합성 윤활기유로서의 알킬벤젠의 분광분석

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Spectroscopic Analysis of Alkylbenzenes as Synthetic Lubricant Base Oils

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요약: 합성 윤활기유로 사용되고 있는 알킬벤젠들 중에 단일, 그리고 이중치환된 알킬벤젠의 양과 알킬사슬에 존재하는 탄소원자의 수를 ^{13}C-NMR, 근적외선 및 UV-Vis 분광법으로 분석하였다. 또한 엔진윤활유에 포함되어 있는 직선형 긴 사슬 알킬벤젠을 적외선분광법으로 분석하였다.

Abstract: Alkylbenzenes used as synthetic lubricant base oils have been analyzed to find the quantity of mono- and di-substituted alkyl aromatic hydrocarbon compositions and the number of carbon atoms in alkyl chains by ^{13}C-NMR, near-infrared, and UV-Vis spectroscopy. Also, linear long chain alkylated benzene in the engine lubricants was analyzed quantitatively by infrared spectroscopy.

Key words: Alkylbenzenes, ^{13}C-NMR, near-infrared, and UV-Vis spectroscopy

1. Introduction

One of the perspective method for producing alkylbenzenes is alkylation of aromatic compounds with olefin by organo-metal catalysts. High molecular weight alkylbenzenes(fractions obtained at 400~475℃ and 450~500℃) were produced by benzene alkylation with α-olefins(fraction obtained at 180~240℃) obtained by thermal cracking of paraffins in the presence of AlCl$_3$ and HF catalysts. The investigation of high molecular weight alkylbenzenes was carried out by the method of thermo-diffusion separation(TDS). Physical properties of alkylbenzenes depend on the number of side branches and also on the number of carbon atoms in alkyl groups. Analytical methods, providing safe and fast ways to find the quantity of mono- and di-substituted alkyl aromatic

substances are important for making decision to select optimum process conditions. Various kinds of analytical methods for alkylbenzenes have been developed with chromatographic[1] and spectroscopic methods. Our investigations were carried out in UV region[2] and near-infrared region[3~5], where spectrum of mono- and di-substituted alkylbenzenes are distinguishable. The number of carbon atoms in alkyl chains of alkylbenzenes were determined by using ^{13}C-NMR[6~9] and near-infrared spectroscopy. Also, linear long chain alkyl substituted benzenes in the engine lubricants containing synthetic lubricant base oil were analyzed quantitatively by infrared spectroscopy.

2. Experimental

2.1. The methods of ^{13}C-NMR, near-infrared, and UV-Vis spectroscopic analysis

In the present study, ^{13}C-NMR spectrometer has been used to identify the carbon type distribution in alkylbenzenes. The ^{13}C-NMR spectra in this study were obtained with a Varian Unity-1 FT-NMR(300MHz) spectrometer at 50.3MHz. Samples were prepared by making a 50vol.% solution with CDCl$_3$ to which 25~30mg/mL of Cr(acac)$_3$ was

added as a relaxation reagent. The inverse gated decoupling program was used to suppress any nuclear overhauser effect(NOE).[10] A pulse delay time of 1 sec. was used to obtain spectra quantitatively. All of the sharp and broad features of each spectrum were zone integrated. The UV and near-infrared spectra in this study were obtained with a Cary 17D UV-Vis-NIR spectrophotometer. In the UV study, alkylbenzene samples were diluted appropriately with n-heptane.

2.2. The method of infrared spectroscopic analysis

Detailed conditions of infrared spectroscopic analysis are as follows: infrared spectrophotometers used were a Perkin-Elmer 883 IR spectrophotometer; slit width was 3nm; scanning time was set at 6; noise filter was set at 2; baseline (90% transmission) was set to 2,000cm^{-1} for each sample; and 0.2mm KBr cell was used.

3. Results and discussion

3.1. Analysis by ^{13}C-NMR, near-infrared, and UV-Vis spectroscopy

The molar absorptivity coefficients at wavelengths selected for alkylbenzene sample analysis are

Table 1. Molar absortivity coefficients of alkylbenzenes in heptane.

