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A Study of the Color of Coal Liquids. II. Involvement of Light, Oxygen, Phenols, and Aromatic Amines in Formation of Colored Materials from Wandoan-Coal-Derived Liquids

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Triggering materials responsible for coloring of coal liquids have been searched by comparing the structures of the colored materials derived from the neutrals, acids, and bases of the coal liquid and the nitrogenous model compounds. Basic constituents of the coal liquid are most prone to photooxidation and afford colored materials of higher molecular weight and stronger absorption in the visible region. Model compound studies suggest that they are predominantly formed in the photoinduced oxidative coupling of aromatic amines.

It has already been reported in our preceding paper that a 10 to 20-fold increase is observed in the contents of nitrogen and oxygen for the colored materials separated from the degraded Wandoan-Coal-derived liquids, compared with those of the fresh sample oils.[1] It has also been shown that they have wider absorption range from the UV to visible region and abound in the constituents of large molecular sizes.

These results further prompted us to separate neutrals, acids, and bases from the fresh sample oils and to investigate their reactivities toward oxygen and/or light. Model compounds were also photooxidized in order to disclose triggering materials responsible for coloring of the coal liquids. The structures of their photooxygenated products were compared with those derived from the constituents of the coal liquids.

In this paper, we present that the above colored materials are principally formed in the oxidative coupling of aromatic amines, minor components of coal liquids.

Experimental

The coal liquid samples used were the kerosene (bp 180—240 °C) and light oil (bp 240—340 °C) fractions of the coal liquid produced from Wandoan-Coal in the 1 t/d PDU of Sumitomo Metal Corporation's. The kerosene and light oil fractions were separated into neutrals, acids, and bases according to the procedure shown in Fig. 1 after the removal of the colored materials by vacuum distillation. The colored materials with the strongest absorption in the visible region were prepared as the methanol-eluted fractions in chromatographing through a silica-gel column the residues obtained in the vacuum distillation (2 mmHg (1 mmHg=133.322 Pa)) of the above degraded kerosene fraction (≈75 °C) and the light oil fraction (≈145 °C), respectively. The colored materials obtained in the photooxidation of the coal liquid constituents and the model compounds were treated and prepared as well as those derived from the original coal liquids.

All the solvents and the model compounds were commercially purchased. Ethanol and tetrahydrofuran of spectrograde were used as received. The following model compounds were further purified by distillation or recrystallization (purity >99%): *p*-toluidine, 2-aminobiphenyl, 1-naphthylamine, 1,2,3,4-tetrahydroquinoline, diphenylamine, isoquinoline, 1-methylindole, and 2,3-dimethylindole.

In order to trace the structural change of the coal liquid constituents or model compounds caused by aerobic irradiation, light from a 200W super-high-pressure mercury arc (Shimadzu-Bausch-Lomb) through a Toshiba glass filter ($\lambda > 310$ nm) was irradiated externally to ethanol solutions (2.5×10^{-3}% v/v) of the coal liquid constituents or the model compounds in Pyrex cells. For preparation of

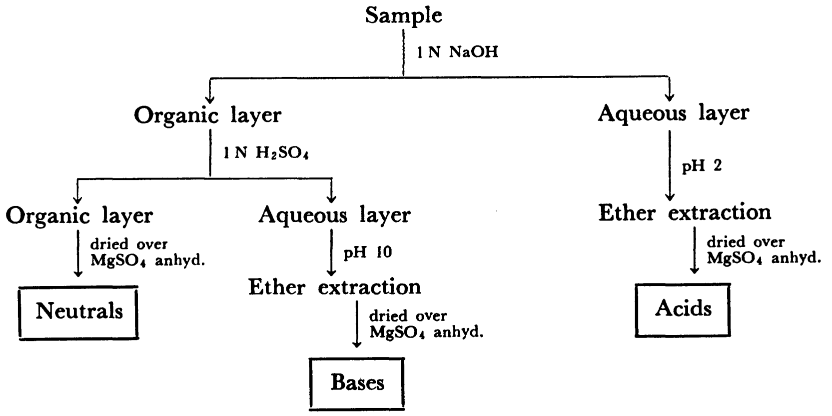

Fig. 1. Scheme for separation of coal liquids.

