphenol	4-EP		122.16	mp: 45 bp: 217.9
2,3,4-trimethylphenol	2,3,4-TMP		136.19	mp: 81 bp: 236
2,3,5-trimethylphenol	2,3,5-TMP		136.19	mp: 94.5 bp: 233
2,3,6-trimethylphenol	2,3,6-TMP		136.19	mp: 63 bp: 215
2,4,5-trimethylphenol	2,4,5-TMP		136.19	mp: 72 bp: 232
2,4,6-trimethylphenol	2,4,6-TMP		136.19	mp: 73 bp: 220
3,4,5-trimethylphenol	3,4,5-TMP		136.19	mp: 108 bp: 248.5

compound	abbreviation	structure	MW (g/mol)	mp/bp (°C)
2-propylphenol	2-PP		136.19	mp: 7 bp: 220
3-propylphenol	3-PP		136.19	mp: 26 bp: 228
4-propylphenol	4-PP		136.19	mp: 22 bp: 232.6
2-isopropylphenol	2-IPP		136.19	mp: 15.5 bp: 213.5
3-isopropylphenol	3-IPP		136.19	mp: 26 bp: 228
4-isopropylphenol	4-IPP		136.19	mp: 62.3 bp: 230

APs are widely occurred by natural and industrial production. They were used as the starting material for the synthesis. Most of them are present in the environmental pollution. In their pure form, most APs are either colorless solid or liquid. They smell like medicine. APs do not attach strongly to soil; therefore, they may move into and contaminate groundwater below the soil surface. For example, half the total amount of MPs will be broken down within a week.

Although APs are corrosive substances, exposures to APs at very low concentration are not harmful. However, breathing, ingesting or applying APs to the

skin at very high concentration could be very harmful. Skin contact with high concentrated APs could cause skin burn. Inhalation of high concentration of APs for a short time could result in eye, nose and throat irritation. Ingestion of high concentrated APs could result in mouth and throat burns, abdominal pain, vomiting, kidney damage, irregular heart beat and effects on the blood and nervous system. In addition, death may occur in some cases. Thus, EPA has determined that cresols are possible human carcinogens. Some applications and toxicity of C_0–C_3 APs are summarized in Table 2.2 [20, 21].

Table 2.2 Some applications and toxicity of C_0–C_3 APs

chemical	application	toxicity
P	bisphenol A, caprolactam, resins, plasticizers, medicines, dyes, pesticides, rubbers, explosives, lubricating oil additives, wood preservatives, pharmaceuticals, leather	- $LD_{50\ (oral,\ rat)}$ = 317 mg/kg - destructive to the tissue of the mucous membranes and upper respiratory tract - irritation to eyes, skin and digestion system
2-MP	resins, plasticizers, plastics, dyes, antiseptics, herbicides, pesticides, lubricating oils, pharmaceuticals	- $LD_{50\ (oral,\ rat)}$ = 121 mg/kg - irritation to respiratory tract, eyes, skin and digestion system
3-MP	resins, plasticizers, plastics, dyes, antiseptics, antioxidants, films, herbicides, pesticides, adhesives, fiber, lubricating oils, explosives, pharmaceuticals, electronic industries, perfume	- $LD_{50\ (oral,\ rat)}$ = 242 mg/kg - destructive to the tissue of the mucous membranes and upper respiratory tract - irritation to eyes, skin and digestion system
4-MP	resins, plastics, dyes, antiseptics, pesticides, solvents, adhesives, fiber, gasoline additives, explosive	- $LD_{50\ (oral,\ rat)}$ = 207 mg/kg - irritation to respiratory tract, eyes, skin and digestion system

chemical	application	toxicity
2,3-DMP	preparation of coal tar disinfectants, perfuming agents, resins, organic synthesis	- $LD_{50\ (intravenous,\ mouse)}$ = 56 mg/kg - destructive to the tissue of the mucous membranes and upper respiratory tract - irritation to eyes, skin and digestion system
2,4-DMP	resins, plasticizers, plastics, dyes, antiseptics, herbicides, rubber, fiber, wood preservatives, photographic chemicals, fungicides, organic synthesis, disinfectant, pharmaceuticals	- $LD_{50\ (oral,\ rat)}$ = 3,200 mg/kg - destructive to the tissue of the mucous membranes and upper respiratory tract - irritation to eyes, skin and digestion system
2,5-DMP	resins, plasticizers, plastics, dyes, antiseptics, herbicides, rubber, fiber, wood preservatives, photographic chemicals, disinfectant, pharmaceuticals	- $LD_{50\ (oral,\ rat)}$ = 444 mg/kg - destructive to the tissue of the mucous membranes and upper respiratory tract - irritation to eyes, skin and digestion system
2,6-DMP	disinfection for lubricants, gasolines, coal tar, intermediate for pesticides, dyes, rubbers, chemical, pharmaceuticals, agrochemical intermediates	- $LD_{50\ (oral,\ rat)}$ = 296 mg/kg - destructive to the tissue of the mucous membranes and upper respiratory tract - irritation to eyes, skin and digestion system
3,4-DMP	imine resin, plastics, disinfectors, pesticides, essence, dyes	- $LD_{50\ (oral,\ rat)}$ = 727 mg/kg - destructive to the tissue of the mucous membranes and upper respiratory tract - irritation to eyes, skin and digestion system

chemical	application	toxicity
3,5-DMP	resins, plasticizers, plastics, dyes, antiseptics, herbicides, pesticides, rubber, fiber, wood preservatives, photographic chemicals, disinfectant, pharmaceuticals	- $LD_{50\ (oral,\ rat)}$ = 608 mg/kg - destructive to the tissue of the mucous membranes and upper respiratory tract - irritation to eyes, skin and digestion system
2-EP	starting material for photochemicals	- $LD_{50\ (oral,\ mouse)}$ = 600 mg/kg - irritation to respiratory tract, eyes, skin and digestion system
3-EP	starting material for photochemicals, production of phenolic resins	- irritation to respiratory tract, eyes, skin and digestion system
4-EP	phenolic resins, rubber anti-aging agent, plastics, surfactants, pesticides, pharmaceuticals, chemical reagents, perfume	- $LD_{50\ (intraperitoneal,\ mouse)}$ = 138 mg/kg - irritation to respiratory tract, eyes, skin and digestion system
2,3,4-TMP	raw material	- $LD_{50\ (oral,\ rat)}$ = 318 mg/kg - irritation to respiratory tract, eyes, skin and digestion system
2,3,5-TMP	resins, pharmaceutical, electronic	- destructive to the tissue of the mucous membranes and upper respiratory tract - irritation to eyes, skin and digestion system
2,3,6-TMP	synthesis of vitamin E, intermediate for antioxidants and plastics	- $LD_{50\ (oral,\ mouse)}$ > 2,000 mg/kg - irritation to respiratory tract, eyes, skin and digestion system

chemical	application	toxicity
2,4,5-TMP	raw material	- $LD_{50\ (intraperitoneal,\ mouse)} > 500$ mg/kg - irritation to respiratory tract, eyes and skin
2,4,6-TMP	petroleum processing industries, wood treatment, raw material	- $LD_{50\ (oral,\ mouse)} = 10{,}000$ mg/kg - destructive to the tissue of the mucous membranes and upper respiratory tract - irritation to eyes, skin and digestion system
3,4,5-TMP	raw material	- destructive to the tissue of the mucous membranes and upper respiratory tract - irritation to eyes, skin and digestion system
2-PP	antioxidants, food flavor	- $LD_{50\ (oral,\ rat)} = 500$ mg/kg - irritation to respiratory tract, eyes, skin and digestion system
3-PP	pesticides, raw material	- destructive to the tissue of the mucous membranes and upper respiratory tract - irritation to eyes, skin and digestion system
4-PP	antioxidants, intermediates of liquid crystals, synthesis of ciprofibrate	- $LD_{50\ (oral,\ mouse)} = 348$ mg/kg - irritation to respiratory tract, eyes, skin and digestion system

chemical	application	toxicity
2-IPP	pesticides, UV stabilizers, polymerization inhibitors, anti-oxidants, pharmaceuticals	- $LD_{50\ (oral,\ rat)}$ > 200–2,000 mg/kg - destructive to the tissue of the mucous membranes and upper respiratory tract - irritation to eyes, skin and digestion system
3-IPP	intermediate of killing vegetation carbamate agents isoprocarb	- $LD_{50\ (oral,\ mouse)}$ = 1,630 mg/kg - destructive to the tissue of the mucous membranes and upper respiratory tract - irritation to eyes, skin and digestion system
4-IPP	organic synthesis	- $LD_{50\ (oral,\ mouse)}$ = 875 mg/kg - destructive to the tissue of the mucous membranes and upper respiratory tract - irritation to eyes, skin and digestion system

2.2 Gas chromatography [24, 25]

Gas chromatography (GC) is one of the most widely used techniques for separation, identification, and determination of volatile and thermally stable compounds. In GC, the components of a vaporized compound are separated based on partition of the analyte between a mobile phase and a stationary phase within the GC column. The mobile phase gas in GC is called the carrier gas and must be chemically inert, whereas the stationary phase is usually a liquid that is retained on the surface of an inert solid support by adsorption or chemical bonding. Two general types of columns are used in GC include packed column and capillary column. The GC column is placed in an oven where the temperature can be controlled. For samples with a wide range of boiling points, it is difficult to select a single temperature

(isothermal) suitable to separate all components. The temperature program is used to improve separation and speed of analysis. After components of the mixture are separated using GC, they must be detected by a detector as they elute from the column and appear as peaks on the chromatogram. Many detectors have been used in gas chromatographic separations. It can be classified into two types: general detectors and specific detectors. The difference of detectors will give different types of selectivity. The main advantages of GC are high efficiency, sensitivity, reproducibility, speed and simplicity.

2.3 Cyclodextrins and their derivatives [26, 27]

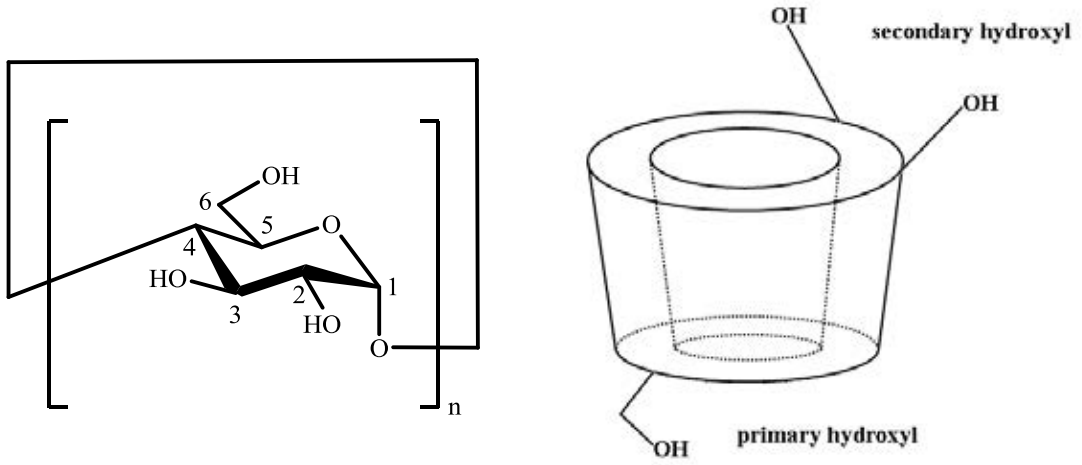
Cyclodextrins (CDs) are cyclic oligosaccharides resulting from the enzymatic degradation of starch by cyclodextrin-glycosyltransferase. These cyclic oligosaccharides consist of α-1,4-linked D-glucopyranose units. Three naturally occurring CDs are α-, β- and γ-CDs which contain six, seven, and eight glucopyranose units, respectively. Some properties of three CDs are summarized in Table 2.3.

Table 2.3 Some properties of α-, β- and γ-CDs

CD	α	β	γ
number of glucose units	6	7	8
anhydrous molecular weight (g/mol)	972	1135	1297
internal diameter (Å)	4.7–5.3	6.0–6.5	7.5–8.3
cavity dept (Å)	7.9	7.9	7.9
cavity volumn $(Å)^3$	174	262	427
solubility in water (g/100 mL, 25 °C)	14.5	1.85	23.3
decomposition temperature (°C)	278	299	267

Considering CD structures, it contains chair conformation of glucopyranose units (Figure 2.1a). CD shape is like a doughnut or truncated cone rather than a perfect cylinder (Figure 2.1b). The hydroxyl functions (-OH) are orientated to the

cone exterior with the primary hydroxyl groups at C6 position of the sugar on the narrow edge of the cone and the secondary hydroxyl groups at C2 and C3 positions on the wider edge. Thus, the exterior of the molecule is hydrophilic, which makes CD soluble in water, whereas the interior surface is relatively hydrophobic. As a result, the hydrophobic internal cavity provides the capability to form inclusion complexes with a wide variety of hydrophobic guest molecules (e.g. aromatics, alcohols, halides, fatty acids, esters).



