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MASTER

HYDROGEN BONDING IN ASPHALTENES AND COAL

Quarterly Report for April 1,1979-June 30,1979

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DISCLAIMER

OBJECTIVE AND SCOPE OF WORK

The objective of this program is to investigate the nature and strength of hydrogen bonding and other molecular interactions that occur in asphaltenes and coal-liquids,and to seek possible correlations with the viscosity of the product oil. During the period April 1,1979-June 30,1979,the paper "Molecular interactions of quinoline with coal-liquid fractions" by K.C. Tewari,J.T.Wang,N.C.Li, and H.J.C.Yeh,appeared in FUEL,vol 58, pp 371-374,1979. Another paper,"Influence of hydrogen bonding on the viscosity of coal liquids",by K.C.Tewari,T.Hara,L.J.S. Yang,and N.C.Li,has been accepted for publication in FUEL PROCESSING TECHNOLOGY.

Report on work in progress is as follows:

(a) Structural analysis of upgraded coal-liquids: Structural analyses have been reported of upgraded coal-liquids derived from catalytic hydroprocessing of a 30-70 blend SRC I with SRC II in a trickle bed reactor under different process conditions. The hydroprocessing conditions,results of solvent fractionation and elemental analysis of upgraded coal liquids are given in Table 1. Representative ir spectra of the coal-liquid before and after upgrading are shown in Fig. 1. The results indicate that along with the decrease in toluene insolubles, heteroatom (O,N,S) content, aromatic content and corresponding increase in aliphatic content, the hydrogen-bonded structure and phenolic OH content of the coal-liquid drastically decrease with increase in contact time and temperature.

Fig. 2 and 3 show that the specific gravity,aromaticity,and atomic C/H ratio of the upgraded liquids decrease linearly with the conversion of pentane-insolubles (TI + A) into pentane-soluble oil (HO). The logarithm of viscosity varies with the extent of hydroprocessing given to the liquid product and shows a rectilinear relationship with the content of toluene-insolubles (Fig. 4), content of total heteroatoms hence the polarity of the molecules (Fig. 5) of the upgraded liquids. Data for the ir absorption ratio A_{CH_3}/A_{CH_2} are also given in Fig. 5. The relative decrease of phenolic OH and atomic N/C ratio in upgrading process follow a first-order kinetics as shown in Fig. 6. The relative reactivity of oxygen removal to nitrogen removal is estimated to be 2:1.

Increase in temperature from 672 K to 694 K,under present hydroprocessing conditions, accelerates thermal hydrocracking and increases the conversion of pentane-insolubles,with a marked decrease in specific gravity,viscosity,heteroatom content,and atomic C/H ratio of the upgraded liquid (Table 1, Fig. 2,3 and 5).

Hydroprocessing conditions greatly influence the properties of asphaltene fractions. Asphaltenes remaining after hydroprocessing contain smaller portion of heteroatoms (O,N) and are of higher average molecular weight than those present before hydroprocessing. The molecular weight increases linearly with decrease in the heteroatom content of the asphaltene fraction (Fig. 7). The results suggest that coal asphaltenes are complex organic mixtures of both less polar materials of high molecular weights and more polar materials of lower molecular weights. Under the present hydroprocessing conditions, the polarity of the molecules plays a dominant role in the conversion of asphaltenes to pentane-soluble oil.

Table 1: Hydroprocessing conditions, material balance and elemental analysis of upgraded coal-liquids

Coal liquid	Feed	U-1	U-2	U-3	U-4
Hydroprocessing conditions:					
Pressure, MPa	-	13.8	13.8	13.8	13.8
LHSV, hr^{-1}	-	1.0	0.75	0.5	0.5
Temperature, K	-	672	672	672	694
Solvent fractionation, wt %:					
Toluene-insolubles (TI)	10.2	1.6	0.2	0.0	0.0
Asphaltenes (A)	18.5	10.9	7.4	5.1	0.5
Pentane-soluble oil (HO)	71.3	87.5	92.4	94.9	99.5
Total liquid product properties:					
Specific gravity (289/289K)	1.068	0.981	0.960	0.942	0.899
Viscosity, cp, 311 K	120	9.5	6.1	5.2	3.0
Heteratom content (O + N + S), wt %	4.15	1.4	0.9	0.6	0.2
Atomic ratio H/C	1.09	1.31	1.36	1.40	1.53
$O/C \times 10^2$	2.13	0.67	0.45	0.40	0.04
$N/C \times 10^2$	1.29	0.59	0.48	0.23	0.15

(b) Self-association of Simple Phenols in Coal-Liquids

SRC II process solvent prepared by Pittsburgh and Midway Coal Company from Kentucky #9 and #14 blend bituminous coal was separated into a number of fractions which differ mainly in their chemical properties. The fractionation was performed, using a Waters Associates Prep LC/System 500, by a sequential elution by solvents through a silica gel column (M.Farcasiu, Fuel, 56,9 (1977)).

Fraction #4 eluted by $CHCl_3/10\%\ Et_2O$, rich in simple phenols, was a major fraction of SRC II (ca. 22%). The NMR spectrum of this fraction showed a distinct concentration-dependent phenolic OH signal in $CDCl_3$. The downfield shift of the OH signal with increasing concentration indicated association of molecules involving phenolic OH.