Table 1. Abbreviations of Coal Liquid Components and Colored Materials

K	Kerosene fraction.	NK	Neutrals of K.
Ak	Acids of K.	BK	Bases of K.
CK	Colored materials derived from K.		
CAK	Colored materials derived from AK.		
L	Light oil fraction	NL	Neutrals of L.
AL	Acids of L.	BL	Bases of L.
CL	Colored materials derived from L.		
NA	Colored materials derived from 1-naphthylamine.		
TOL	Colored materials derived from *p*-toluidine.		
THQ	Colored materials derived from 1,2,3,4-tetrahydroquinoline.		
MI	Colored materials derived from 1-methylindole.		
DMI	Colored materials derived from 2,3-dimethylindole.		

Table 2. Composition of Kerosene and Light Oil Fractions

Component	Kerosene	Light oil
Neutrals	83.6%	85.7%
Acids	14.8	11.2
Bases	1.6	3.1

Table 3. Elemental Analyses of Kerosene and Light Oil Components

	C	H	N	O(diff.)
K	88.2%	9.2%	0.21%	1.9%
NK	90.07	9.52	<0.1	0.41
AK	78.34	8.10	0.14	13.42
BK	81.09	8.26	8.93	1.72
L	89.2	8.3	0.47	1.7
NL	88.76	8.67	<0.1	2.57
AL	80.97	8.68	0	10.35
BL	82.04	8.20	8.06	1.70

the photooxygenated products, light from a 400W high-pressure mercury arc (Riko Kagaku) through a 75% aqueous $NaNO_2$ solution was irradiated externally to the above sample solutions (λ>400 nm).

The UV spectra were recorded on a JASCO RC-200. Ethanol was used as solvent. The gel permeation chromatograms were obtained on a Dupont 830 liquid chromatograph equipped with a column of HSG 15+20. Tetrahydrofuran was used as carrier. The IR spectra were taken on a Shimadzu IR-420 infrared spectrophotometer.

Results and Discussion

Table 1 summarizes the abbreviations of the coal liquid components and the colored materials. Table 2 shows the chemical compositions of the kerosene and light oil fractions. Both oils contain almost the same amounts of neutrals and acids. Bases occupy only 1.6 and 3.1 weight% of each oil. Table 3 shows the elemental analyses of the kerosene fraction and the light oil fraction. These data show that nitrogen and oxygen in coal liquids are concentrated into bases and acids, respectively. Comparison of the two bases by IR confirmed that the absorption ascribed to the pyrrolic N–H stretching band can be observed at 3480 cm^{-1} for BK,[2] while the absorption of basic N–H are stronger for BL. Difference in the chemical compositions between BK and BL affects the amounts and chemical structures of the colored materials. This point will be discussed later. Absorptions ascribed to the phenolic O–H stretching band can be observed at around 3600 cm^{-1} for both of AK and AL, and they cannot be differentiated by IR.

Mechanism for Coloring of Coal Liquids. Mechanisms for oxidative degradation of coal liquids can be classified into two reaction modes as shown in Fig. 2. One is oxygen incorporation, and the other is oxidative coupling. The former reaction can be exemplified as the decomposition of hydroperoxides produced in the autoxidation of hydrocarbons, affording carbonyl compounds and alcohols. This reaction proceeds under ordinary storage conditions since the colored materials obtained contain much oxygen.[1] However, it is improbable that this reaction is responsible for formation of the colored materials with strong absorption in the visible region. On the other hand, the latter reaction affords compounds with extended conjugated systems from phenolics and aromatic amines. For example, oxidative dimerization of substituted phenols give diphenoquinones. These compounds absorb at longer wavelengths (λ_{max}=420 nm) with stronger absorption (ε=70800 M^{-1} cm^{-1}) than benzoquinones (λ_{max}=400 nm).[3] Photooxidation of 2-naphthylamine affords dibenzophenazine,[4] which can be expected to absorb at longer wavelengths than phenazine ($\lambda_{abs}\approx$440 nm). The colored materials of large molecular sizes occupy only a little less than 1 weight% of the degraded coal liquids, and these colored materials could be formed in the oxidative coupling of polar compounds at room temperature.