(a) (b)

Figure 2.1 (a) Structure of a CD molecule with n glucose unit; (b) Side view of CD showing primary hydroxyls on a narrow rim and secondary hydroxyls on a larger rim of a ring

CDs can be modified by various functional groups on the primary and/or secondary hydroxyl groups to improve their physical and chemical properties. The purposes of development focus on modified chelating ability, altered solubility, complex stability, and increase separation activity. Modified CDs are molecular chelating agents of growing importance in food, agricultural, pharmaceutical and chromatographic industries. Modified CDs have application in analytical chemistry. These applications include gas and liquid chromatography, separation techniques and other miscellaneous analytical techniques. They were used as stationary phases in enantiomeric separations or separation of specific components from a mixture and show increased enantioselectivity over native CDs.

2.4 Gas chromatographic separation of C_0–C_3 alkylphenols

Separations of APs by GC using polysiloxane as stationary phases were reviewed as follow:

Ioppolo and coworkers [28] reported the analysis of 19 phenols in crude oil including phenol, 12 methylphenols, 3 ethylphenols and 3 isopropylphenols. They were determined by capillary gas chromatography-flame ionization detection (GC-FID) using 60 m × 0.22 mm i.d. with three different stationary phases: nonpolar BP1 (dimethylsiloxane), BP5 (5% phenyl-95% methyl polysiloxane) and medium polarity DB1701 (14% cyanopropylphenyl siloxane). For nonpolar BP1 and BP5 capillary columns, a temperature program from 40–300 °C was used to separate the mixture in 20 minutes. The elution order of alkylphenols on both columns are similar with exception of 2,4,6-TMP and 2-IPP. The 3-EP and 3,5-DMP were co-eluted on two stationary phases. Incomplete separations were observed for 4-MP/3-MP and 2,4-DMP/2,5-DMP. On DB1701 capillary column, a temperature program from 50–280 °C was used to separate the mixture in 20 minutes. The elution order was different from BP1 and BP5 capillary columns. The 2,4-DMP/2,5-DMP and 3,5-DMP/2,3-DMP were co-eluted and incomplete separations were observed for 4-MP/3-MP; 4-EP/3-EP; 2-IPP/2,3,6-TMP and 4-IPP/3-IPP. The DB1701 column was less efficient than the BP1 and BP5 columns as incomplete separations of several compounds were observed.

Pino and coworkers [29] using gas chromatography-mass spectrometry (GC-MS) for determination of 13 methylphenols, 2 ethylphenols, 3-methoxyphenol, 2,6-dimethoxyphenol, 4-chloro-3-methoxyphenol, eugenol and vanillin in wood extractives. The separation was achieved on a 30 m × 0.25 mm i.d. capillary column coated with nonpolar VF-5ms (5% phenyl-95% methyl polysiloxane) as a stationary phase. Under the optimum condition, a temperature program from 60–280 °C, the 3-MP/4-MP and 2,4-DMP/2,5-DMP were co-eluted and incomplete separations were observed for 3-EP/3,5-DMP/2,3-DMP.

Bernado and coworkers [30] determine 11 methylphenols in eluates from pyrolysis solid residue by dispersive liquid-liquid microextraction coupled with GC-MS. A nonpolar TR-5MS (5% phenyl polysilphenylene-siloxane) stationary phase was used to coat a 30 m × 0.25 mm i.d. column. The analysis was completed in 23 minutes using a temperature program from 35–220 °C. The separation of *m*-MP from *p*-MP was not achieved and incomplete separation between 2,4-DMP and 2,5-DMP was observed.

Separations of derivatized APs, such as silylated or acylated APs, by GC using polysiloxane as stationary phases were discussed below:

Bennett and coworkers [31] analyzed crude oils and waters for 19 APs, including phenol, 13 methylphenols, 2 ethylphenols, propylphenol and 2 isopropylphenols. They used two capillary column of different stationary phase: DB-5 (5% phenyl-95% dimethyl polysiloxane, 30 m × 0.32 mm i.d.) and HP-1 (dimethylsiloxane, 25 m × 0.25 mm i.d.). APs were analyzed as the trimethylsilyl derivatives using GC-FID for DB-5 and using GC-MS for HP-1 capillary columns with the same temperature program from 35–300 ºC. Incomplete separations were observed for 2,4-DMP/3,5-DMP and 2,4,6-TMP/2,3,5-TMP on DB-5 column; and for 2,4-DMP/2,6-DMP/3,5-DMP on HP-1 column.

Llompart and coworkers [32] used solid-phase microextraction (SPME) coupled with GC-MS for determination of phenol, 11 methylphenols and 18 chlorophenols in water samples. Phenols were analyzed as acetyl derivatives using 30 m × 0.25 mm i.d., nonpolar VA-5MS (5% phenyl-95% dimethyl polysiloxane) capillary column. The GC temperature program was 60–250 °C. The separation of isomer of cresols was finished in 6 minutes but the separation of *m*-cresol from *p*-cresol was not observed. For separation of five isomers of dimethylphenols (except 3,5-DMP) was complete in 14 minutes and incomplete separation were observed for 2,3-DMP/2,6-DMP. The chromatograms obtained from this column showed tailing peaks.

Vermeulen and coworkers [4] presented a GC-MS method for the analysis of 35 phenols in water. The mixture of phenols includes phenol, 11 methylphenols, 3 ethylphenols, isopropylphenol and 19 chlorophenols. Phenols were acetylated with acetic anhydride and analyzed by a 30 m × 0.25 mm i.d., slightly polar DB-XLB (14% -diphenyl-methyl polysiloxane) capillary column. The separation of all APs was done in 36 minutes using a temperature program from 40–320 °C. The incomplete separations were *m*-EP/2-IPP and 2,3-DMP/3,5-DMP/*p*-EP.

Jonsson and coworkers [14] studied the solid-phase analytical derivatization with bis(trimethylsilyl)trifluoroacetamide (BSTFA) for determination of 21 C_1–C_9 APs in fish bile. Derivatized APs were analyzed by GC-MS using a 50 m × 0.25 mm i.d., nonpolar CP-SIL 8 CB-MS (5% phenyl-95% dimethyl polysiloxane) capillary column. Chromatographic separation was performed with a temperature program from 50–300 °C in 30 minutes and symmetric peak shapes were observed. The results showed the incomplete separation of 3,5-DMP/2,4-DMP.

Previous studies concerning the separation of APs with GC using cyclodextrin derivatives as stationary phases are summarized as follow:

Jing and coworkers [33] separated isomer of xylenes, dichlorobenzenes, dibromobenzenes, nitrobromobenzenes, cresols, chlorotoluenes, nitrotoluenes, bromotoluenes, nitrochlorobenzenes and dinitrotoluenes with three derivatized-β-CDs as stationary phases: heptakis(2,3,6-tri-*O*-ethyl)-β-CD; heptakis(2,3,6-tri-*O*-butyl)-β-CD and heptakis(2,3,6-tri-*O*-octyl)-β-CD. All compounds were separated on 10 m × 0.25 mm i.d. capillary columns using GC-FID. The results showed that all stationary phases could completely resolve the three isomers of cresols with the same elution order (*otho*-, *para*-, *meta*-) at 130 °C. Furthermore, other isomers such as xylenes, dichrorobenzenes, nitrobromobenzenes, nitrotoluenes and chlorotoluenes were well separated on these stationary phases with the different elution order.

Zhang and coworkers [34] synthesized a new stationary phase, bikis(2,6-di-*O*-pentyl-3-*O*-hex-6-enyl)-pentakis(2,6-di-*O*-pentyl-3-*O*-methyl)-β-CD linked to the polysiloxane, and applied it to GC-FID for the separation of chiral compounds and isomers. This new stationary phase column (30 m × 0.25 mm i.d.) has an excellent selectivity for the separation of phenols and disubstituted benzenes. The analysis times of each isomer of cresols and dimethylphenols were complete in 15 minutes. For the separation of cresols, they were separated at 150 ºC with the elution order of *otho*-, *para*- and *meta*-substitution position, respectively. Dimethylphenols were also successfully separated at 160 ºC with the elution order of substitution position at 2,6-/2,4-/2,5-/2,3-/3,5- and 3,4-, respectively. In addition, other isomers including xylenes, chlorotoluenes, bromotoluenes, dimethoxybenzenes and nitrotoluenes showed complete separation on this stationary phase.

Pothisamutyothin and Hublee [17] studied the separation of cresol isomers by GC-FID using heptakis(2,3-di-*O*-methyl-6-*O*-*tert*-butyldimethylsilyl)-β-cyclodextrin mixed in OV-1701 as a stationary phase. The determination of cresols was completed at 160 °C within 1.5 minutes with elution order of *otho*-, *para*- and *meta*-, respectively and consistent with previous results [33, 34].

2.5 Thermodynamic study

In this research, thermodynamic parameters are acquired through van't Hoff equation and are used to evaluate the interaction between analytes and stationary phases.

The dependencies of the natural logarithms of retention factor (k′) on the inverse of temperature (1/T) are used to determine thermodynamic parameters on each column [35].

$$\ln k' = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} - \ln \beta$$

Where ΔH is enthalpy change resulting from the interaction of analyte with the stationary phase. ΔH value describes the degree of the interaction strength. The large negative ΔH value indicates high strength of interaction between an analyte and a stationary phase.

ΔS is entropy change resulting from the interaction of the analyte with the stationary phase. ΔS value describes the degree of which the solute structure influences the interaction.

k' is a retention factor or capacity factor.

$$k' = \frac{t_R - t_M}{t_M}$$

t_R is the retention time of analyte.

t_M is the time for mobile phase or unretained compound to travel at the same distance as analyte.

R is the universal gas constant (1.987 cal/mol·K).

β is a constant called phase ratio (the ratio of mobile phase volume to stationary phase volume). It is related to the stationary phase film thickness (d_f) and the column diameter (d_c).

$$\beta = \frac{d_c}{4d_f}$$

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

All phenols and solvent were purchased from various vendors such as Hopkin & Williams, Acros, Fluka, Tokyo Chemical Industries (TCI) and J.T. Baker and were used without further purification. Some APs are not commercially available: 2,3,4-trimethylphenol; 2,4,5-trimethylphenol; and 3-propylphenol.

3.1.1 Phenol and alkylphenols

- phenol [108-95-2], 99%,
- 2-methylphenol [95-48-7], 99%,
- 3-methylphenol [108-39-4], 98%
- 4-methylphenol [106-44-5], 99%
- 2,3-dimethylphenol [526-75-0], 99%
- 2,4-dimethylphenol [105-67-9], 97%
- 2,5-dimethylphenol [95-87-4], 97%
- 2,6-dimethylphenol [527-26-1], 98%
- 3,4-dimethylphenol [95-65-8], 98%
- 3,5-dimethylphenol [108-68-9], 98%
- 2,3,5-trimethylphenol [697-82-5], 98%
- 2,3,6-trimethylphenol [2416-94-6], 95%
- 2,4,6-trimethylphenol [527-60-6], 99%
- 3,4,5-trimethylphenol [527-54-8], 95%
- 2-ethylphenol [90-00-6], 97%
- 3-ethylphenol [620-17-7], 95%
- 4-ethylphenol [123-07-9], 97%
- 2-propylphenol [644-35-9], 98%

- 4-propylphenol [645-56-7], 99%
- 2-isopropylphenol [88-69-7], 98%
- 3-isopropylphenol [618-45-1], 98%
- 4-isopropylphenol [99-89-8], 98%

3.1.2 Solvent

- dichloromethane, analytical reagent grade

3.2 Gas chromatographic analysis

All chromatographic analyses were performed on an Agilent 6890 series gas chromatograph, equipped with a split injector and a flame ionization detector (FID). The injector and detector temperatures were set at 250 ºC. A split ratio was adjusted to 100:1. Hydrogen was used as a carrier gas with an average linear velocity of 50 cm/s. The separation was carried out on the 15 m long × 0.25 mm i.d. capillary column coated with 0.25 μm thick film of stationary phases. Four types of stationary phases were used in this research:

- **OV-1701**: poly(14 %-cyanopropylphenyl-86 %-dimethyl siloxane)
- **ASiMe**: 26.8 % hexakis(2,3-di-*O*-methyl-6-*O*-*tert*-butyldimethylsilyl)cyclomaltohexaose mixed in OV-1701
- **BSiMe**: 30.0 % heptakis(2,3-di-*O*-methyl-6-*O*-*tert*-butyldimethylsilyl)cyclomaltoheptaose mixed in OV-1701
- **GSiMe**: 32.8 % octakis(2,3-di-*O*-methyl-6-*O*-*tert*-butyldimethylsilyl)cyclomaltooctaose mixed in OV-1701

All columns were conditioned at 220 ºC until a stable baseline was observed.

3.2.1 GC separation of the mixture of C_0–C_3 alkylphenols

Each analyte was dissolved in dichloromethane and was injected at least in duplicate at isothermal temperature in the range of 70–190 ºC with 10 ºC difference. Retention factors (k′) of all analytes at each temperature were calculated from the chromatograms. Relationships between ln k′ *vs.* 1/T of all analytes were used to determine the optimum condition for the separation of a mixture of phenol and 21 APs.

3.2.2 Thermodynamic studies

The enthalpy (ΔH) and entropy (ΔS) changes for all analytes were determined from the ln k′ *vs.* 1/T of van't Hoff equation.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 GC separation of mixtures of C_0–C_3 alkylphenols

Each analyte was injected at least in duplicate at isothermal temperature, in the range of 70–190 ºC with 10 ºC difference, on four types of GC capillary columns namely polysiloxane stationary phase (OV-1701 column) and three CD–based stationary phases (ASiMe, BSiMe and GSiMe columns). The retention factors (k′) of all analytes at each temperature were determined from the chromatograms. A plot of ln k′ *vs.* 1/T of all APs was constructed. The optimum condition for the separation of the mixture of 22 APs was adjusted to obtain the temperature that showed no or minimum interception of ln k′ *vs.* 1/T lines and gave shortest analysis time.