Infrared measurements of OH-stretching band at 3600 cm^{-1} were used to determine self-association constant of this phenolic fraction. The variation of absorbance of carbon disulfide solutions of the fraction with concentration is shown in Fig. 8(a). Above 0.01 M, the negative deviation in the slope indicates self-association of phenolic OH. Since at very low concentrations the dimer is expected to be the dominant species, the association constant for the dimer was calculated from the intensity of the monomer band at 3600 cm^{-1} by use of limiting slope method of U. Liddel and E.D.Becker (Spectrochim. Acta,10,70 (1957)). In this method,the apparent molar extinction coefficient of the monomer band is plotted against the concentration of the absorbing solute and the dimerization constant, K_d, is obtained from the limiting slope of the resulting curve by use of eq (1)

$$(d\epsilon_m / dc)_{c \to 0} = -2 K_d \epsilon^o_m \qquad (1)$$

where ϵ^o_m is the molar extinction coefficient of the monomer extrapolated to infinite dilution (c = 0). A typical curve obtained is shown in Fig. 8(b).

Eq (1) holds good only for cyclic dimers where the OH groups of the dimer would make no contribution to the absorbance of the monomer peak. In case of open-chain dimer, the free OH group of the dimer will also absorb in the region of the monomer peak. If one assumes that absorption coefficient of the free OH group of the dimer is the same as that of the monomer OH,the dimerization constant, K_d,will be given by (Liddel and Becker,1957)

$$(d\epsilon_m / dc)_{c \to 0} = - K_d \epsilon^o_m$$

i.e.,the equilibrium constant will be twice that for the case of cyclic dimer.

The calculated value of dimerization constant for the fraction #4, on the basis of an open-chain dimer at 24°C, is 7.6 l mole^{-1}. As comparison, the value of 4.5 l. mole^{-1} for the open-chain dimerization constant of cholesterol at 23° has been reported (F.S.Parker and K.R. Bhaskar, Biochemistry,7,1286 (1968)).

PLANS FOR THE COMING YEAR: We plan further work on the characterization and structural analysis of the coal-liquids and their fractions, both before and after upgrading. The effects of residence time, temperature, catalyst, hydrogen pressure on improving the quality of upgraded liquids will be investigated.

PERSONNEL: The Principal Investigator devoted an average of 1/3 time, during April-June,1979, to the work of this contract. Dr. K.C.Tewari and Dr. T. Hara devoted 40 hrs/week in this period. The following students participated: Lilly Young, Dan Croitura and David Susco.

Legends of Figures

Fig. 1. IR spectra of a 30-70 blend of SRC I with SRC II before and after upgrading at 694 K, LHSV 0.5 hr^{-1}.

Fig. 2. Plots of heteroatoms (wt %) in product oil and of specific gravity vs. pentane-insolubles removed (% of initial concentration in feed). Open circles, 672K; closed circles, 694 K.

Fig. 3. Plots of aromaticity and of atomic H/C ratio vs. pentane-insolubles removed (% of initial concentration in feed). ▲, 694 K; circles, 672 K.

Fig. 4 Plots of $\ln \eta$, cp, vs. pentane-insolubles (% wt) for TI and (TI + A). Data from Table 1.

Fig. 5. Plots of $\ln \eta$, cp, and of ir absorbance ratio, A_{CH_3}/A_{CH_2}, vs. heteroatom content (% wt). ▲ 694 K; circles, 672 K.

Fig. 6. First-order plot of removal of oxygen and nitrogen vs. contact time for Feed F-1, 672 K. x = % removal.

Fig. 7. Plot of asphaltene molecular weight vs. heteroatom content (% wt).

Fig. 8. Plots of (a) absorbance and (b) ϵ_m at 3600 cm^{-1} vs. concentration, M, of fraction #4 in CS_2. Mol. wt. of Fraction #4, 195.