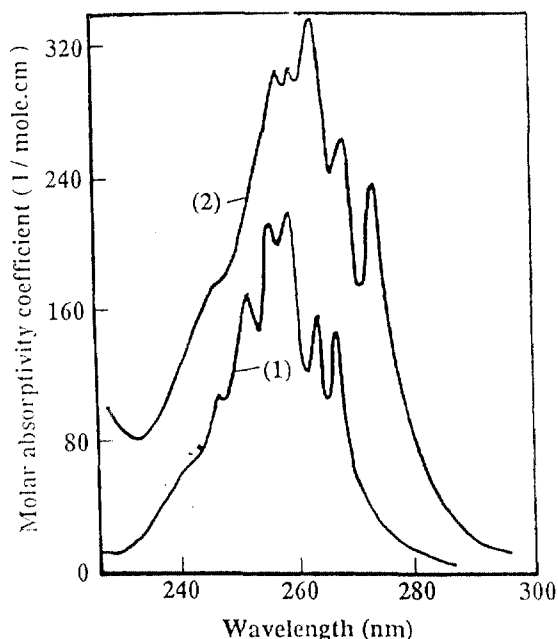| Alkylbenzene	Molar absortivity coefficient ε(L/mol.cm)			
	252nm	264nm	268nm	272nm
heptylbenzene	154	156	138	33.6
octylbenzene	159	155	140	33.7
decylbenzene	158	157	142	34.0
	157±1%	156±0.7%	140±0.7%	33±0.4%
Diheptylbenzene				
I	172.0	318.0	250.0	207.0
II	170.9	323.0	253.6	249.0
III	175.0	298.0	241.0	236.0
didecylbenzene	193.6	307.5	245.3	222.5
	177.9±4.7%	311.6±2.8%	247.5±1.5%	228.8±3.1%

Fig. 1. Typical UV-absorption spectrum of mono-alkylbenzene (1) and dialkylbenzene (2).

shown in *Table* 1. Typical UV-spectrum of mono- and dialkylbenzene are shown in *Fig.* 1. In case of mono-alkylbenzenes, it is clear that the deviations of each molar absorptivity coefficient from its average value were no more than 1%. In case of dialkylbenzene, the IR^{12} spectrum data show that the sample is a mixture of ortho-, meta-, and para-isomers with different quantitative compositions. The deviations of each molar absorptivity coefficient from the average value were approached to 5%. It was impossible to obtain the characteristic spectrum for each dialkylbenzenes with mixed state of substituents. Using absorptivity coefficients in *Table* 1 and solving Firodot's equation for 4 wavelengthes, we obtained equations for the calculation of concentrations(mole/L) of the sum of mono- and di-alkylbenzenes.

$$C_M = 0.1226\ \varepsilon_{\lambda1} + 0.0055\ \varepsilon_{\lambda2} + 0.0326\ \varepsilon_{\lambda3} - 0.1381\ \varepsilon_{\lambda4} \quad (1)$$

$$C_D = -0.0455\ \varepsilon_{\lambda1} + 0.0230\ \varepsilon_{\lambda2} + 0.0044\ \varepsilon_{\lambda3} - 0.0866\ \varepsilon_{\lambda4} \quad (2)$$

Using values calculated by eq.(1) and (2) the contents of benzene rings(in %) in samples with mono- and di-alkylbenzene substituents are :

$$B_M = (72 \times C_M \times V) \times 100 / (1000 \times a) \quad (3)$$

$$B_D = (72 \times C_D \times V) \times 100 / (1000 \times a) \quad (4)$$

where a is the weight of analyzed mixtures(in VmL of n-heptane).

Test sample mixtures consisting individual alkylbenzenes have been prepared and analyzed. According to the proposed UV spectrum analysis scheme, the test samples of alkylbenzenes were analyzed. Analytical results obtained with test samples are shown in *Table* 2. The sample mixtures have been fractionated before analysis based on the boiling point to find the length of alkyl chain of basic components that exist in the fractions. Analytical results of the sample mixtures were shown in *Table* 3. In the *Table* 3, the contents of mono- and dialkylbenzenes having different length of alkylchain were the calculated and compared with the experimentally obtained contents.

Alkylbenzenes containing the linear alkyl chain have lower freezing point, better viscosity index and more thermal stability than those with the branched alkyl chain structure. For the selection of the lubricant base material, the main criteria considered are the sufficient viscosity at higher temperatures and lower freezing point. In *Table* 4, kinematic viscosities at 99°C and freezing point of mono-, di-, and tri-alkylbenzenes with the linear alkyl groups having carbon atoms C_6-C_{16} are presented. The freezing points of di-alkylbenzenes which had the alkyl substituents length C_{10}-C_{13} of showed much lower freezing points.

