Determination of the Composition of Post Dodecyl Benzene by IR Spectroscopy

BILSEN BEŞERGIL, *Central Quality Control Laboratories, Petkim, Petrochemical Corporation, P.K. 12, Izmir, Turkey* and BAHATTIN M. BAYSAL, *Department of Chemical Engineering and Polymer Research Center, 80815 Bebek-Istanbul, Turkey*

Synopsis

The purpose of this study is to determine if the chemical composition of post dodecyl benzene (PDB) which is obtained as the by product during the production of dodecyl benzene (DDB) at PETKIM, Petrochemical Corporation, is a suitable raw material for the production of alkyl benzene sulphonic acids of high molecular weights. In this work, physical and chemical properties of PDB are determined and results are compared with literature values. Chemical composition analysis are done by IR spectroscopy. Thus, the types of alkylates in PDB are determined both qualitatively and quantitatively, the results showed that PDB consist mainly of mono- and m-di-alkyl benzenes, only a small amount of p-di-alkyl benzenes are also present.

INTRODUCTION

Post dodecyl benzene (PDB) which is a mixture of alkyl benzenes is a suitable raw material for the production of detergent additives for lubricating oils. These additives are the rare earth metal salts of alkyl benzene sulphonic acid.[1] This active material must be compatible with the mineral oil and must not separate out by time. In addition, it has to have properties such as molecular weight and viscosity within certain limits to sustain particles of certain salts such as $CaCO_3$ and $BaCO_3$ in colloidal sizes. These properties of the final product, namely the active material, is dependent on the properties of the raw material.[2,3]

The heavier by product of PETKIM dodecyl benzene (DDB) plant is PDB, which is produced by alkylation of branched parafines to benzene.[4,5] The molecular weight of PDB effects the properties of the final product in a direct way. In addition, its sulphonation yield must be high. The unsulphonable portion of PDB effects the properties of the active material in an undesirable way. The yield of sulphonation of PDB, on the other hand, depends on its content of alkylate types and concentrations. In this work the chemical structure, physical, and chemical properties of PDB is determined. The results obtained are compared with the properties of the raw materials used for the production of mineral oil detergent additives and found suitable for such production.

EXPERIMENTAL

Materials

Dodecyl benzene (DDB), post dodecyl benzene (PDB), and oleum (26%) are obtained from PETKIM, Petrochemical Corporation, Izmit, Turkey; spindle

Journal of Applied Polymer Science, Vol. 40, 1871–1879 (1990)
 CCC 0021-8995/90/11-121871-09$04.00

oil is obtained from ALIAĞA Refinary Corporation, Izmir, Turkey; Analitical grades of o-, m-, and p-xylenes are used.

Equipments

A Perkin Elmer 377 model IR spectrophotometer is used. For the determination of the physical and chemical properties of PDB and spindle oil the equipments suggested by the relevant ASTM and UOP test methods are used. These are given in Table I.

Preparation of the Samples

For the qualitative analysis of PDB, toluene as low molecular weight monoalkyl benzene, and o-, m-, and p-xylenes as di-alkyl benzenes are used without further treatment. For the quantitative analysis, the solutions of DDB, PDB, and PDAB (p-di-alkyl benzene of high molecular weight) of various concentrations in spindle oil are used. PDAB is prepared by sulphonation of PDB and separation of sulphonation products subsequently.[6]

The spectrums of the samples are obtained by using KBr cells of the same thicknesses. Preliminary studies to determine the cell thickness showed that the thickness of 0.03 mm is suitable enough to obtain good quality spectra at all concentrations used during our experiments. Therefore, 0.03 mm KBr/Air cells are used throughout the experiments.

Tests

For the determination of physical and chemical properties of the materials, various test methods are used which are tabulated in Table I. The qualitative

TABLE I
Properties of PDB and Spindle Oil

Properties	PDB	Spindle oil	Test methods
Sp.Gr., g/cm^3 15°C	0.880	0.860	ASTM D 1298
API, 15°C	29.15	29.71	
Flash Point, °C	160	200	ASTM D 92
Pour Point, °C	−25	−15	ASTM D 97
Viscosity, CSt			ASTM D 445
20°C	357.1	33	
40°C	77.8	16	
Anilin Point, °C	69	—	ASTM D 611
Distillation			ASTM D 1160
I.B.P. °C	371	270	
%5 °C	390	375	
%10 °C	393	380	
%30 °C	403	390	
%50 °C	407	396	
%70 °C	415	410	
%90 °C	445	424	
F.B.P. °C	477	456	
Yield, %	98.5	99.0	
Molecular Weight	370	380	UOP 375/59
Bromine Number	0.312	—	—
Acidity	0.059	0.053	ASTM D 664

analysis and quantitative chemical composition of PDB is determined by IR spectroscopy.[7,9]