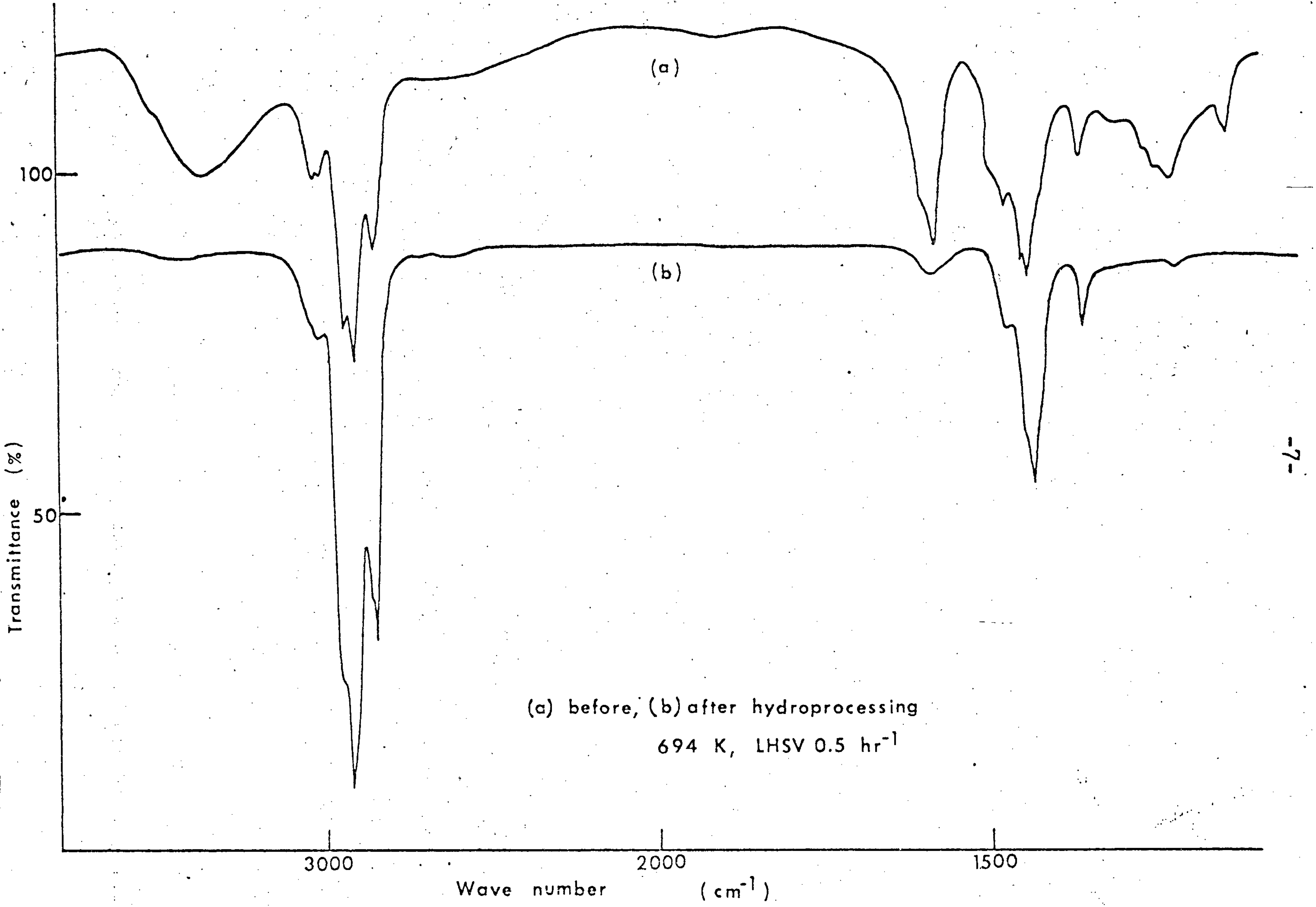

Fig. 1 IR spectra of the blend of SRC I with SRC II before and after upgrading

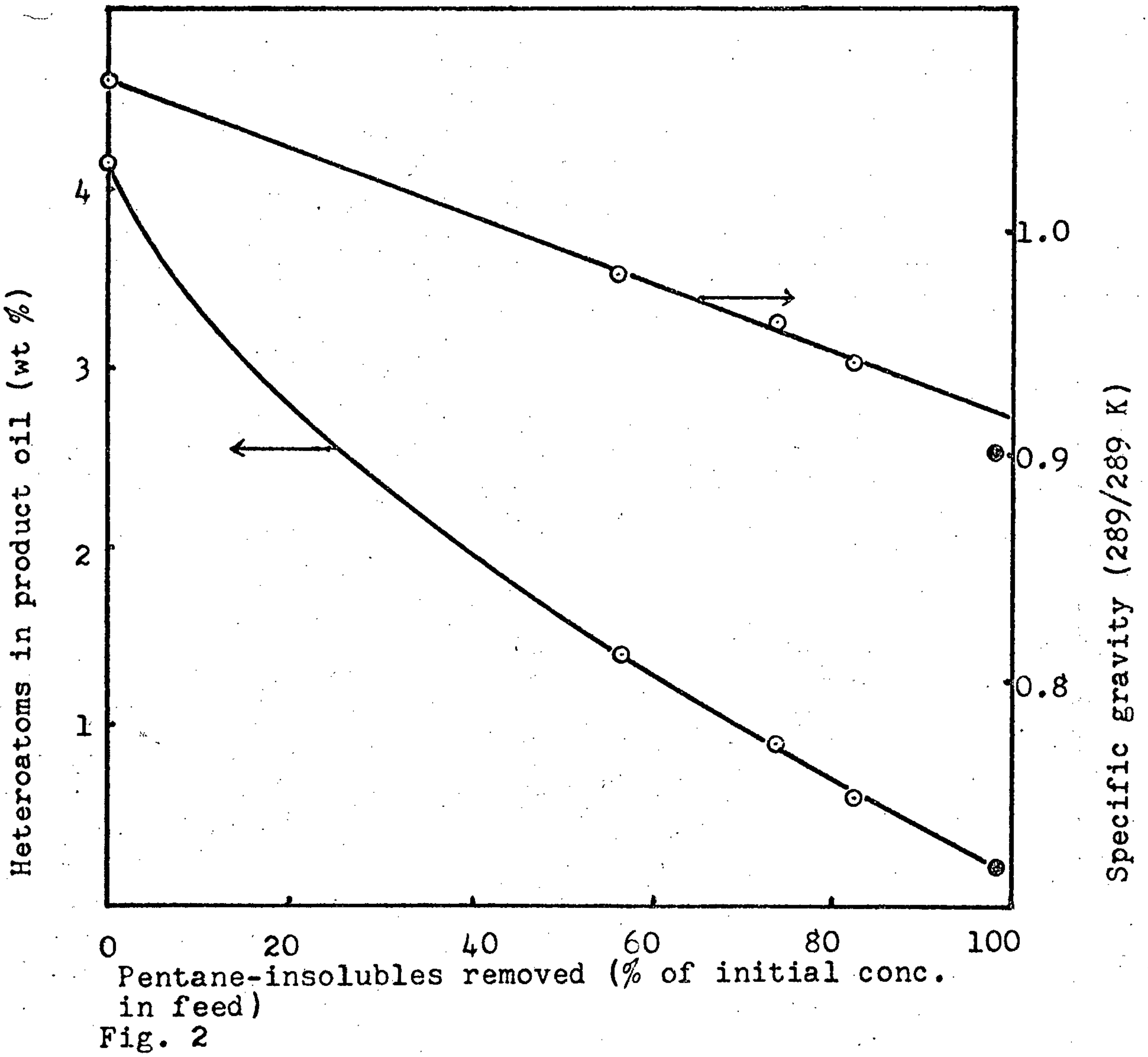
Heteroatoms in product oil (wt %)
4
3
2
1
Specific gravity (289/289 K)
1.0
0.9
0.8
0
20
40
60
80
100
Pentane-insolubles removed (% of initial conc. in feed)