Structural Change Accompanied by Photooxidation of the Coal Liquid. Seven samples such as L, NL, AL, BL, (NL+AL) (5.6:1.0 weight ratio), (NL+BL) (50:1.0 weight ratio), (AL+BL) (9.3:1.0 weight ratio) were stored in the dark under oxygen at room temperature for 5 d, but all the samples were colorless and no change was observed in their UV spectra. These results show that each component of the coal liquid is rather stable under oxygen without light. Then, all the above samples were irradiated under air. Figure 3a shows that the absorption of NL at longer than 300 nm grows with irradiation time and it levels off after 8 h. The original light oil fraction showed almost the same UV spectral change as NL. As Fig. 3b shows, increase in the absorbance in the visible region was only small on irradiating AL under air. On the other hand, BL was extremely unstable under the photooxidation conditions. As Fig. 3c shows, aerobic irradiation decreased its absorption at 280—320 nm and increased that at longer than 320 nm. The increasing rate for the absorption at 400 nm is 4 to 8 times larger for BL than for NL and AL. The UV spectrum obtained by irradiating BL under argon for 7 h (dotted line in Fig. 3c) shows that BL is sensitive to anaerobic irradiation while the absorption at longer wavelengths is much weaker than under air. These results reveal that BL is most prone to structural change induced by irradiation and that oxygen promotes the formation of chromophores with the absorption from the UV to visible region. Furthermore, on 6 h irradiation, BL comes to take almost the same spectral pattern as that of CL(Fig. 3c). All of these results suggest that BL is predominantly involved in formation of colored materials with stronger absorption in the visible region. Mixing of AL and BL had no synergistic effect on increasing the rate of the absorbance at 400 nm. This finding suggests that acid-base interaction is negligible in photoinduced formation of colored materials.

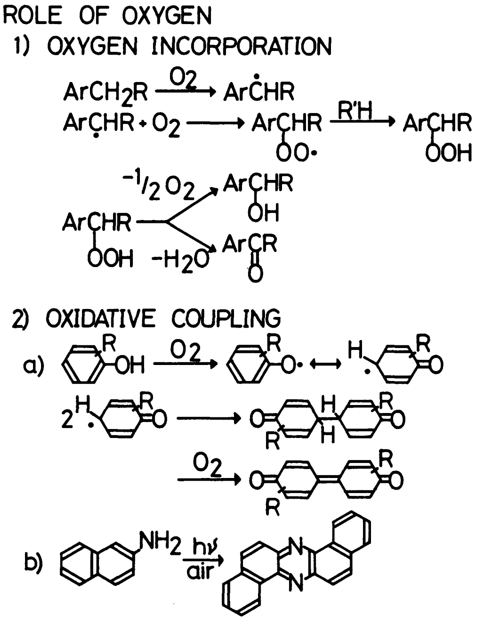

Fig. 2. Reaction modes for oxidation of coal liquids.

Comparison of Kerosene and Light Oil Fractions. The UV spectrum of the kerosene fraction remained unchanged on aerobic irradiation for 20 h. This fact coincides well with the fact that the kerosene fraction is more stable than the light oil fraction under ordinary storage conditions. NK and AK showed a similar UV spectral change on aerobic irradiation, but their absorption range did not extend to wavelengths longer than 350 nm. Aerobic irradiation of BK shifted the absorption range up to visible region, but the increasing rate of the absorbance at 400 nm was only 1/5 of that for BL. In this case, oxygen did not promote formation of colored materials. It is interesting that such difference was observed in the increasing rate of the absorption at 400 nm for pyrrole-rich BK and amine-rich BL.