Spectroscopic Analyses

The types of alkylates present in PDB are determined by the comparison of the absorbtion peaks of PDB IR spectrum with the data obtained from the IR spectrums of known, standard alkylates. For this purpose, toluene and DDB as mono-alkyl benzene, o-, m-xylenes as o-di- and m-di-alkyl benzene, PDAB as p-di-alkyl benzene are used as standard materials.

IR measurements are made at the region of 1100-650 cm^{-1} which are characteristic for alkyl groups. All spectrums are obtained against air except the spectrum of PDAB which is obtained against spindle oil.

DDB and PDAB standard materials are used for quantitative analysis. IR analysis are performed by using 1030 cm^{-1} and 765 cm^{-1} peaks for mono-alkyl benzenes, whereas 1015 cm^{-1} and 830 cm^{-1} for p-di-alkyl benzenes. The m-di-alkyl benzenes content are calculated by substracting the sum of the other alkyl benzenes from 100.

The baseline method is used to evaluate the IR spectrum of standards and unknown.

RESULTS AND DISCUSSIONS

Qualitative Analyses

IR spectra of toluene and DDB are given in Figure 1. The following characteristic absorbtion peaks are obtained:

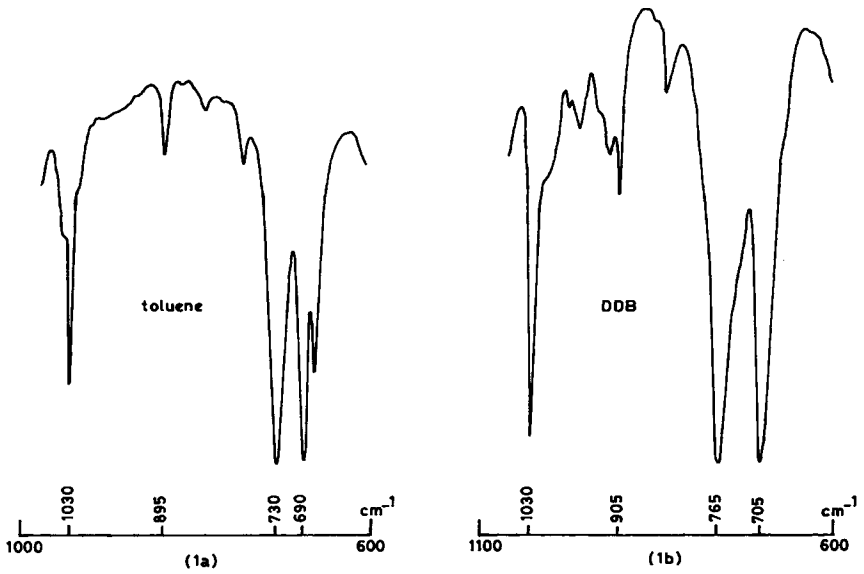

Fig. 1a. Toluene (0.03 mm)/Air.
Fig. 1b. DDB (0.10 mm)/Air.