Fig. 2

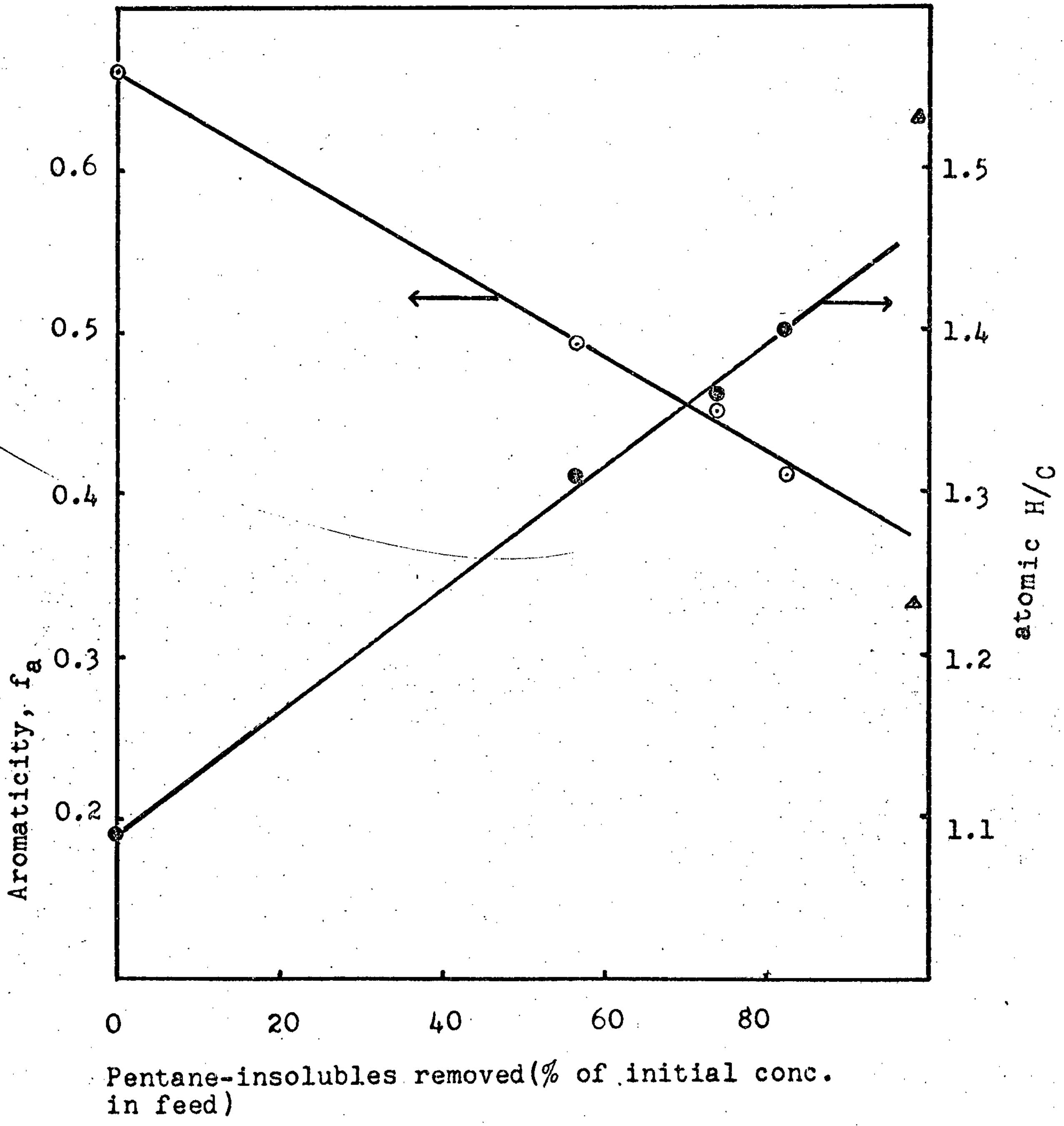
0.6
0.5
0.4
0.3
0.2
Aromaticity, f_a
1.5
1.4
1.3
1.2
1.1
atomic H/C
0
20
40
60
80
Pentane-insolubles removed(% of initial conc.
in feed)