4.1.1 polysiloxane stationary phase

A plot of ln k′ *vs.* 1/T of C_0–C_3 APs obtained from OV-1701 column was constructed and shown in Figure 4.1. From the graph, the appropriate column temperature was determined. With some adjustments, the optimum condition could be obtained. The mixture of C_0–C_3 AP isomers could be separated within 22 minutes using the temperature program from 80–90 ºC at 4 ºC/min, held for 17 min; then to 220 ºC at 40 ºC/min (Figure 4.2). The elution order and retention times of all analytes are shown in Table 4.1. From the chromatogram, the separation of 2,4-DMP from 2,5-DMP was not achieved on this column. Incomplete separations (resolution < 1.5) were observed for 4-MP/3-MP; 2-EP/2,4-DMP/2,5-DMP; 2,3-DMP/2,3,6-TMP/3,5-DMP; 4-EP/3-EP and 4-IPP/3-IPP.

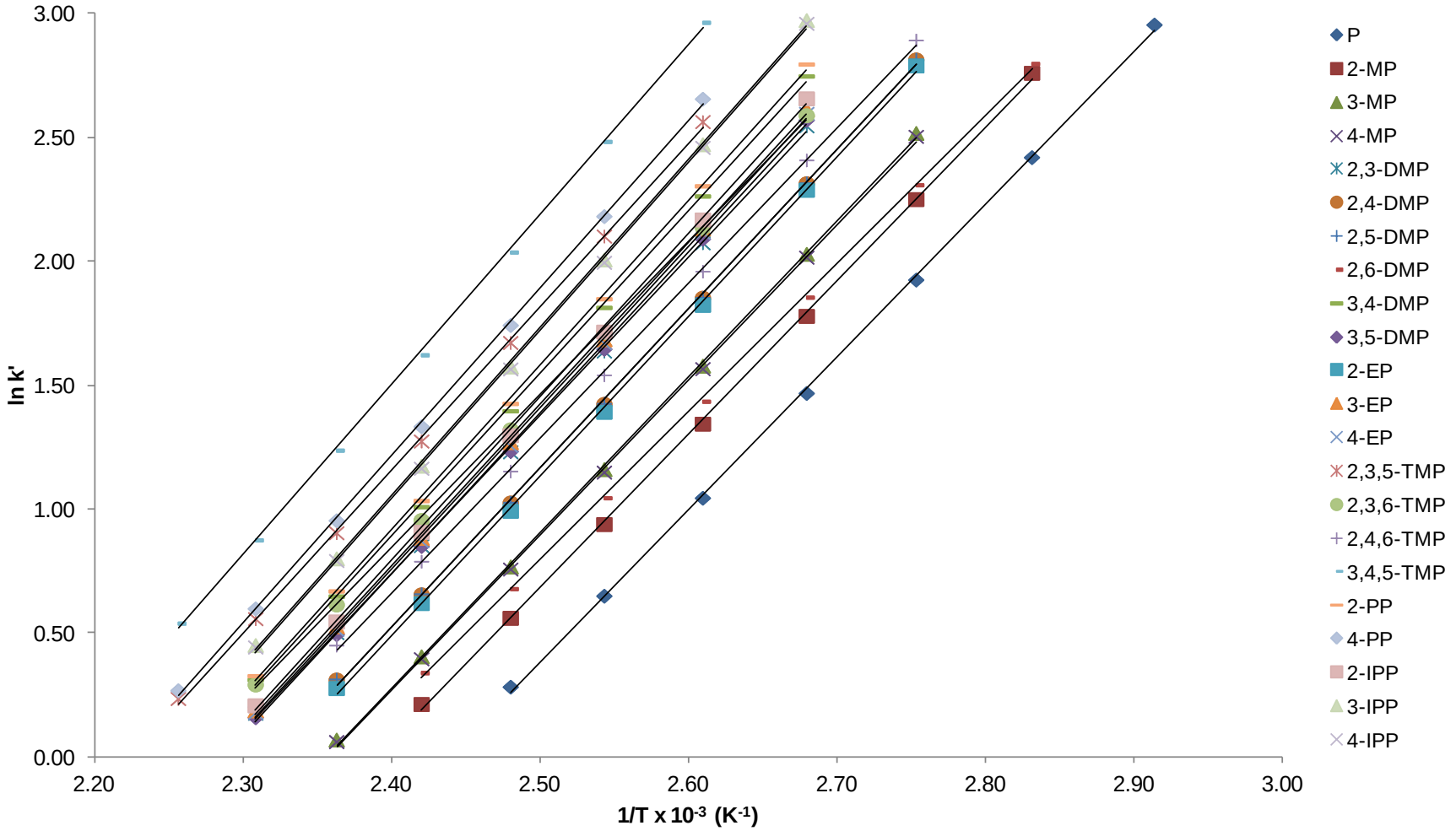


Figure 4.1 Relationship of ln k′ *vs.* 1/T of C_0–C_3 APs on OV-1701 column

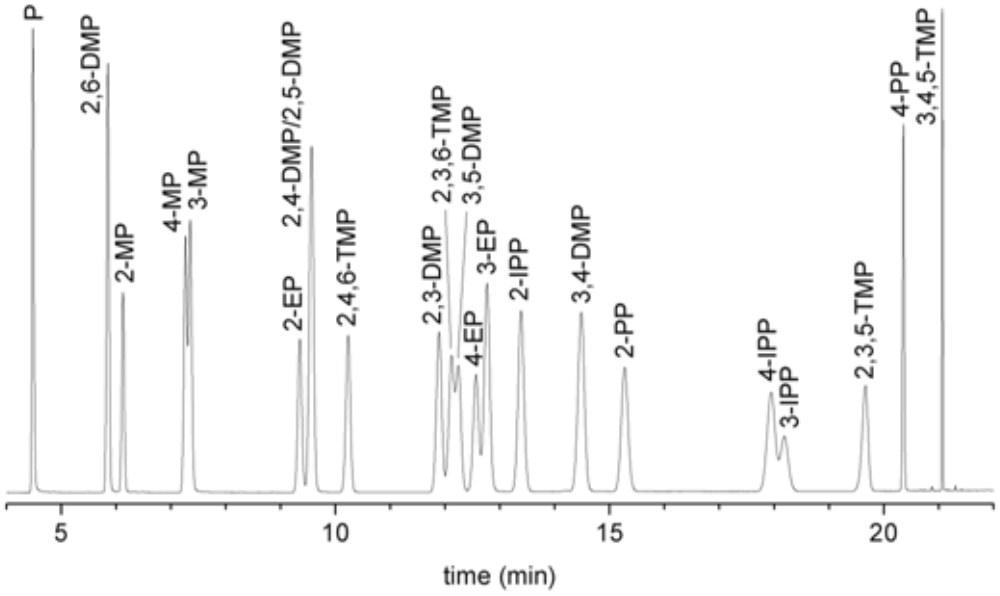


Figure 4.2 Separation of the mixture of C_0–C_3 APs on OV-1701 column (condition: 80–90 ºC at 4 ºC/min, held for 17 min; then to 220 ºC at 40 ºC/min)

Table 4.1 Retention times of C_0–C_3 APs on OV-1701 column

elution order	retention time (min)	compound
1	4.484	P
2	5.850	2,6-DMP
3	6.127	2-MP
4	7.267	4-MP
5	7.352	3-MP
6	9.352	2-EP
7	9.566	2,4-DMP/2,5-DMP
9	10.233	2,4,6-TMP
10	11.891	2,3-DMP
11	12.120	2,3,6-TMP
12	12.241	3,5-DMP
13	12.564	4-EP
14	12.766	3-EP
15	13.386	2-IPP
16	14.485	3,4-DMP
17	15.276	2-PP
18	17.946	4-IPP
19	18.186	3-IPP
20	19.668	2,3,5-TMP
21	20.359	4-PP
22	21.070	3,4,5-TMP

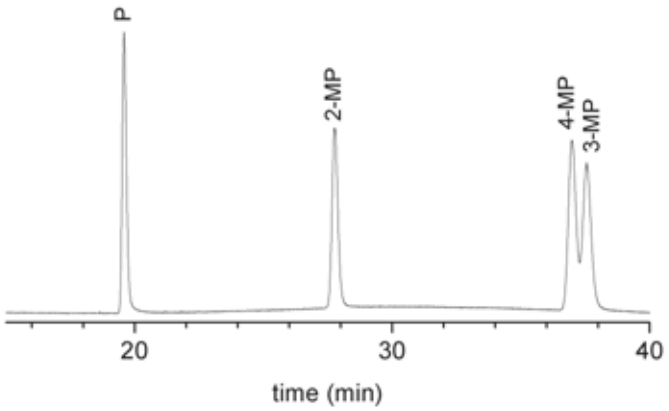
The optimum conditions for the separation of each group of AP isomers were also acquired from the ln k′ *vs.* 1/T plots with shortest analysis time.

The mixture of C_0–C_1 APs could be separated in 38 minutes using the column temperature from 50–60 ºC at 2 ºC/min and held for 40 min with the elution order of P > 2-MP > 4-MP > 3-MP (Figure 4.3 a).

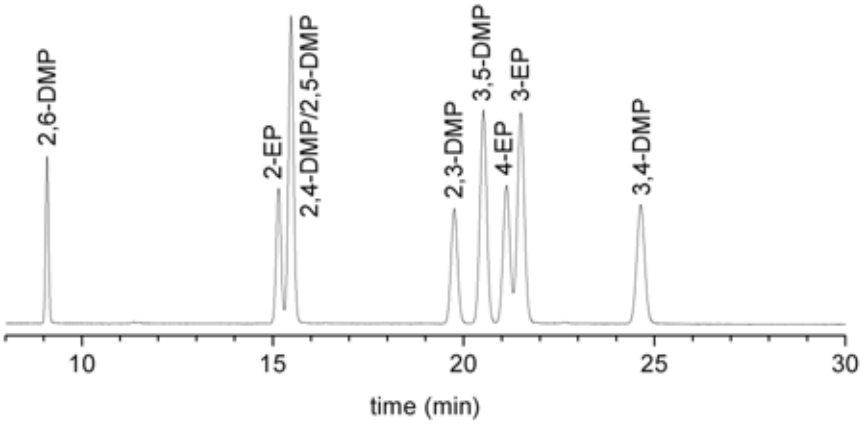
The optimum column temperature for separation of C_2 APs was at 80 ºC in 25 minutes with the elution order of 2,6-DMP > 2-EP > 2,4-DMP/2,5-DMP > 2,3-DMP > 3,5-DMP > 4-EP > 3-EP > 3,4-DMP (Figure 4.3 b). Under the optimum condition, the separation of 2,4-DMP from 2,5-DMP was not achieved and incomplete separations were observed for 2-EP/2,4-DMP/2,5-DMP and 4-EP/3-EP. Further adjustment of column temperature led to poorer separation or longer analysis time.

Finally, the separation of C_3 APs could be achieved using the column temperature at 80 ºC, held for 32 min; then to 140 ºC at 20 ºC/min. The total analysis time for C_3 APs was 35 minutes with the elution order of 2,4,6-TMP > 2,3,6-TMP > 2-IPP > 2-PP > 4-IPP > 3-IPP > 2,3,5-TMP > 4-PP > 3,4,5-TMP (Figure 4.3 c).

(a)



(b)



(c)

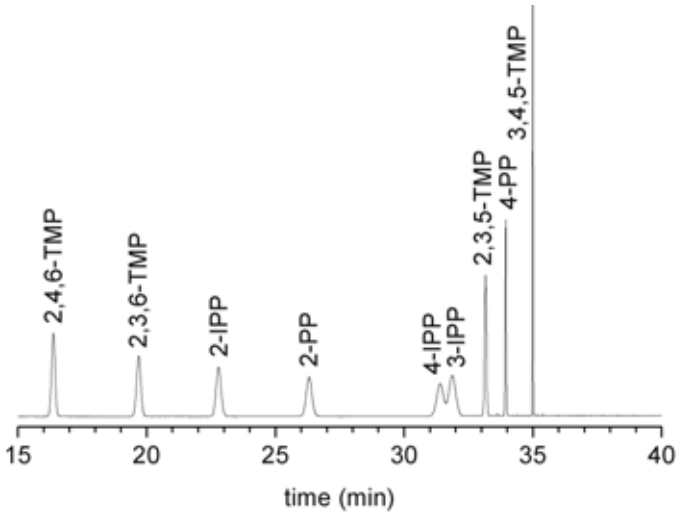


Figure 4.3 Separation of (a) the mixture of four C_0–C_1 AP isomers (condition: from 50–60 ºC at 2 ºC/min, held for 40 min); (b) the mixture of nine C_2 AP isomers (condition: 80 ºC); and (c) the mixture of nine C_3 AP isomers (condition: from 80 ºC, held for 32 min; then to 140 ºC at 20 ºC/min) on OV-1701 column

4.1.2 Cyclodextrin-based stationary phases

In this research, derivatized α-, β- and γ-cyclodextrins separately mixed with polysiloxane OV-1701 were used as stationary phases to improve the separation of the AP mixture. A variety of interaction between the derivatized CDs and the analytes leads to good separation of isomers. Additionally, the separation of all phenols obtained from polysiloxane (OV-1701 column) in this study were compared to CD–based stationary phases (ASiMe, BSiMe and GSiMe columns).