Fig. 2 shows the near-infrared spectra of alkylbenzenes produced by the alkylation of benzene with α-olefin in the presence of HF catalyst in the 1650~1800nm wavelength range. This wavelength

Table 2. Analytical results of artificial mixtures of mono- and di-hepthlybenzenes.

sample	Contents(%)		Mono-heptylbenzene			Di-heptylbenzene		
	monohept-ylbenzene	diheptyl-benzene	# of measure-ments	average contents (%)	relative error(%)	# of measure-ments	average contents (%)	relative error(%)
1	81.4	18.6	7	79.5	2.3	7	17.7	4.9
2	91.9	8.1	2	88.9	3.7	2	8.0	1.9
3	53.2	46.8	2	56.5	6.1	2	45.1	3.7
4	34.2	65.8	2	43.1	6.1	2	69.5	5.6

Table 3. Analytical results of alkylbenzene's fraction

	Contents of benzene rings (calculated)		# of carbons in alkylbenzene	Contents of benzene rings (experimantal)	
	mono-alkylbenzene	di-alkylbenzene		mono-alkylbenzene	di-alkylbenzene
C_4	54.1	37.9	C_4-C_6	43.0	3.3
C_6	44.7	28.8	C_6-C_8	31.2	5.2
C_8	37.9	23.8	C_{10}-C_{12}	19.0	12.5
C_{10}	33.1	20.1	C_{14}-C_{16}	14.3	13.1
C_{12}	29.0	17.4	C_{16}	8.3	13.5
C_{14}	26.3	15.3	C_{18}-C_{20}	7.2	14.7

range is the C-H first overtone region of the methyl, methylene, and aromatic of alkylbenzenes. From the relative absorbance ratio of the near infrared spectrum in the first overtone region, we can calculate the number of methylene carbon atoms in alkyl chain of the alkylbenzenes.

Fig. 3 shows the ^{13}C-NMR spectra of 4 kinds of alkylbenzenes produced by Friedel-Craft alkylation process using HF catalyst. The ^{13}C-NMR spectra may provide the direct information about the number of carbon atoms in alkyl chains, the degree of substitution and position in alkyl chains, the degree of branching in alkyl chains of alkylbenzenes.

3.2. Analysis by infrared spectroscopy

3.2.1. Calibration

Three standard oil samples having 7.5%, 10%, and 12.5% of linear long chain alkyl substituted benzene were prepared. Necessary conditions of standard oil samples and prodecures for calibration are as follows :

(i) Grade of sample oil for calibration=SAE 30.

(ii) The oil sample having linear long chain alkyl substituted benzene(HLAB) must be a representative of the average production.

(iii) Plot an IR spectrum(900cm^{-1}~600cm^{-1} spectral region).

Table 4. Viscosity and freezing point of linear alkylbenzenes

Alkyl group	Kinematic viscosity at 99℃ (cSt)			Freezing point (℃)		
	mono-alkylbenzene	di-alkylbenzene	tri-alkylbenzene	mono-alkylbenzene	di-alkylbenzene	tri-alkylbenzene
C_6H_{13}	0.75		2.4			−40
C_7H_{15}	0.83		3.2			−40
C_8H_{17}	0.95		3.9			−60
$C_{10}H_{21}$	1.0	3.1			−62	
$C_{12}H_{23}$	1.5	4.0			−62	
$C_{13}H_{25}$	1.6	5.0		−79	−54	
$C_{14}H_{29}$	1.9	5.7			−29	
$C_{16}H_{33}$	2.0	7.0			−12	
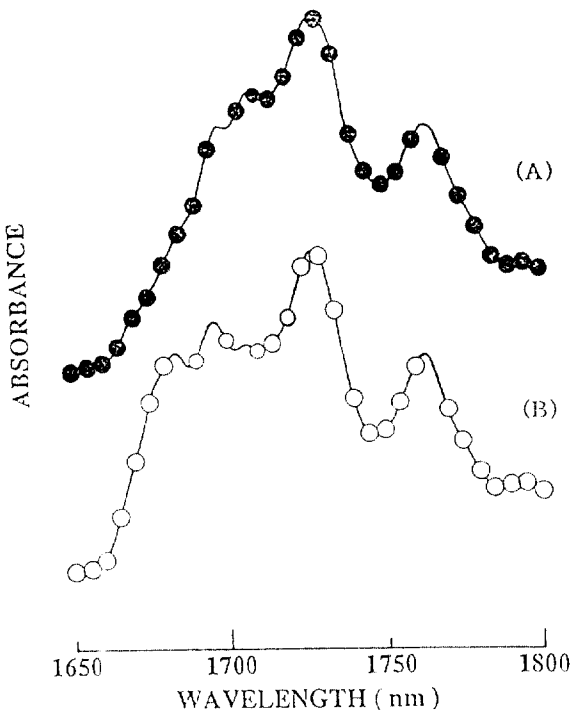
Fig. 2. Near-IR spectrum of alkylbenzenes in the 1650~1800nm wavelength region.(A- fractionated linear monoalkylbenzene heavy fraction, B-linear C_{10}-C_{12} monoalkylbenzene).