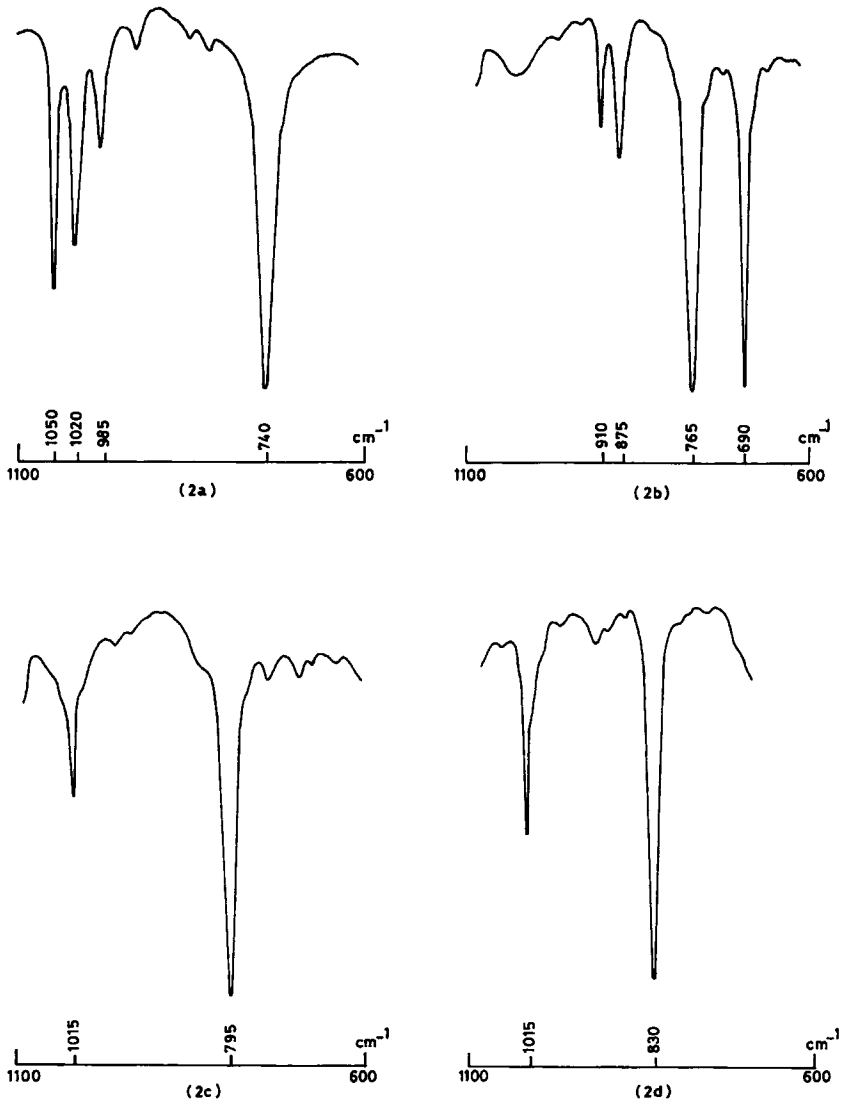

Fig. 2a. o-Xylene (0.03 mm)/Air.
Fig. 2b. m-Xylene (0.03 mm)/Air.
Fig. 2c. p-Xylene (0.03 mm)/Air.
Fig. 2d. Unsulphonated oil, PDAB (0.10 mm)/Spindle oil (0.10 mm).

Toluene (0.03 mm KBr/Air)	DDB (0.1 mm KBr/Air)
1030 cm^{-1} (s)	1030 cm^{-1} (s)
895 cm^{-1} (m)	905 cm^{-1} (m)
730 cm^{-1} (s)	765 cm^{-1} (s)
690 cm^{-1} (s)	705 cm^{-1} (m)

At the spectrum of toluene and dodecyl benzene there are three strong (s) and one medium strong (m) absorbtion peaks which are related to mono-alkyl ben-