Firstly, a plot of ln k′ *vs.* 1/T of all analytes on ASiMe column is shown in Figure 4.4. The best separation condition could be achieved at 90 ºC for 17 min; then to 120 ºC at 20 ºC/min, held for 3 min; then to 200 ºC at 20 ºC/min. The total analysis time was 24 minutes. Under the optimum condition, the 3-MP/2-EP and 4-IPP/3,4-DMP were co-eluted and incomplete separations were observed for 2,4,6-TMP and 3-EP (Figure 4.5). The elution order and retention times of all analytes on ASiMe column were shown in Table 4.2.

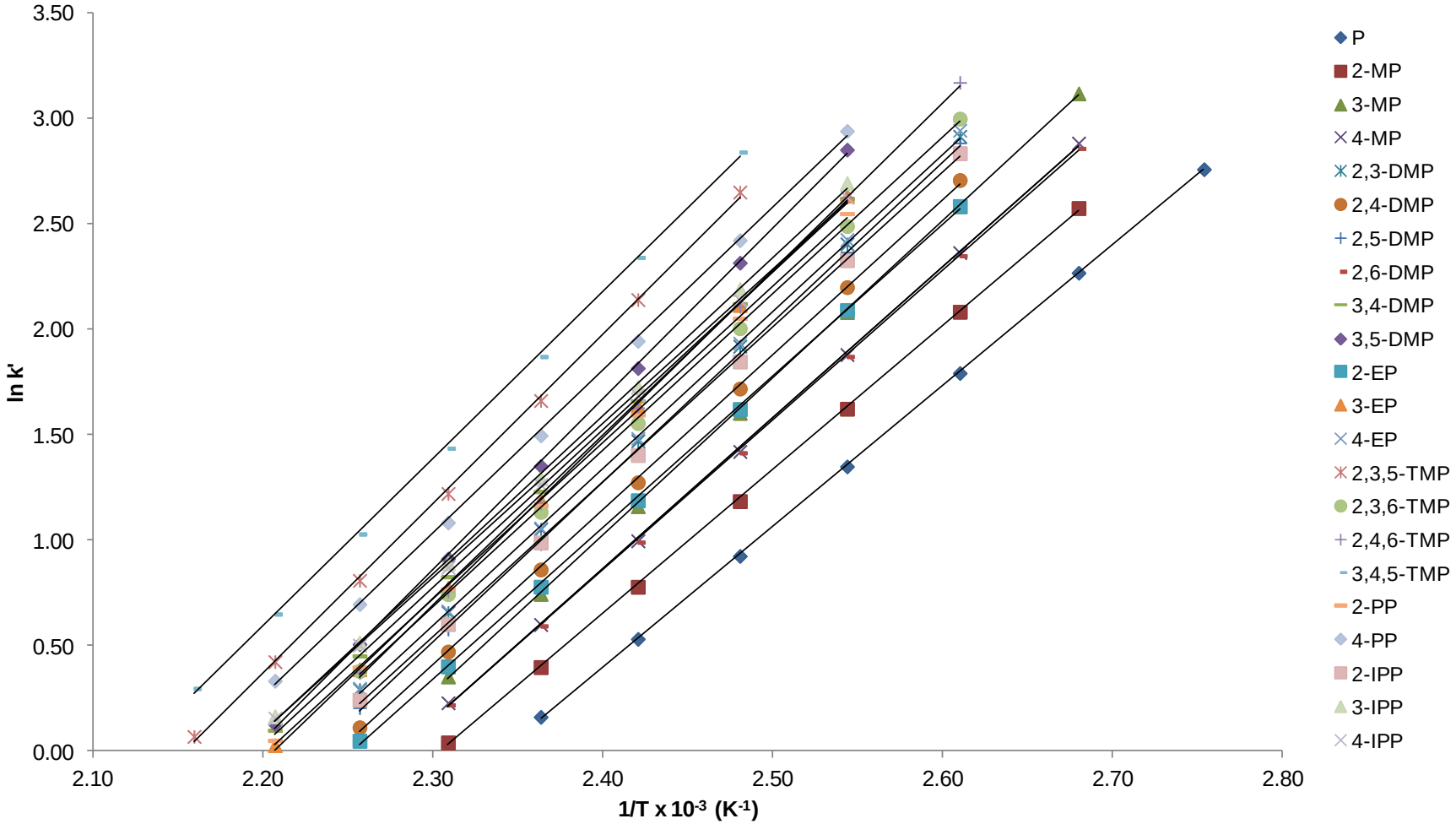


Figure 4.4 Relationship of ln k′ *vs.* 1/T of C_0–C_3 APs on ASiMe column

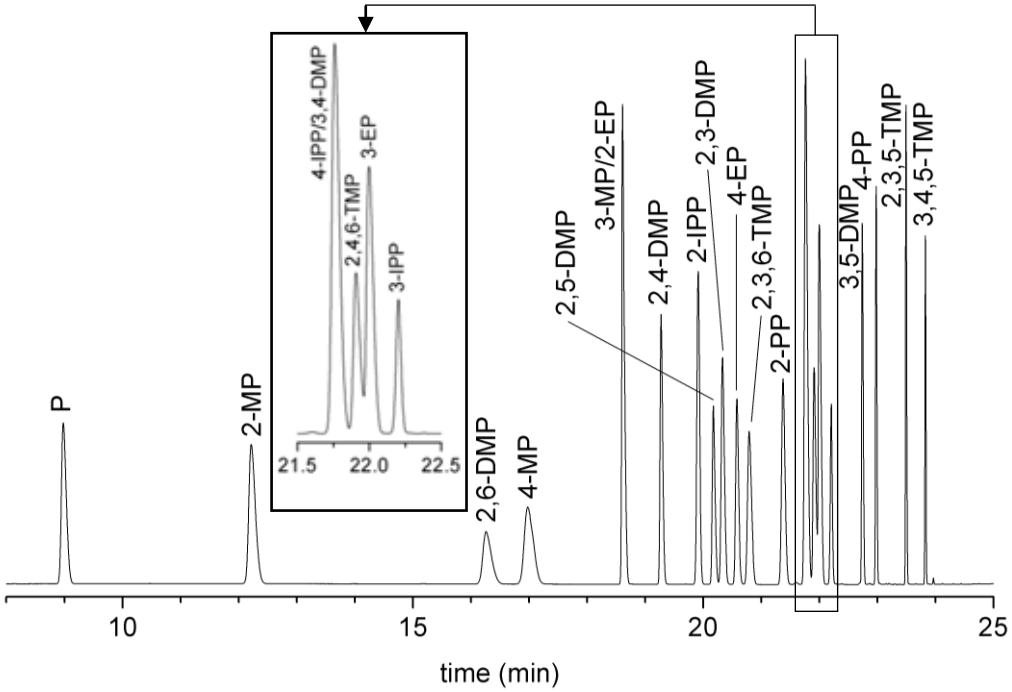


Figure 4.5 Separation of the mixture of C_0–C_3 APs on ASiMe column (condition: 90 ºC, held for 17 min; then to 120 ºC at 20 ºC/min, held for 3 min; then to 200 ºC)

Table 4.2 Retention times of C_0–C_3 APs on ASiMe column

elution order	retention time (min)	compound
1	8.980	P
2	12.215	2-MP
3	16.260	2,6-DMP
4	16.976	4-MP
5	18.611	3-MP/2-EP
7	19.273	2,4-DMP
8	19.911	2-IPP
9	20.173	2,5-DMP
10	20.330	2,3-DMP
11	20.578	4-EP
12	20.788	2,3,6-TMP
13	21.373	2-PP
14	21.759	4-IPP/3,4-DMP
16	21.907	2,4,6-TMP
17	21.998	3-EP
18	22.202	3-IPP
19	22.737	3,5-DMP
20	22.976	4-PP
21	23.489	2,3,5-TMP
22	23.825	3,4,5-TMP

On BSiMe column, a plot of ln k′ *vs.* 1/T of C_0–C_3 APs is shown in Figure 4.6. Chromatographic separation was achieved with a temperature program at 120 ºC for 11 min and then programmed from 120–180 ºC at 25 ºC/min. The separation was completed in 13 minutes. All analytes could be separated on this column. The results showed the incomplete separation of 3-MP/2,4-DMP; 2,3,6-TMP/2,3-DMP; 2-IPP/3-EP/4-IPP and 4-PP/2,3,5-TMP (Figure 4.7). The elution order and retention time of phenol and 21 APs on BSiMe column were shown in Table 4.3.

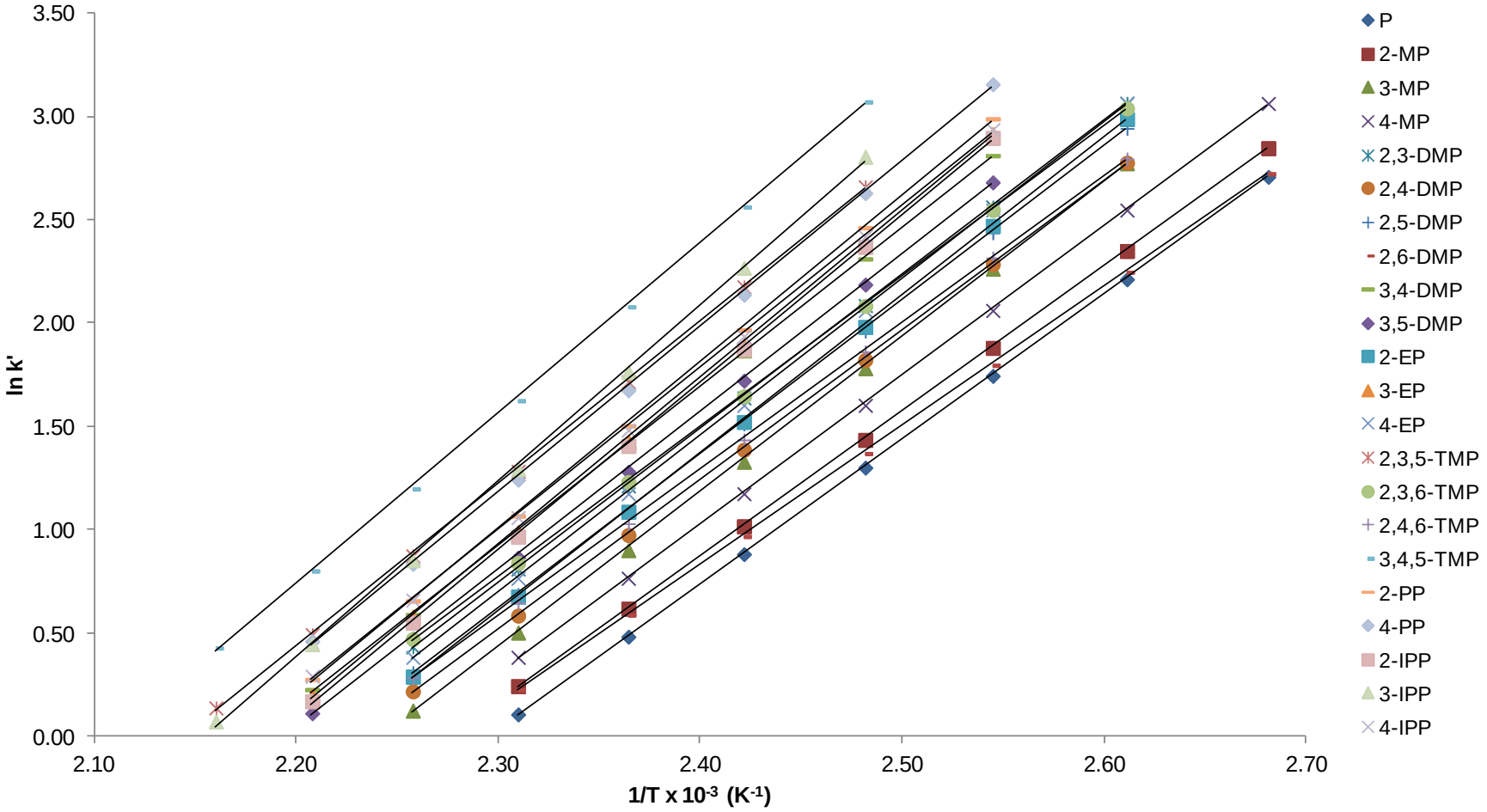


Figure 4.6 Relationship of ln k′ *vs.* 1/T of C_0–C_3 APs on BSiMe column

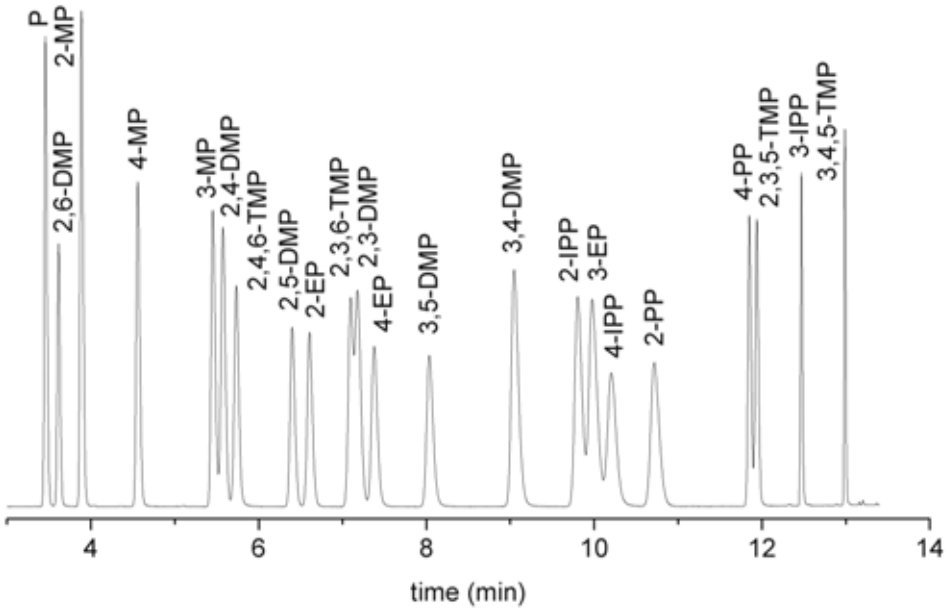


Figure 4.7 Separation of the mixture of C_0–C_3 APs on BSiMe column (condition: 120 ºC, held for 11 min; then to 180 ºC at 25 ºC/min)