(iv) Draw a horizontal tangent at $705cm^{-1}$ (T2) and measure the optical density(O.D.) of the peak at $700cm^{-1}$ (T1) as shown in *Fig.* 4.

(v) Draw the calibration curve(O.D.=f(% HLAB)).

3.2.2. Calculation of the percentage of H-LAB in engine lubricant

(i) Plot the near-IR spectrum in the region of $900cm^{-1}$~$600cm^{-1}$(use the same cell as the one used for the calibration without any change of the experimental settings).

(ii) Measure the optical density of the peak at $700cm^{-1}$ as mentioned above.

(iii) By using the calibration curve, calculate the percentage of H-LAB corresponding to the measured O.D. using equation(5). (see the example in *Fig.* 5).

$$O.\ D.=Log(T_2/T_1)$$
$$=-4.1806\times e^{-2}+4.3702\times e^{-2}\times HLAB(wt.\%) \quad (5)$$

4. Conclusions

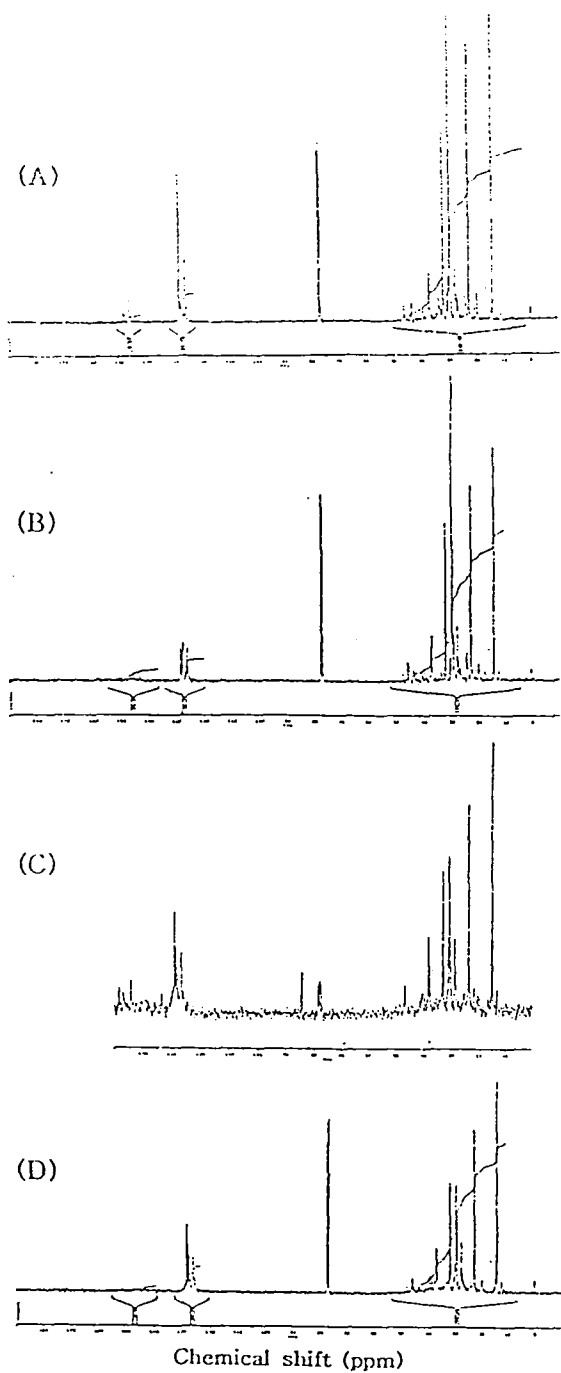Fig. 3. ^{13}C-NMR spectrum of alkylbenzenes.(A: dialkylbenzene with HF catalyst, B: dialkylbenzene with AlCl₃ catalyst, C: fractionated linear mono-alkylbenzene heavy fraction, D: linear monoalkyl-benzene heavy fraction).
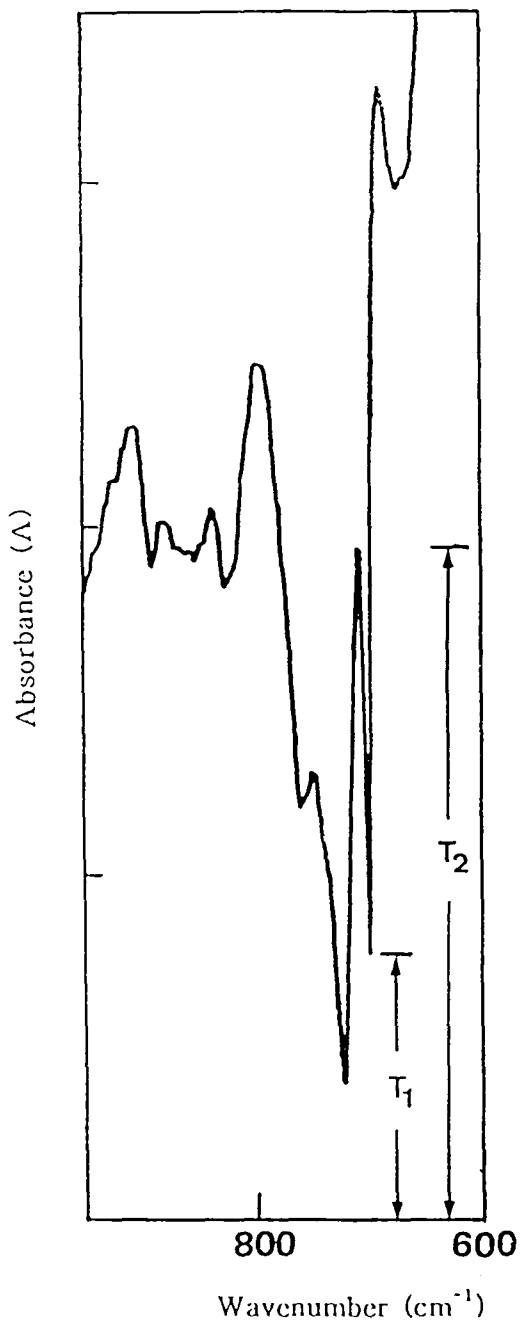