Structural Change Accompanied by Photooxidation of Nitrogen Compounds. Predominant involvement of nitrogen compounds has been suggested in coloring of coal liquids, and the following model compounds have been chosen and subjected to photooxidation by taking account of the GC-MS analyses of the coal liquids used and the product analyses of the polar compounds contained in the SRC-II coal liquids.[5]: *p*-toluidine, 1-naphthylamine, 1,2,3,4-tetrahydroquinoline, diphenylamine, and iso-

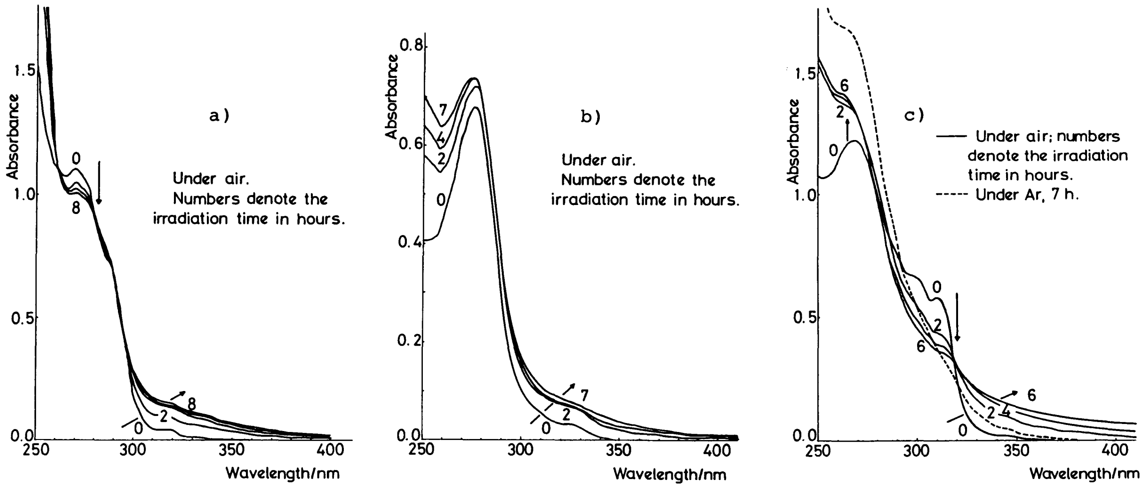

Fig. 3. UV spectral change induced by aerobic irradiation in ethanol.
a): NL, b): AL, c): BL.

quinoline. As to pyrrole-type nitrogen heterocycles, 2,3-dimethylindole and 1-methylindole have been chosen. The former compound has been reported to be deleterious in deposit formation in oil shale.[6] 1-Methylindole has been chosen as one of the *N*-alkylindoles for comparison of its reactivity toward photooxidation with that of 2,3-dimethylindole. Figure 4 shows the UV spectral changes of isoquinoline, diphenylamine, 1-naphthylamine, and 2,3-dimethylindole induced by aerobic irradiation, respectively. Any of them disappeared within 6 h, but the pattern of UV spectral change is quite different from each other. In the case of isoquinoline, no absorption can be observed at longer wavelengths. The increasing rate of the absorbance at 400 nm is 6 times larger for 1-naphthylamine and 2,3-dimethylindole than for diphenylamine. It is also interesting to note that aerobic irradiation of 1-naphthylamine for 3 h gives almost the same UV spectral pattern as that of CL.

Wright et al.[7] have alreadv pointed out that under air at 100 °C, anilines and indoles are the most reactive among the nitrogen compounds contained in the SRC-II coal liquid, and that their concentrations decrease to 1.4 and 11% after 112 d, respectively. Our results clearly show that the above compounds are photosensitive even at room temperature, forming colored materials more rapidly than aromatic secondary and tertiary amines under air.