Table 4.3 Retention times of C_0–C_3 APs on BSiMe column

elution order	retention time (min)	compound
1	3.457	P
2	3.615	2,6-DMP
3	3.886	2-MP
4	4.558	4-MP
5	5.452	3-MP
6	5.573	2,4-DMP
7	5.733	2,4,6-TMP
8	6.399	2,5-DMP
9	6.606	2-EP
10	7.097	2,3,6-TMP
11	7.178	2,3-DMP
12	7.376	4-EP
13	8.034	3,5-DMP
14	9.045	3,4-DMP
15	9.803	2-IPP
16	9.975	3-EP
17	10.203	4-IPP
18	10.717	2-PP
19	11.849	4-PP
20	11.937	2,3,5-TMP
21	12.469	3-IPP
22	12.988	3,4,5-TMP

The relationships between ln k′ *vs.* 1/T of all phenols on GSiMe column is shown in Figure 4.8. The optimum column temperature for the separation was at 90 ºC for 22 min and then programmed from 90–170 ºC at 10 ºC/min. The mixture could be separated in 29 minutes. The separation of 3,5-DMP/4-EP and 3-EP/2-IPP were co-eluted and incomplete separation between 2-EP and 2,3,6-TMP were observed (Figure 4.9). The elution order and retention times of all phenols on GSiMe column were shown in Table 4.4.

Among four columns tested, BSiMe gave the best single-run separation for the mixture of twenty-two C_0–C_3 APs with shortest analysis time of 13 minutes. Other derivatized CD stationary phases, ASiMe and GSiMe, as well as polysiloxane OV-1701 did not give sufficiently separations as co-elution of some isomers were still observed.

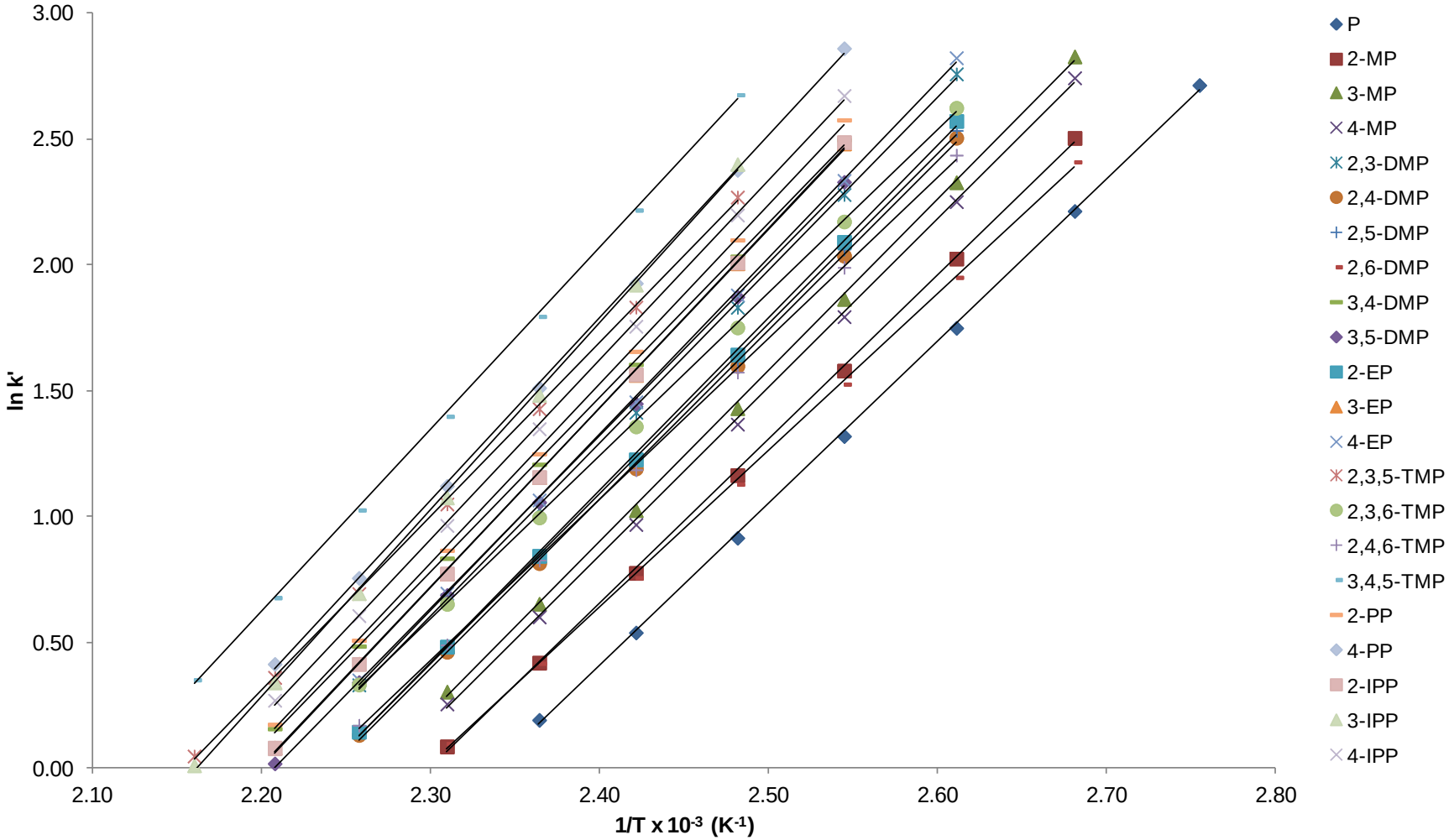


Figure 4.8 Relationship of ln k′ *vs.* 1/T of C_0–C_3 APs on GSiMe column

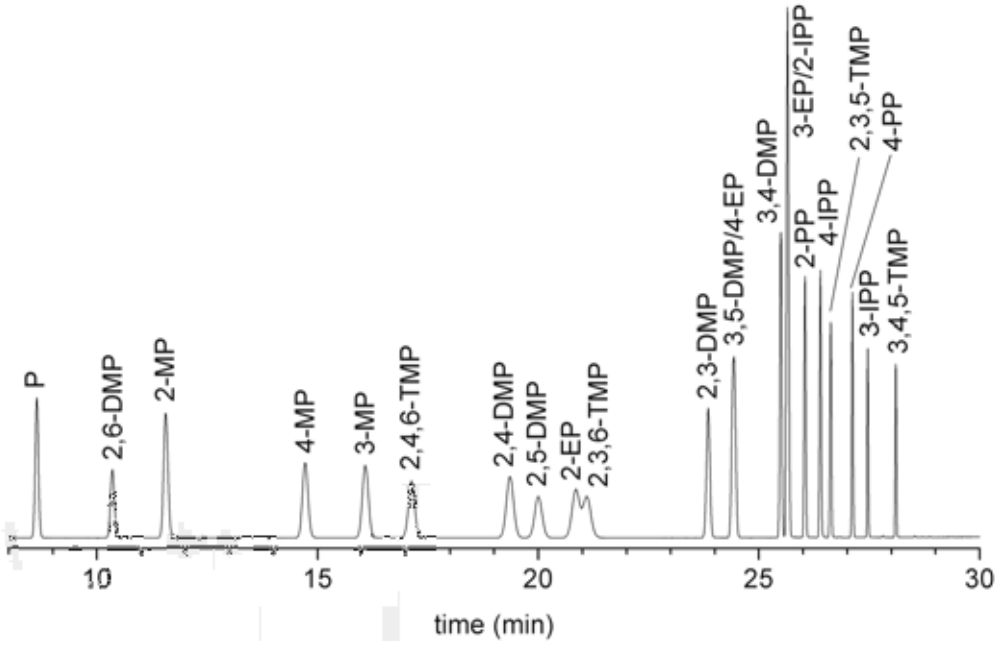


Figure 4.9 Separation of the mixture of C_0–C_3 APs on GSiMe column (condition: from 90 ºC, held for 22 min; then to 170 ºC at 10 ºC/min)

Table 4.4 Retention times of C_0–C_3 APs on GSiMe column

elution order	retention time (min)	compound
1	8.634	P
2	10.349	2,6-DMP
3	11.554	2-MP
4	14.717	4-MP
5	16.075	3-MP
6	17.126	2,4,6-TMP
7	19.358	2,4-DMP
8	20.000	2,5-DMP
9	20.849	2-EP
10	21.089	2,3,6-TMP
11	23.848	2,3-DMP
12	24.431	3,5-DMP/4-EP
14	25.493	3,4-DMP
15	25.645	3-EP/2-IPP
17	26.042	2-PP
18	26.389	4-IPP
19	26.625	2,3,5-TMP
20	27.114	4-PP
21	27.463	3-IPP
22	28.099	3,4,5-TMP

The elution order and total analysis time of the separation of all analytes on four columns are compared and shown in Table 4.5.

Table 4.5 The elution order and total analysis times of C_0–C_3 APs on OV-1701, ASiMe, BSiMe and GSiMe columns

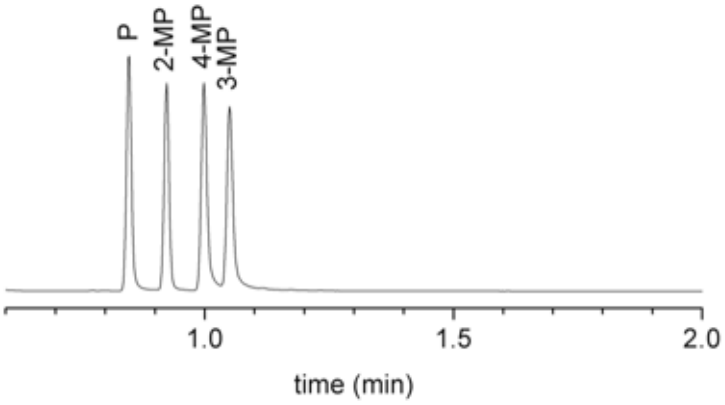
elution order	OV-1701	ASiMe	BSiMe	GSiMe
1	P	P	P	P
2	2,6-DMP	2-MP	2,6-DMP	2,6-DMP
3	2-MP	2,6-DMP	2-MP	2-MP
4	4-MP	4-MP	4-MP	4-MP
5	3-MP	3-MP/2-EP	3-MP	3-MP
6	2-EP	-	2,4-DMP	2,4,6-TMP
7	2,4-/2,5-DMP	2,4-DMP	2,4,6-TMP	2,4-DMP
8	-	2-IPP	2,5-DMP	2,5-DMP
9	2,4,6-TMP	2,5-DMP	2-EP	2-EP
10	2,3-DMP	2,3-DMP	2,3,6-TMP	2,3,6-TMP
11	2,3,6-TMP	4-EP	2,3-DMP	2,3-DMP
12	3,5-DMP	2,3,6-TMP	4-EP	3,5-DMP/4-EP
13	4-EP	2-PP	3,5-DMP	-
14	3-EP	4-IPP/3,4-DMP	3,4-DMP	3,4-DMP
15	2-IPP	-	2-IPP	3-EP/2-IPP
16	3,4-DMP	2,4,6-TMP	3-EP	-
17	2-PP	3-EP	4-IPP	2-PP
18	4-IPP	3-IPP	2-PP	4-IPP
19	3-IPP	3,5-DMP	4-PP	2,3,5-TMP
20	2,3,5-TMP	4-PP	2,3,5-TMP	4-PP
21	4-PP	2,3,5-TMP	3-IPP	3-IPP
22	3,4,5-TMP	3,4,5-TMP	3,4,5-TMP	3,4,5-TMP
total analysis time (min)	21.070	23.825	12.988	28.099

As seen from Table 4.5, the elution orders of C_0–C_3 APs on four columns were quite different. The relationship between elution order and analyte properties (e.g. boiling point, molecular weight, type and number of substituents or analyte volumn) on four columns could not be concluded.