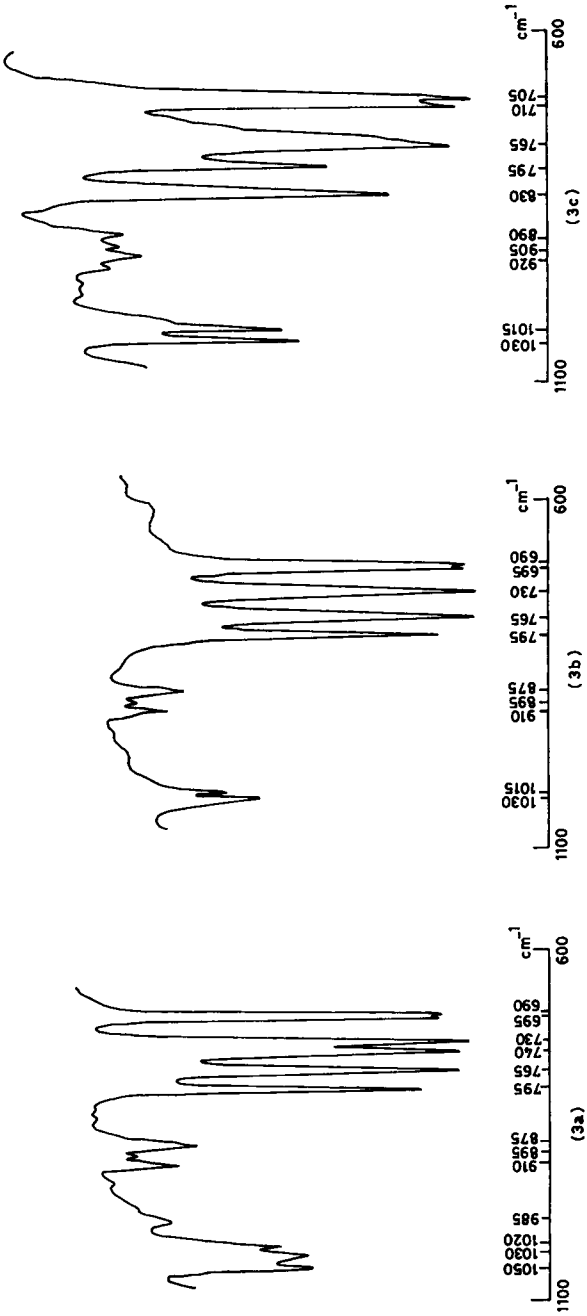

Fig. 3a. Toluene + (o-m-p) Xylene (0.03 mm)/Air.
Fig. 3b. Toluene + (m-p) Xylene (0.03 mm)/Air.
Fig. 3c. PDB (0.03 mm)/Air.

TABLE II
Absorption Peaks for Toluene and Xylene Mixtures

Toluene and o-, m-, p-xylenes		Toluene and m-, p-xylenes	
1050 cm^{-1} (m) ortho-di-alkyl	(o-xylene)	1030 cm^{-1} (m) mono-alkyl	(toluene)
1030 cm^{-1} (m) mono-di-alkyl	(toluene)	1015 cm^{-1} (m) p-di-alkyl	(p-xylene)
1020 cm^{-1} (m) o-di and p-di mixed	(o- and p-xylenes)	910 cm^{-1} (m) m-di-alkyl	(m-xylene)
		895 cm^{-1} (w) mono-alkyl	(toluene)
985 cm^{-1} (w) o-di-alkyl	(o-xylene)	875 cm^{-1} (m) m-di-alkyl	(m-xylene)
910 cm^{-1} (m) m-di-alkyl	(m-xylene)	795 cm^{-1} (s) p-di-alkyl	(p-xylene)
895 cm^{-1} (w) mono-alkyl	(toluene)	765 cm^{-1} (s) m-di-alkyl	(m-xylene)
875 cm^{-1} (m) m-di-alkyl	(m-xylene)	730 cm^{-1} (s) mono-alkyl	(toluene)
795 cm^{-1} (s) p-di-alkyl	(p-xylene)	695 cm^{-1} (s) m-di-alkyl	(m-xylene)
765 cm^{-1} (s) m-di-alkyl	(m-xylene)	690 cm^{-1} (s) mono-alkyl	(toluene)
740 cm^{-1} (s) o-di-alkyl	(o-xylene)		
730 cm^{-1} (s) mono-alkyl	(toluene)		
695 cm^{-1} (s) m-di-alkyl	(m-xylene)		
690 cm^{-1} (s) mono-alkyl	(toluene)		

zenes. From the above figures, it will be seen that only the peak at 1030 cm^{-1} is the same for the two chemicals. This peak, although characteristic for the mono-alkyl benzenes, is not effected by the size of the alkyl group. Since both chemicals in question are mono-alkyl benzenes, the differences at their absorbtion peaks are due to difference in size of the alkyl groups they have. Therefore, the last three absorbtion peaks reflects the effects of the size of the alkyl group.

Characteristic absorbtion peaks of the IR spectra of p-xylene and PDAB are obtained from Figure 2.