Table 4. Weight Ratio of Colored Materials(CM)[a] to Substrate

Substrate	CM/Subst.
AK	0.16
BK	0.43
p-Toluidine	0.15
1-Naphthylamine	0.50
1,2,3,4-Tetrahydroquinoline	0.24
1-Methylindole	0.43
2,3-Dimethylindole	1.42

a) Prepared as the residue in the vacuum distillation of the reaction mixture obtained in the photooxidation of each sample in EtOH for 5 h.

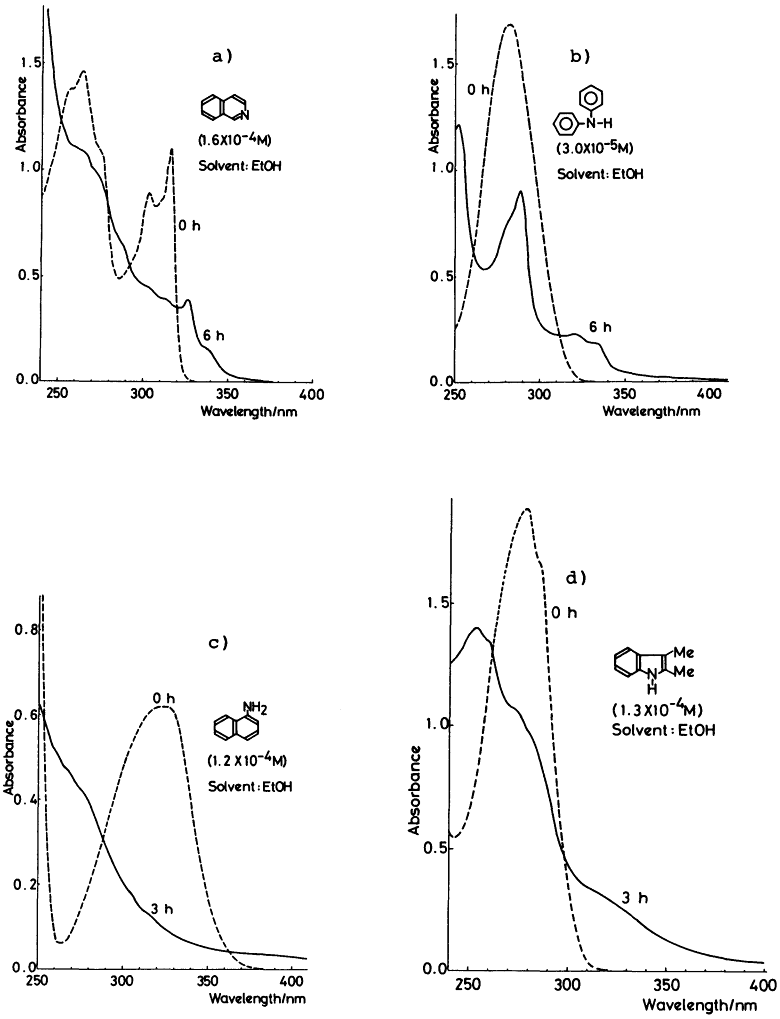

Fig. 4. UV spectral change induced by aerobic irradiation in ethanol(1 M = 1 mol dm^{-3}).
a): Isoquinoline, b): diphenylamine, c): 1-naphthylamine, d): 2,3-dimethylindole.