Fig. 3

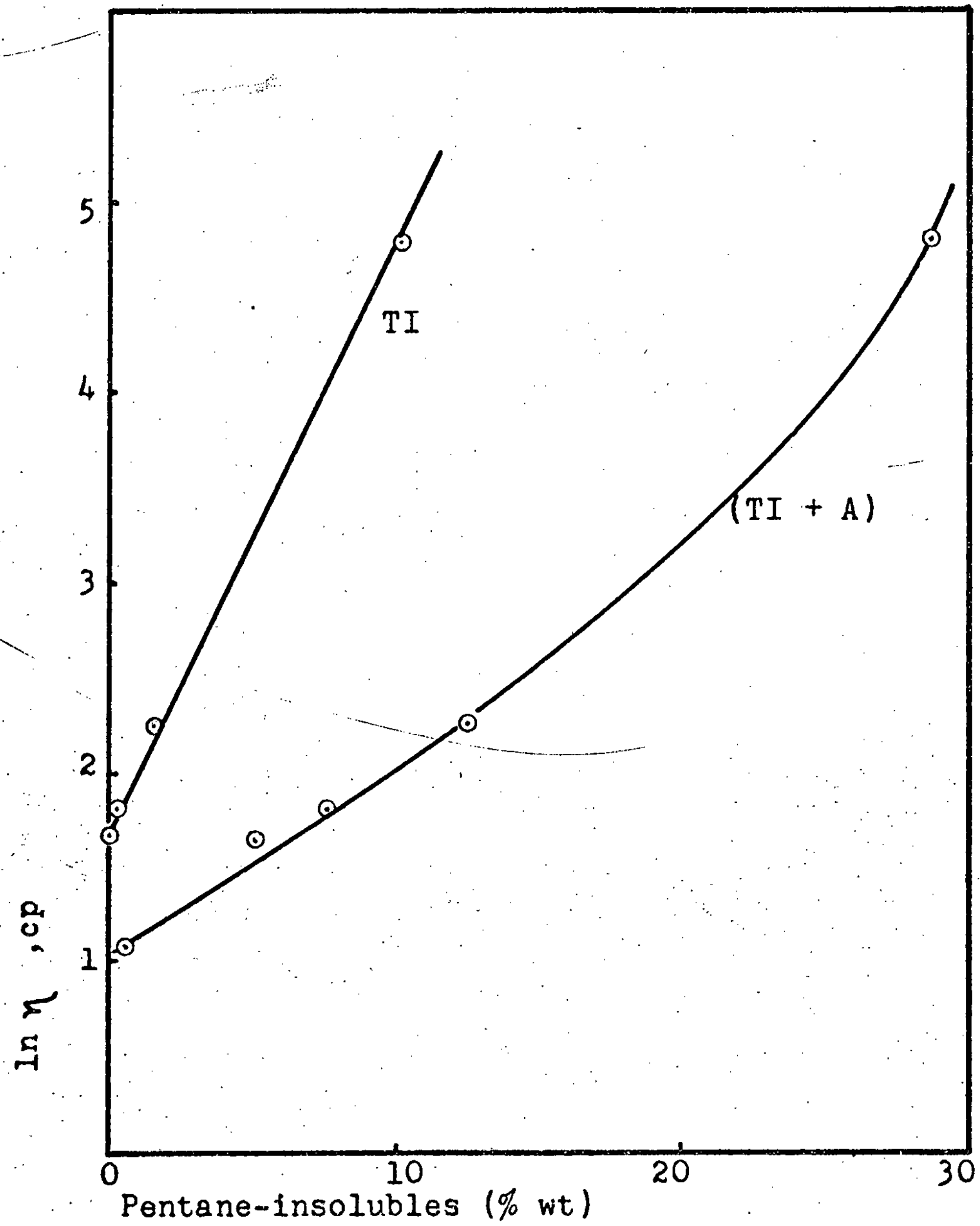

Fig. 4

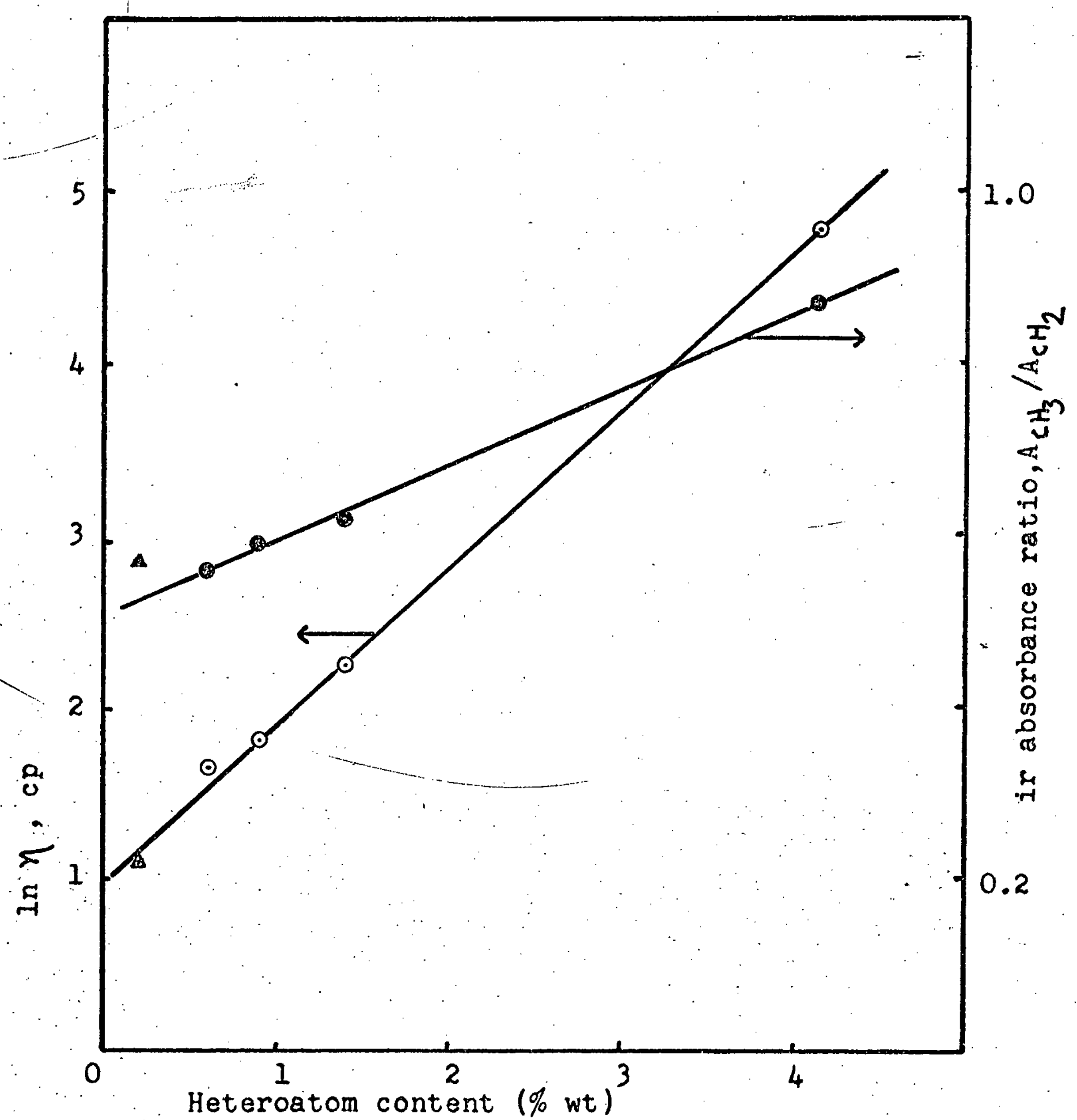
ln η , cp
1
2
3
4
5
0
1
2
3
4
Heteroatom content (% wt)
ir absorbance ratio, A_{CH_3}/A_{CH_2}
0.2
1.0