Fig. 4. Infrared spectrum of engine lubricant containing HLAB in the 900~600cm^{-1} region.

$y = -4.1806e\text{-}2 + 4.3702e\text{-}2x$
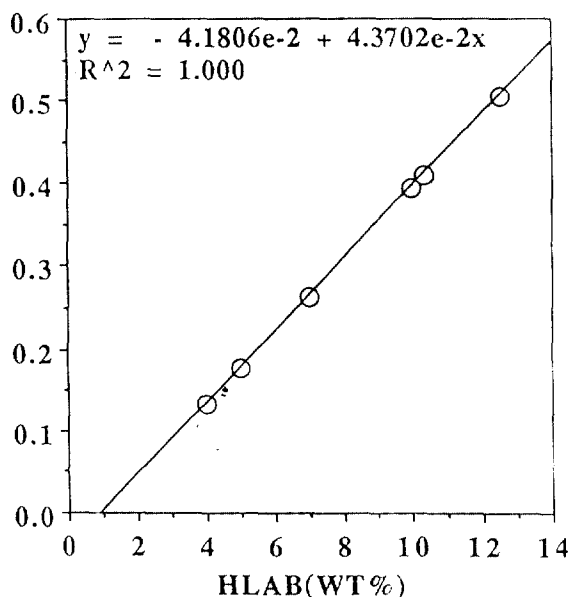
$R^2 = 1.000$

Fig. 5. Calibration curve for H-LAB in engine oil.

Alkylbenzenes used as synthetic lubricant base oils have been analyzed to find the quantity of mono- and di-substituted alkyl aromatic hydrocarbon compositions and the number of carbon atoms in alkyl chains by ^{13}C-NMR, near-infrared, and UV spectroscopy. The relative error of measurements of mono- and di-substituted alkyl aromatic hydrocarbon compositions and the number of carbon atoms in alkyl chains by spectroscopic analysis was in the range of 3~5%. It was attributed to the existence of absorption coefficient deviation of each components in the given alkylbenzene mixtures from the average absorption coefficient values. Our investigations found that the most valuable components of alkylbenzene oils were dialkylbenzenes which had the alkyl substituents length of C_{10}-C_{13}.

Acknowledgment

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