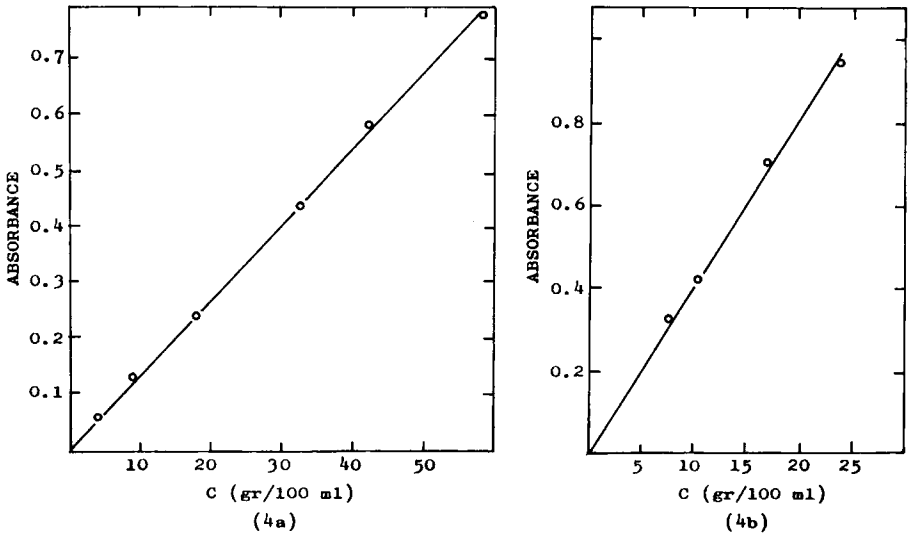

Fig. 4a. Calibration Curve for DDB ($\tilde{\nu}$ = 1030 cm^{-1}).
Fig. 4b. Calibration Curve for PDAB ($\tilde{\nu}$ = 830 cm^{-1}).

TABLE III
Composition of Alkylates Obtained From Various Industrial Sources

Alkyl benzene	mono-alkyl (%)	m-di-alkyl (%)	p-di-alkyl (%)	mono- + m-di- (%)	Yield of sulphonic acid (%)	References
A	36	47	17	83	87	3, 10, 12
B	32	33	35	65	78	3, 12
C	48	32	20	80	88	3, 12
D	20	47	33	67	70	3, 12
E	35	20	45	55	63	3, 11, 12
PDB	30	49	21	79	—	This work

p-Xylene (0.03 mm KBr/Air)	PDAB/S. oil (0.10 mm/0.01 KBr)
1015 cm^{-1} (m)	1015 cm^{-1} (m)
795 cm^{-1} (s)	830 cm^{-1} (s)

Both p-xylene and PDAB are para-di-alkyl benzenes and have one strong and one medium strong absorbtion peaks. It is seen that the peak at 1015 cm^{-1} retains its position while the peak at 795 cm^{-1} of p-xylene shifts 35 units to 830 cm^{-1} in the case of PDAB.

IR spectra of ortho- and meta-xylenes are also included in Fig. 2.

o-Xylene (0.03 mm KBr/Air)	m-Xylene (0.03 mm KBr/Air)
1050 cm^{-1} (s)	910 cm^{-1} (m)
1020 cm^{-1} (s)	875 cm^{-1} (m)
985 cm^{-1} (m)	765 cm^{-1} (s)
740 cm^{-1} (s)	695 cm^{-1} (s)

The comparison of the above peaks which belong to small molecular weight ortho- and meta-di-alkyl benzenes with higher side chain compounds could not be made due to absence of standard chemicals.

IR Spectrum of Toluene and Xylenes Mixtures (Figure 3a, 0.03 mm KBr/Air)

The mixture consists of small molecular weight mono-, ortho-di, para-di-alkyl benzenes. The place of the absorption peaks and their sequence in accordance with the alkyl benzene type is important.

The absorption peaks of the spectrum at Fig. 3a are identified as of Table II by making use of the spectrum separately obtained for the alkyl benzenes in the mixture:

- Each compound in the mixture has retained its original absorption frequencies. Only the absorption peaks at 1020 cm^{-1} (ortho-di) and 1015 cm^{-1} (para-di) are overlapped.

- The doublet observed at 695/690 cm^{-1} which corresponds to m-xylene and toluene is characteristic enough for identification of mixtures.

IR Spectra of Toluene, m-Xylene, and p-Xylene Mixtures (Figure 3b, 0.03 mm KBr/Air)

Absorption peaks are also included in Table II.

IR Spectrum of PDB (Figure 3c, 0.1 KBr/Air)

Some of the absorption peaks at the spectrum of PDB are identified by making use of the DDB and PDAB spectra,

1030 cm^{-1} (m)	mono-alkyl
1015 cm^{-1} (m)	p-di-alkyl
920 cm^{-1} (w)	—
905 cm^{-1} (w)	mono-alkyl
890 cm^{-1} (w)	—
830 cm^{-1} (s)	p-di-alkyl
795 cm^{-1} (s)	—
765 cm^{-1} (s)	mono-alkyl
710/705 cm^{-1} (s)	doublet

The peaks observed at 920, 890, and 795 cm^{-1} are identified by the evaluation of the data obtained from the standard chemical spectra.