Gravimetrical Analysis of the Colored Materials. Next, the structures of the colored materials were compared, taking AK, BK, *p*-toluidine, 1-naphthylamine, 1-methylindole, 2,3-dimethylindole, and 1,2,3,4-tetrahydroquinoline as substrate. Table 4 summarizes the gravimetrical analyses of the colored materials. Minor component BK affords more colored materials than AK. Among the model compounds, an unusually large amount of colored materials is obtained from 2,3-dimethylindole, suggesting considerable oxygen uptake. Among the primary amines, 1-naphthylamine seems to give more colored materials than *p*-toluidine. It may reflect their different reactivities toward oxidative coupling. Figure 5 shows the UV spectra of the colored materials obtained in the photooxidations of AK, BK, and the model compounds. CBK is stronger in absorption in the visible region than CAK, and the UV spectrum of the former is more similar to that of CK. Absorption intensity at 400 nm of the colored materials derived from the model compounds decreases in the order of NA>TOL>THQ>DMI>MI.

Comparison of Figs. 4 and 5 indicates that among the nitrogen compounds, aromatic primary amines are most responsible for coloring of coal liquids.

Elemental Analysis of the Colored Materials. Table 5 shows the results of the elemental analyses of the colored materials. CAK contains almost no nitrogen, indicating that acids contribute to a lesser extent for coloring of coal liquids. The oxygen content of CK is larger than that of CL by about 10%. It is most likely that this was induced by the different chemical compositions of pyrrole-rich BK and amine-rich BL. In fact, the colored materials derived from the indoles tend to contain more oxygen than those from the amines by 4.6—15%.

IR Analysis. Figure 6 shows the IR spectra of the colored materials. Absorption of conjugated carbonyls can be observed at around 1680 cm^{-1} for CBK and its spectral pattern coincides well with that of CK.

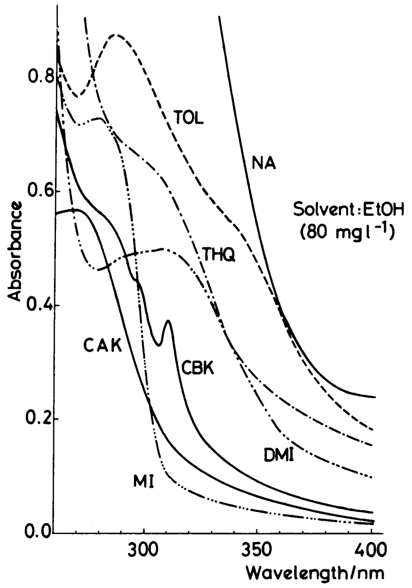

Fig. 5. UV spectra of the colored materials (concn: 80 mg l^{-1}).

Table 5. Elemental Analyses of Colored Materials(CM)$^{a)}$

CM	C	H	N	O(diff.)
CK	60.66%	7.54%	4.91%	26.89%
CAK	61.13	6.83	0	32.04
CBK	69.53	6.91	7.72	15.84
CL	68.65	8.82	5.57	16.96
TOL	73.48	7.04	9.30	10.18
NA	79.81	4.73	7.45	8.01
THQ	75.76	6.85	8.54	8.85
MI	70.60	6.69	7.97	14.74
DMI	64.26	5.93	6.78	23.03

a) Dried in vacuo at room temperature for 6 h.

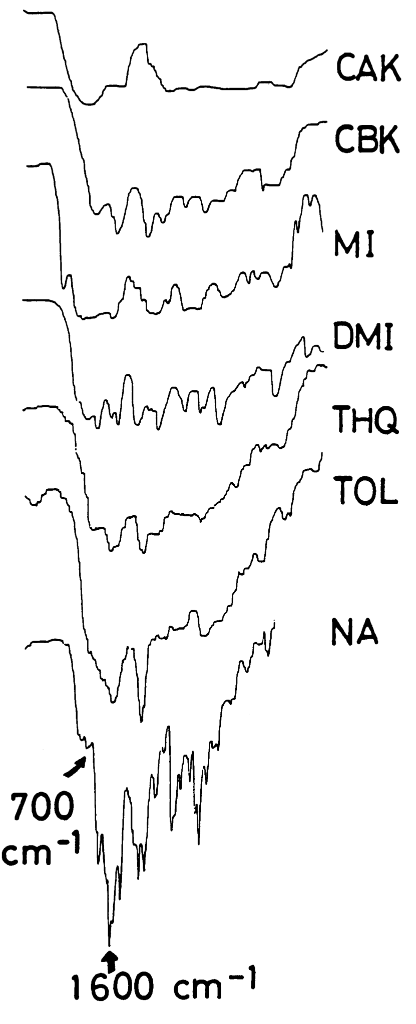

Fig. 6. IR spectra of the colored materials.