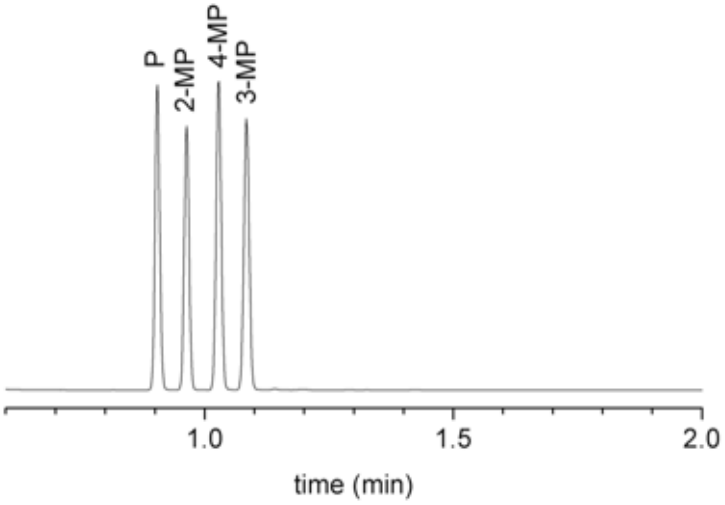
The separations of each group of isomers on three derivatized CD columns were investigated as well.

The mixture of C_0–C_1 APs could be excellently separated on derivatized CD columns in less than 2 minutes, about 19 times faster than the separation on OV-1701 column. The optimum column temperature was 170 ºC for ASiMe and BSiMe columns and was 150 ºC for GSiMe column. The elution order of C_0–C_1 APs on three columns are similar in the order of P > 2-MP > 4-MP > 3-MP (Figure 4.10). Interestingly, the elution order for each group of mono-substituted APs isomers on four columns were similar depending on the position of methyl substitution of *ortho*-, *para*- and *meta*-, respectively.

(a)



(b)



(c)

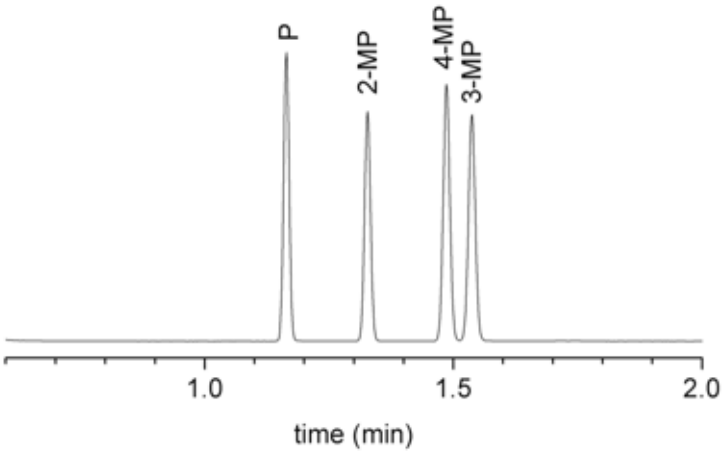


Figure 4.10 Separation of C_0–C_1 APs on derivatized CD columns: (a) ASiMe (170 ºC); (b) BSiMe (170 ºC); (c) GSiMe (150 ºC)

The optimum column temperature for separation of six isomers of C_2 APs on ASiMe column was at 110 ºC. The total analysis time on this column was 17 minutes with the elution order of 2,6-DMP > 2-EP > 2,4-DMP > 2,5-DMP > 2,3-DMP > 4-EP > 3,4-DMP > 3-EP > 3,5-DMP (Figure 4.11 a). On BSiMe column, the mixture could be completely resolved in 10 minutes using isothermal temperature at 120 ºC with the elution order of 2,6-DMP > 2,4-DMP > 2,5-DMP > 2-EP > 2,3-DMP > 4-EP > 3,5-DMP > 3,4-DMP > 3-EP (Figure 4.11 b). The mixture could be separated using isothermal temperature at 100 ºC on GSiMe column. The analysis time was completed in 20 minutes with the elution order of 2,6-DMP > 2,4-DMP > 2,5-DMP > 2-EP > 2,3-DMP > 3,5-DMP/4-EP > 3,4-DMP > 3-EP (Figure 4.11 c). The 3,5-DMP and 4-EP were the only analytes that co-eluted on GSiMe column. The elution order on BSiMe and GSiMe columns were similar. Besides, the separations of C_2 APs on CD columns were better and faster than on OV-1701 column.

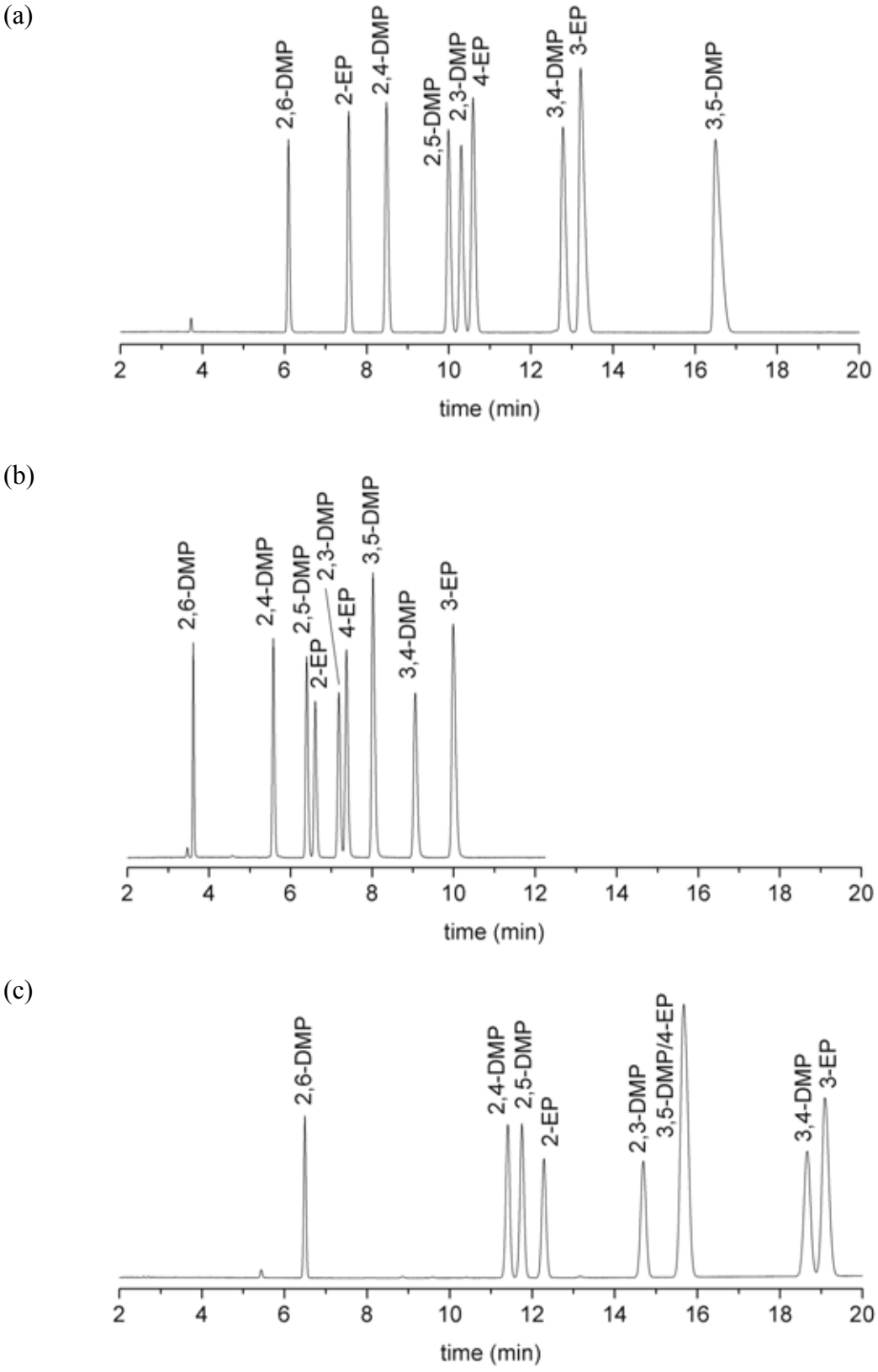


Figure 4.11 Separation of C_2 APs on derivatized CD columns: (a) ASiMe (110 ºC); (b) BSiMe (120 ºC); (c) GSiMe (100 ºC)

Finally, the separation of nine isomers of C_3 APs could be completely separated on three columns with the difference in the elution order. The total analysis time on ASiMe column was only 5 minutes, about 1.5 times and 3 times faster than the separation on BSiMe (8 minutes) and GSiMe column (14 minutes), respectively. On ASiMe column, the optimum column temperature was at 140 ºC for 4 min and then programmed from 140–180 ºC at 40 ºC/min. The separation gave the elution order of 2-IPP > 2,3,6-TMP > 2-PP > 2,4,6-TMP > 4-IPP > 3-IPP > 4-PP > 2,3,5-TMP > 3,4,5-TMP (Figure 4.12 a). The separation on BSiMe column, with isothermal temperature at 140 ºC, gave the elution order of 2,4,6-TMP > 2,3,6-TMP > 2-IPP > 4-IPP > 2-PP > 4-PP > 2,3,5-TMP > 3-IPP > 3,4,5-TMP (Figure 4.12 b). Finally, the separation on GSiMe column, with isothermal temperature at 120 ºC, gave the elution order of 2,4,6-TMP > 2,3,6-TMP > 2-IPP > 2-PP > 4-IPP > 2,3,5-TMP > 4-PP > 3-IPP > 3,4,5-TMP (Figure 4.12 c).

The separations of each group of isomers on columns that contain cyclodextrin derivatives as stationary phase gave better resolution and shorter analysis time than on polysiloxane column. Additionally, direct analysis of APs without derivatization gave acceptable peak shapes on all columns.

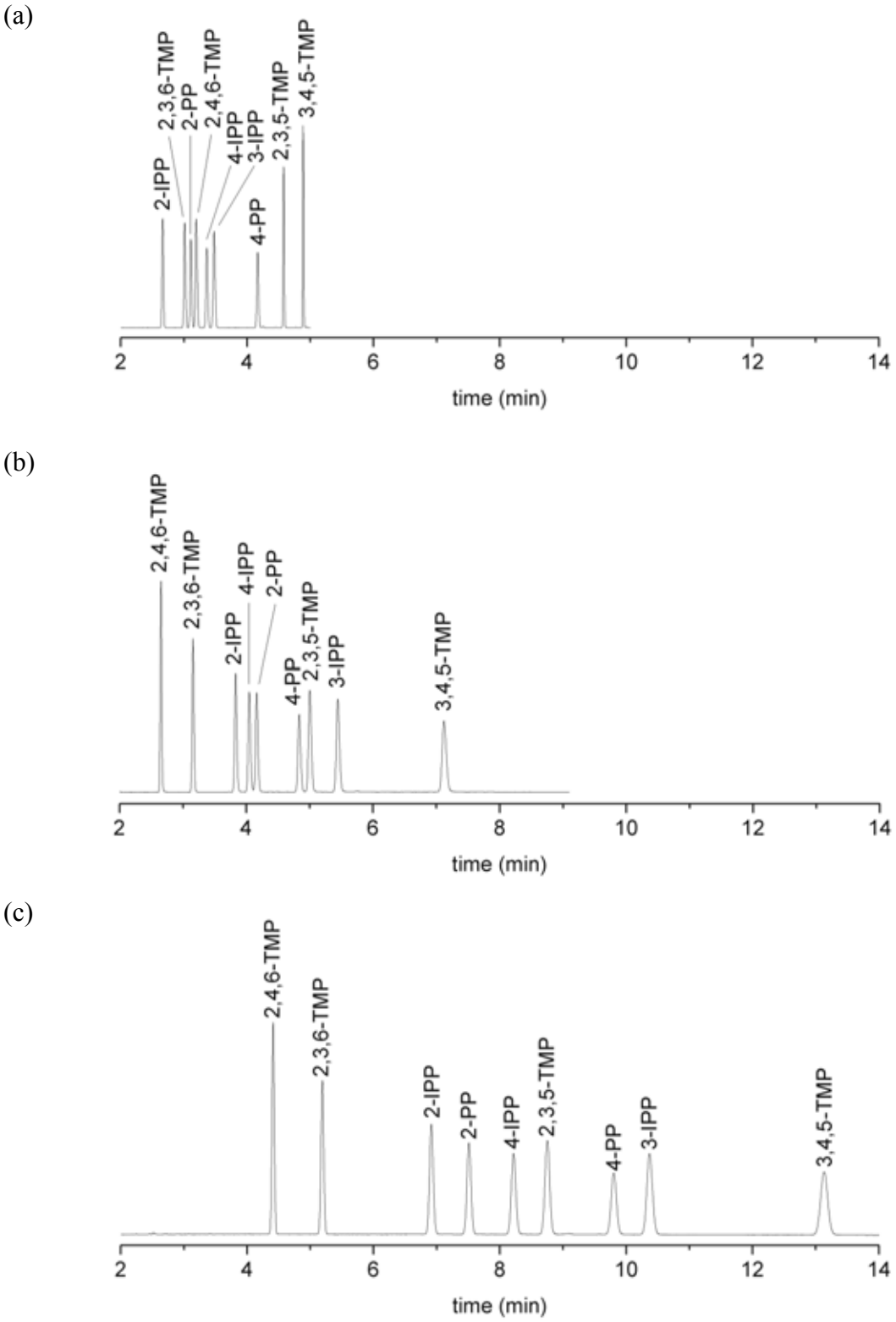


Figure 4.12 Separation of C_3 APs on derivatized CD columns: (a) ASiMe (140 ºC for 4 min; then to 180 ºC at 40 ºC/min); (b) BSiMe (140 ºC); (c) GSiMe (120 ºC)

4.2 Thermodynamic studies

Thermodynamic parameters described the interaction between phenols and stationary phases could be achieved through the van't Hoff plot of ln k´ *vs.* 1/T. All ln k´ *vs.* 1/T plots of all analytes showed linear relationship with correlation coefficient value (R^2) greater than 0.9995. From these plots, the enthalpy (ΔH) and entropy (ΔS) change values for each analyte could be calculated from slope and y-intercept, respectively.