From above data which is based on careful IR analysis, it is seen that PDB certainly contains mono- and p-di alkyl benzenes. For the presence of m-di and o-di alkyl benzenes Figs. 3a and 3b are to be compared with Fig. 3c which indicates, in addition to mono- and p-di-alkylates, the presence of m-di-alkyl benzenes only. Therefore, it can be concluded that, PDB contains a mixture of mono-, m-di-, and p-di-alkyl benzenes, but does not contain any o-Substituted compound.

Quantitative Analyses

Since post dodecyl benzene consists of three different alkyl benzene for the quantitative analysis of PDB two standard chemicals are sufficient. These are DDB (mono-alkyl) and PDAB (para-di-alkyl). Therefore, quantitative analyses are performed depending on the peaks of the PDB spectrum corresponding to mono- and para-di-alkyl benzenes. Mono-alkyl and p-di-alkyl peaks of PDB are observed at 1030, 905, 765 cm^{-1} and 1015, 830 cm^{-1}, respectively. The peak at 905 cm^{-1} is a weak one and it is not suitable for quantitative analyses. However, the other peaks are strong enough for this purpose. In this work, the peaks appear at 1030, 765 cm^{-1} and the peaks at 1015, 830 cm^{-1} are used for the quantitative determination of mono-alkyl and p-di-alkyl benzenes, respectively (Fig. 3c).

The determinations are done in two steps: First, calibration graphs are constructed from solutions of standards (DDB and PDAB) in spindle oil which has no absorption peaks at the part of the spectra of our concern. Sample calibration graphs for 1030 cm^{-1} and 765 cm^{-1} are given in Figure 4a and Figure

4b which are obtained by plotting absorbance values evaluated in accordance with the baseline method versus concentration. The observed straight line relation indicates quantitative determinations with precision. The second step involves obtaining the spectrum of PDB, evaluating the absorbance values of the peak in question then reading the concentration values from the calibration graphs corresponding to these absorbance values.

The results of quantitative IR spectral analyses show that PDB is a mixture of 30% mono-alkyl benzene, 49% m-di-alkyl benzene, and 21% p-di-alkyl benzene. The analytical results of alkylates obtained from various industrial sources are given in Table III together with the results obtained in this work.

It is seen that PDB has a composition very similar to A type alkylate and is expected to be sulphonated with a yield of 87% which makes a suitable raw material for sulphonation processes. We will present the results of sulphonation in a subsequent paper.

References

1. Overbased di-alkyl benzene sulphonates, U.S. Patent 3 470 097 Sept., 1969.
2. Prepation of basic barium sulphonates in a non volatile solvent, U.S. Patent 2 982 726, May, 1969.
3. E. Gilbert and B. Veldhuis, *Ind. Eng. Chem.*, **50,** 997 (1958).
4. R. H. Rosenwald, in *Encyclopedia of Polymer Science and Technology,* H. F. Mark, N. G. Gaylord, and N. M. Bikales, Eds., Vol. 2, p. 50–72, Interscience, New York, 1978.
5. B. T. Brooks, S. S. Kurtz, C. E. Boord, and L. Schmerling, *The Chemistry of Petroleum Hydrocarbons,* Vol. 3, Reinhold, New York, 1955.
6. E. Gilbert, B. Veldhuis, E. J. Carlson, and S. L. Giolite, *Ind. Eng. Chem.*, **45,** 2068 (1953).
7. C. N. Rao, *Chemical Application of IR Spectroscopy,* Academic Press, New York, 1963.
8. R. M. Silverstein, C. G. Bassler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds,* John Willey and Sons., Inc., New York, 1974.
9. C. N. Rao, *Chemical Application of IR Spectroscopy,* Academic Press, New York, 1963.
10. W. J. Sweeney and B. E. Hudson, *Sci. Petroleum,* **5,** 329 (1955).
11. H. S. Bloch and G. L. Hervert, Div. of Petroleum Chemistry, 124th Meeting, ACS, 1953.
12. J. C. Kirk and A. Shadan, Div. of Petroleum Chemistry, 129th Meeting, ACS, 1956.

Received February 16, 1989
Accepted July 13, 1989