Fig. 5

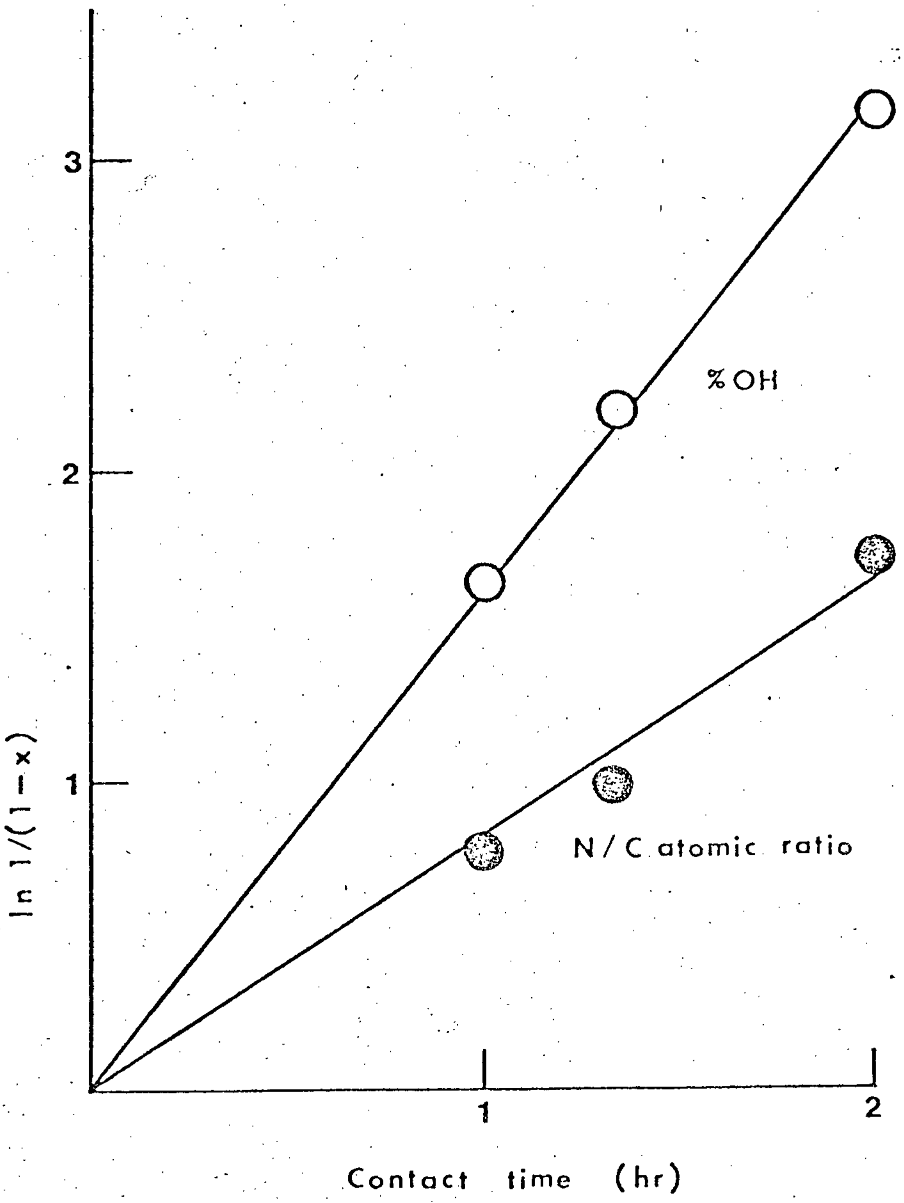

Fig. 6 First-order plot of removal of oxygen and nitrogen

Feed F−1, 672 K

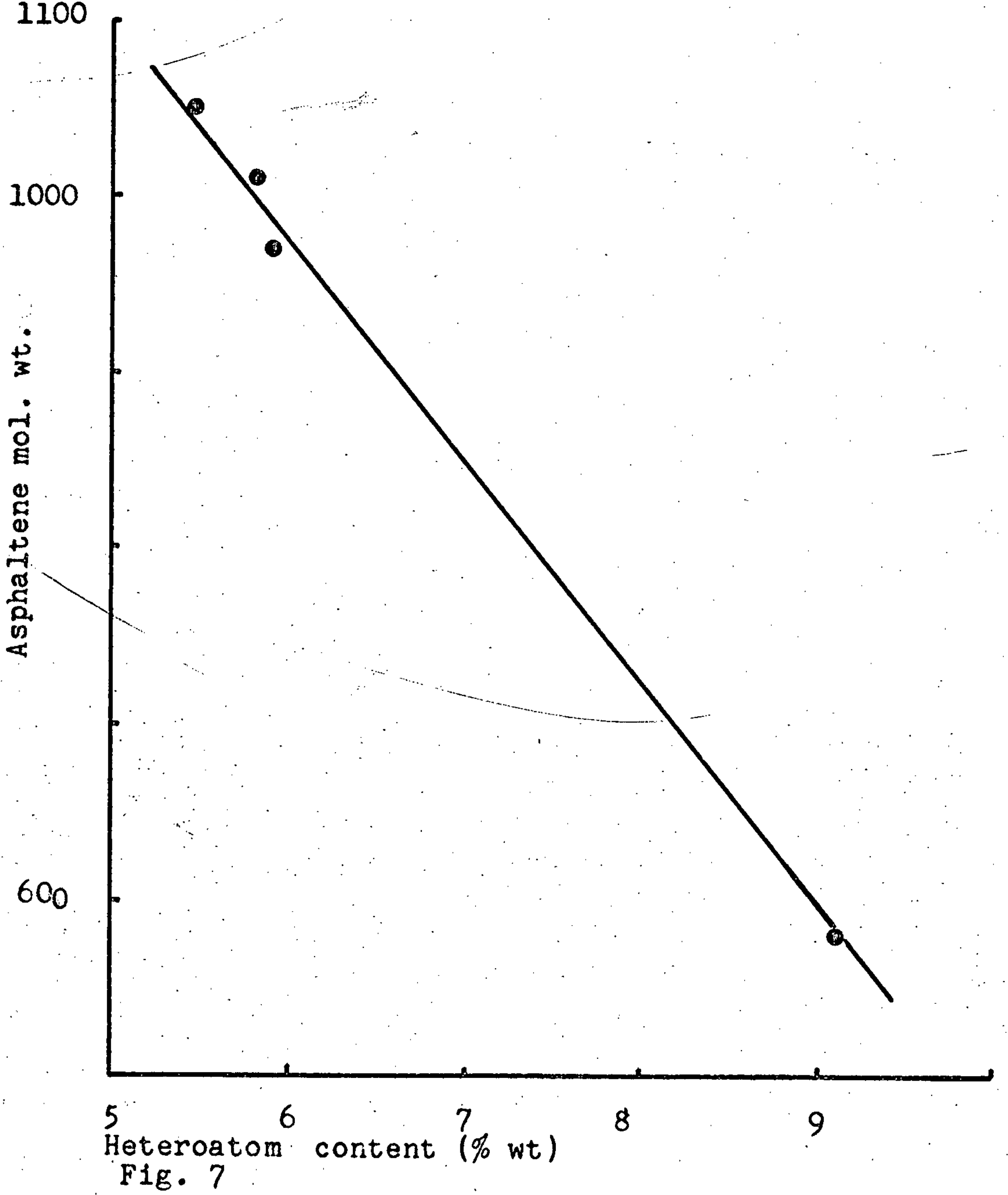
1100
1000
600
Asphaltene mol. wt.
5
6
7
8
9
Heteroatom content (% wt)