The enthalpy change (ΔH) value describes the degree of the interaction strength. The large negative ΔH value indicates strong interaction between an analyte and a stationary phase. While the entropy change (ΔS) value describes the degree of which the solute structure influences the interaction. The large negative ΔS value indicates high loss of degree of freedom.

4.2.1 Polysiloxane

The −ΔH and −ΔS values of C_0–C_3 APs on OV-1701 column are shown in Figure 4.13. In general, all APs showed similar −ΔH and −ΔS values, indicating that the major interaction came from aromatic ring and hydroxyl group of analytes. However, some trends were observed. For the methyl-substituted phenols (MPs, DMPs and TMPs), the −ΔH values slightly increase in the order of MPs < DMPs < TMPs with the increasing number of methyl substitution. While the −ΔS values insignificantly increase in the order of TMPs < DMPs < MPs with the decreasing number of methyl substitution. The −ΔH and −ΔS values of isomers of most mono-substituted APs (MPs, EPs, PPs and IPPs) on OV-1701 column slightly increase in the order of *ortho-* < *para-* < *meta-*, except for the −ΔS values of MPs and EPs (*para-* < *meta-* < *ortho-*). For all C_0–C_3 APs, the interaction increase in the order of $C_0 < C_1 < C_2 < C_3$ following the size and molecular weight of substituent.

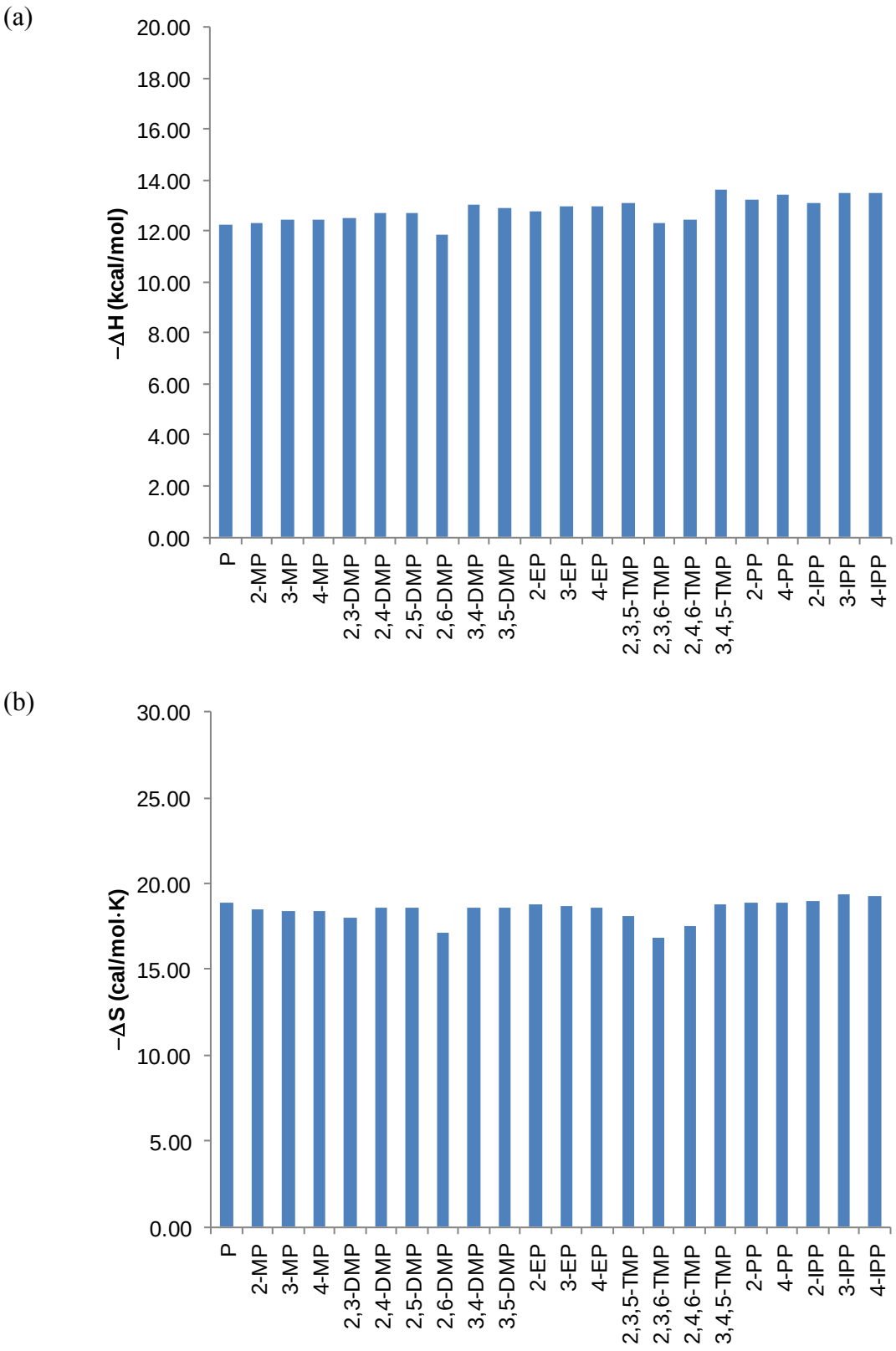


Figure 4.13 (a) Enthalpy and (b) entropy changes of C_0–C_3 APs on OV-1701 column

4.2.2 Cyclodextrin–based stationary phases

The −ΔH and −ΔS values of C_0–C_3 APs on derivatized CD columns are shown in Figure 4.14 and Figure 4.15, respectively. From these graphs, the −ΔH and −ΔS values on each column showed similar trend. The −ΔH and −ΔS values of most methyl-substituted phenols increase in the order of MPs < DMPs < TMPs with the increasing number of methyl substitution, except for the −ΔS values on GSiMe column (TMPs < DMPs < MPs). For the same type of mono-substituted, isomer with *meta*-substitution showed slightly higher −ΔH and −ΔS values. For all analytes, larger substituents showed higher −ΔH values in the order of $C_0 < C_1 < C_2 < C_3$ following the size and molecular weight of substituent. Similar trend was observed for the −ΔS values. These results are consistent with OV-1701 column.

The −ΔH and −ΔS values of all analytes obtained from derivatized CDs were compared to those obtained from polysiloxane stationary phase. It was found that the average −ΔH and −ΔS values increase in the order of OV-1701 < GSiMe < ASiMe < BSiMe. This indicates that analytes interact on column that contains cyclodextrin derivatives more strongly than on polysiloxane column.

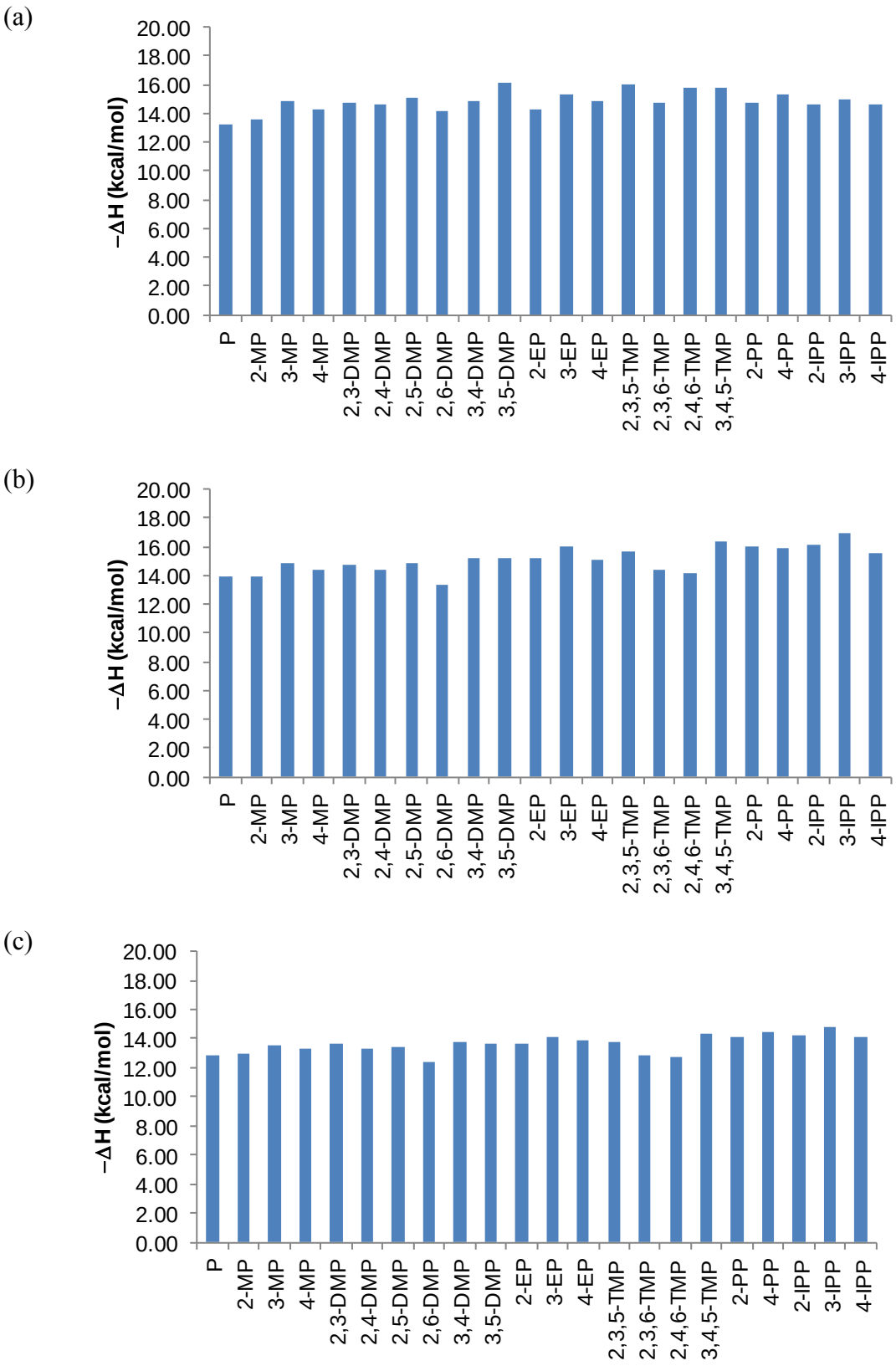


Figure 4.14 Enthalpy changes of C_0–C_3 APs on (a) ASiMe; (b) BSiMe; (c) GSiMe columns