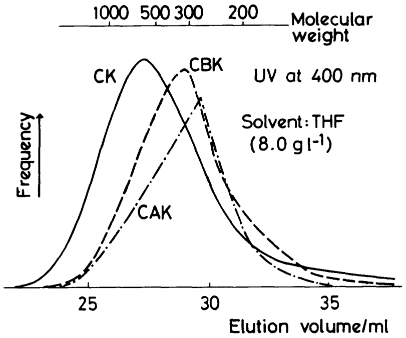

Fig. 7. GPC profiles of the colored materials derived from the kerosene fraction (concn: 8.0 g l^{-1}, detected with UV at 400 nm).

On the other hand, the carbonylic absorption of CAK shifts to higher wavenumbers. As to the model compounds, relative intensity of the absorption at 1680 cm^{-1} to that at 1600 cm^{-1} decreases in the order of MI>DMI>THQ>TOL>NA. This order is reversed against that of the UV absorption intensity at 400 nm (see Fig. 5). This fact clearly shows that the degree of photooxygenation does not parallel formation of chromophores with absorption at longer wavelengths. Therefore, it is most likely that oxidative coupling of aromatic primary amines afford colored materials of higher molecular weight with stronger absorption in the visible region.

GPC Analysis. Figures 7 and 8 show the GPC profiles of the colored materials. As to the colored materials derived from the coal liquids, nominal peak molecular weights of CK, CBK, and CAK are 580, 330, and 250, respectively (polystyrene standards). CBK is more similar to CK than CAK in molecular weight distribution. Among the colored materials derived from the model compounds, the scan of DMI extends to an area of the most highest molecular weight with a shoulder at nominal molecular weight 600. Oxidative trimers and tetramers could be formed. The molecular weight distributions of NA and TOL also suggest the formation of the constituents with higher molecular weight in the cases of 1-naphthylamine and *p*-toluidine. The scan of THQ has a wide molecular weight distribution with two peaks in the area of lower molecular weight. MI is considered to contain only a small amount of high molecular weight compounds.

All of these results show that the colored materials with the stronger absorption in the visible region tends to be of higher molecular weight.

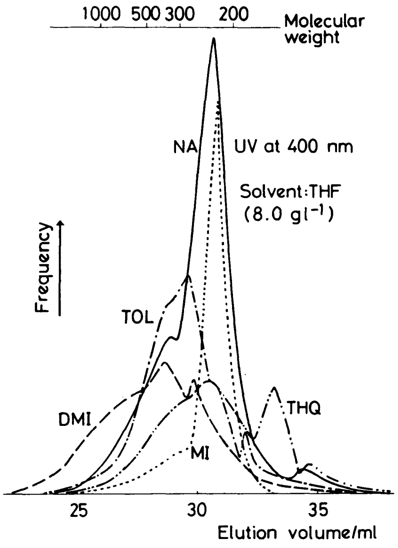

Fig. 8. GPC profiles of the colored materials derived from the model compounds (concn: 8.0 g l^{-1}, detected with UV at 400 nm).

In this paper, we have shown that coloring of coal liquids is induced by light and greatly promoted by oxygen. Bases in coal liquids are most liable to photooxidation and affords colored materials of higher molecular weight and stronger absorption in the visible region than neutrals and acids. Among the nitrogen compounds, aromatic primary amines are most deleterious and the above colored materials could be afforded predominantly in their oxidative coupling although they are only minor components in coal liquids.

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