Fig. 7

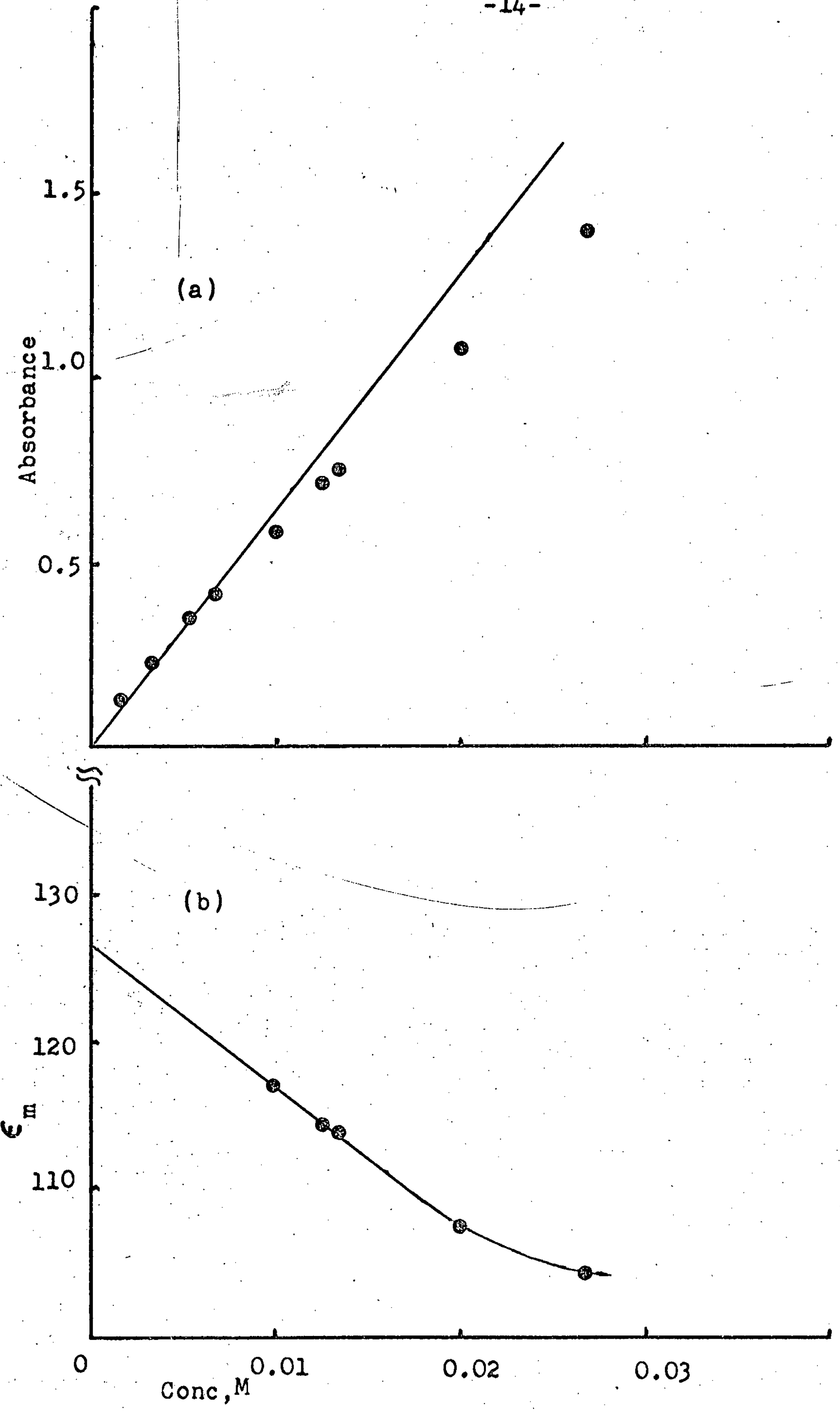
(a)
Absorbance
1.5
1.0
0.5
(b)
ϵ_m
130
120
110
0
0.01
0.02
0.03
Conc,M

Fig.8