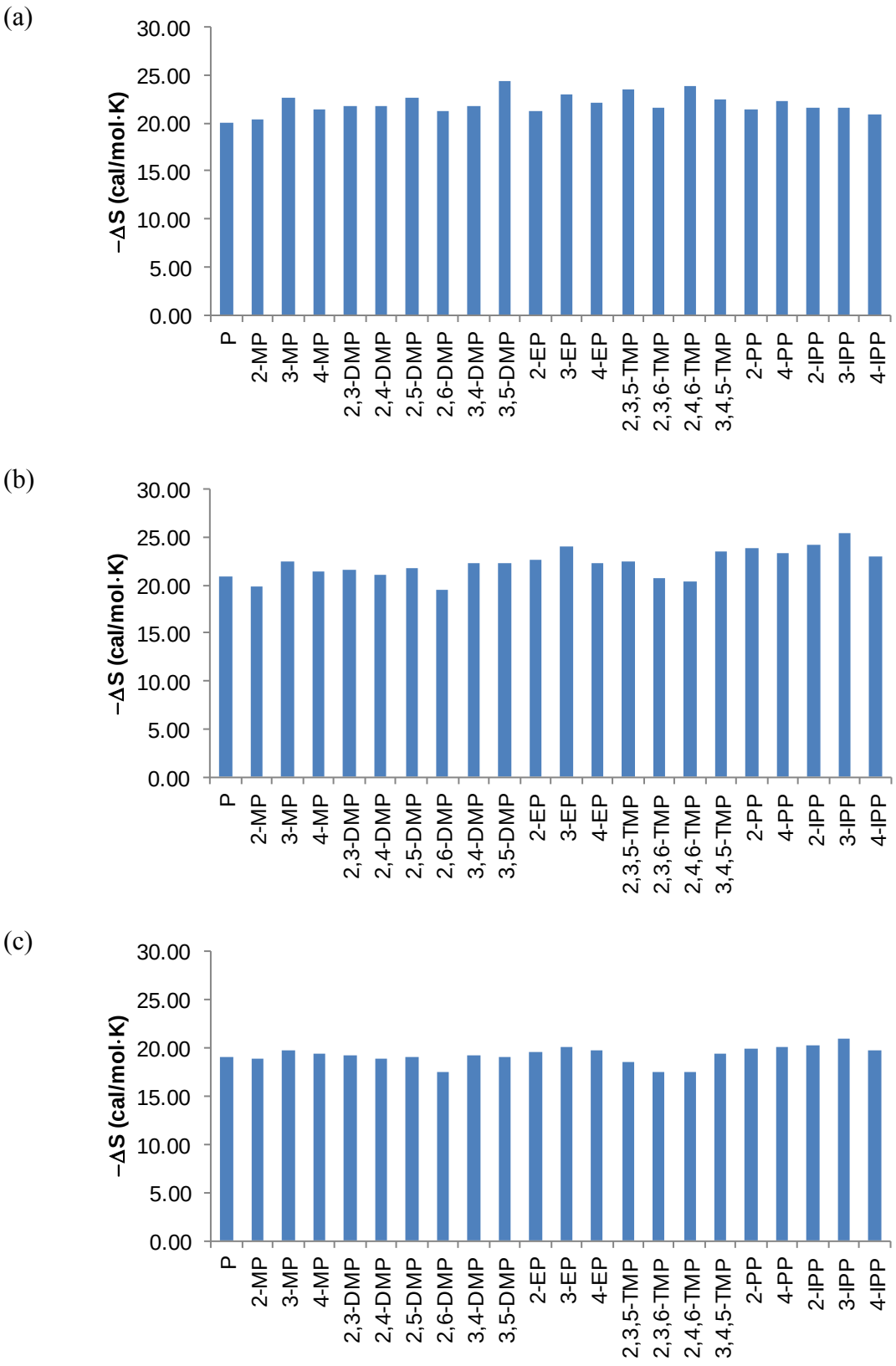


Figure 4.15 Entropy changes of C_0–C_3 APs on (a) ASiMe; (b) BSiMe; (c) GSiMe columns

CHAPTER V

CONCLUSIONS

The mixture of C_0–C_3 AP isomers was separated by GC using polysiloxane (OV-1701) and derivatized CDs as stationary phases. Three types of derivatized CDs used in this study were hexakis(2,3-di-*O*-methyl-6-*O*-*tert*-butyldimethylsilyl)-α-cyclodextrin (ASiMe), heptakis(2,3-di-*O*-methyl-6-*O*-*tert*-butyldimethylsilyl)-β-cyclodextrin (BSiMe) and octakis(2,3-di-*O*-methyl-6-*O*-*tert*-butyldimethylsilyl)-γ-cyclodextrin (GSiMe). All phenols were individually analyzed isothermally in the temperature range of 70–190 ºC with 10 ºC difference. From the chromatograms obtained from each run, the retention factors (k´) of all analytes at each temperature were determined to construct a plot of ln k´ *vs.* 1/T. These graphs were used to determine the optimum condition for the separation of a mixture of C_0–C_3 APs.

The separation of a mixture of C_0–C_3 APs on OV-1701 column could be achieved in 22 minutes. Under the optimum condition, co-elution and incomplete separations were observed. Therefore, CD columns were used to improve the resolution of the mixture.

Upon analyses of twenty-two C_0–C_3 APs on CD columns, the best single-run separation was achieved on BSiMe column in 13 minutes with a temperature program from 120 ºC for 11 min and then programmed from 120–180 ºC at 25 ºC/min. However, ASiMe and GSiMe did not give satisfactory results.

Each group of AP isomers was not resolved on OV-1701 column but they were well separated on CD columns. The separation of analytes on CD columns showed better resolution and shorter analysis time than OV-1701 column. The chromatograms obtained from all columns showed acceptable peak shapes, although APs were directly analyzed without derivatization.

Thermodynamic parameters described the interaction between analytes and stationary phases could be achieved through the van't Hoff plot of ln k´ vs. 1/T. The results indicated that, the interactions of analytes on CD columns were stronger than on polysiloxane column. Moreover, BSiMe columns showed strongest interaction among CD columns in the order of GSiMe < ASiMe < BSiMe, respectively.

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APPENDIX

APPENDIX

Thermodynamic study

Table 1 Equations, correlation coefficient and thermodynamic parameters of C_0–C_3 APs obtained from van't Hoff plots of ln k′ *vs.* 1/T plots on OV-1701 column

compound	temperature range (°C)	ln k′ = m(1/T) + c		R^2	−ΔH (kcal/mol)	−ΔS (cal/mol·K)
		m	c			
P	70–130	6160.7	-15.021	0.9996	12.24	18.88
2-MP	80–140	6196.8	-14.809	0.9996	12.31	18.45
3-MP	90–150	6273.6	-14.779	0.9996	12.47	18.39
4-MP	90–150	6259.8	-14.755	0.9996	12.44	18.35
2,3-DMP	100–160	6309.3	-14.600	0.9996	12.54	18.04
2,4-DMP	90–150	6411.5	-14.863	0.9996	12.74	18.56
2,5-DMP	90–150	6409.2	-14.855	0.9996	12.74	18.55
2,6-DMP	80–140	5978.0	-14.149	0.9997	11.88	17.14
3,4-DMP	100–160	6563.1	-14.862	0.9996	13.04	18.56
3,5-DMP	100–160	6493.4	-14.852	0.9996	12.90	18.54
2-EP	90–150	6439.4	-14.965	0.9996	12.80	18.76
3-EP	100–160	6533.1	-14.915	0.9996	12.98	18.66
4-EP	100–160	6514.2	-14.882	0.9996	12.94	18.60
2,3,5-TMP	110–170	6588.6	-14.653	0.9996	13.09	18.14
2,3,6-TMP	100–160	6187.5	-14.009	0.9997	12.29	16.86
2,4,6-TMP	90–150	6255.3	-14.351	0.9997	12.43	17.54
3,4,5-TMP	110–170	6862.0	-14.966	0.9996	13.63	18.77
2-PP	100–160	6648.6	-15.044	0.9996	13.21	18.92
4-PP	110–170	6756.5	-15.000	0.9996	13.43	18.83
2-IPP	100–160	6597.7	-15.047	0.9996	13.11	18.93
3-IPP	100–160	6793.8	-15.255	0.9996	13.50	19.34
4-IPP	100–160	6779.8	-15.231	0.9996	13.47	19.29
				$\bar{x}$	12.83	18.46
				S.D.	0.47	0.61

Table 2 Equations, correlation coefficient and thermodynamic parameters of C_0–C_3 APs obtained from van't Hoff plots of ln k′ *vs.* 1/T plots on ASiMe column

compound	temperature range (°C)	ln k′ = m(1/T) + c		R^2	−ΔH (kcal/mol)	−ΔS (cal/mol·K)
		m	c			
P	90–150	6459.1	-15.098	0.9997	13.25	20.04
2-MP	100–160	6514.9	-14.982	0.9996	13.58	20.33
3-MP	100–160	6799.1	-15.420	0.9996	14.82	22.56
4-MP	100–160	6700.5	-15.240	0.9997	14.22	21.44
2,3-DMP	110–170	6865.4	-15.187	0.9996	14.77	21.82
2,4-DMP	110–170	6709.6	-15.034	0.9996	14.61	21.82
2,5-DMP	110–170	6741.5	-15.088	0.9996	15.09	22.70
2,6-DMP	100–160	6227.5	-14.305	0.9996	14.14	21.27
3,4-DMP	120–180	6937.4	-15.175	0.9996	14.87	21.68
3,5-DMP	120–180	6852.9	-15.127	0.9997	16.08	24.31
2-EP	110–170	6861.0	-15.363	0.9996	14.28	21.20
3-EP	120–180	7118.0	-15.652	0.9996	15.38	22.95
4-EP	110–170	6990.5	-15.449	0.9997	14.90	22.10
2,3,5-TMP	130–190	6903.7	-14.878	0.9997	15.98	23.44
2,3,6-TMP	110–170	6478.6	-14.309	0.9997	14.75	21.61
2,4,6-TMP	110–170	6401.8	-14.296	0.9997	15.77	23.92
3,4,5-TMP	130–190	7226.0	-15.273	0.9997	15.74	22.47
2-PP	120–180	7123.2	-15.571	0.9996	14.73	21.49
4-PP	120–180	7254.9	-15.620	0.9996	15.38	22.34
2-IPP	110–170	7138.2	-15.699	0.9996	14.59	21.52
3-IPP	120–180	7422.9	-16.045	0.9995	14.92	21.67
4-IPP	120–180	7125.6	-15.479	0.9996	14.57	20.91
				$\bar{x}$	14.84	21.98
				S.D.	0.71	1.05

Table 3 Equations, correlation coefficient and thermodynamic parameters of C_0–C_3 APs obtained from van't Hoff plots of ln k′ *vs.* 1/T plots on BSiMe column

compound	temperature range (°C)	ln k′ = m(1/T) + c		R^2	−ΔH (kcal/mol)	−ΔS (cal/mol·K)
		m	c			
P	100–160	7003.4	-16.070	1.0000	13.92	20.96
2-MP	100–160	7009.7	-15.494	1.0000	13.93	19.82
3-MP	110–170	7493.9	-16.802	0.9999	14.89	22.41
4-MP	100–160	7216.5	-16.291	0.9999	14.34	21.40
2,3-DMP	110–170	7444.2	-16.377	0.9999	14.79	21.57
2,4-DMP	110–170	7234.9	-16.120	0.9999	14.38	21.06
2,5-DMP	110–170	7448.4	-16.512	0.9999	14.80	21.84
2,6-DMP	100–160	6721.4	-15.300	1.0000	13.36	19.43
3,4-DMP	120–180	7676.3	-16.733	0.9998	15.25	22.28
3,5-DMP	120–180	7634.6	-16.754	0.9999	15.17	22.32
2-EP	110–170	7631.4	-16.945	0.9999	15.16	22.70
3-EP	120–180	8068.0	-17.629	0.9998	16.03	24.06
4-EP	110–170	7600.0	-16.745	0.9999	15.10	22.30
2,3,5-TMP	130–190	7857.7	-16.849	0.9998	15.61	22.51
2,3,6-TMP	110–170	7265.9	-15.937	0.9999	14.44	20.70
2,4,6-TMP	110–170	7099.9	-15.747	1.0000	14.11	20.32
3,4,5-TMP	130–190	8230.7	-17.366	0.9998	16.35	23.54
2-PP	120–180	8057.0	-17.527	0.9998	16.01	23.86
4-PP	120–180	8007.0	-17.235	0.9997	15.91	23.27
2-IPP	120–180	8100.7	-17.728	0.9998	16.10	24.25
3-IPP	130–190	8512.7	-18.341	0.9995	16.91	25.47
4-IPP	120–180	7853.8	-17.065	0.9997	15.61	22.94
				$\bar{x}$	15.10	22.23
				S.D.	0.91	1.51

Table 4 Equations, correlation coefficient and thermodynamic parameters of C_0–C_3 APs obtained from van't Hoff plots of ln k′ *vs.* 1/T plots on GSiMe column

compound	temperature range (°C)	ln k′ = m(1/T) + c		R^2	−ΔH (kcal/mol)	−ΔS (cal/mol·K)
		m	c			
P	100–160	6459.1	-15.098	0.9997	12.83	19.03
2-MP	100–160	6514.9	-14.982	0.9996	12.95	18.80
3-MP	100–160	6799.1	-15.420	0.9996	13.51	19.67
4-MP	100–160	6700.5	-15.240	0.9997	13.31	19.31
2,3-DMP	110–170	6865.4	-15.187	0.9996	13.64	19.21
2,4-DMP	110–170	6709.6	-15.034	0.9996	13.33	18.90
2,5-DMP	110–170	6741.5	-15.088	0.9996	13.40	19.01
2,6-DMP	100–160	6227.5	-14.305	0.9996	12.37	17.45
3,4-DMP	120–180	6937.4	-15.175	0.9996	13.78	19.18
3,5-DMP	120–180	6852.9	-15.127	0.9997	13.62	19.09
2-EP	110–170	6861.0	-15.363	0.9996	13.63	19.56
3-EP	120–180	7118.0	-15.652	0.9996	14.14	20.13
4-EP	110–170	6990.5	-15.449	0.9997	13.89	19.73
2,3,5-TMP	130–190	6903.7	-14.878	0.9997	13.72	18.59
2,3,6-TMP	110–170	6478.6	-14.309	0.9997	12.87	17.46
2,4,6-TMP	110–170	6401.8	-14.296	0.9997	12.72	17.44
3,4,5-TMP	130–190	7226.0	-15.273	0.9997	14.36	19.38
2-PP	120–180	7123.2	-15.571	0.9996	14.15	19.97
4-PP	120–180	7254.9	-15.620	0.9996	14.42	20.07
2-IPP	120–180	7138.2	-15.699	0.9996	14.18	20.22
3-IPP	130–190	7422.9	-16.045	0.9995	14.75	20.91
4-IPP	120–180	7125.6	-15.479	0.9996	14.16	19.79
				$\bar{x}$	13.62	19.22
				S.D.	0.62	0.90

VITA

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