

FTIR EXTERNAL REFLECTION STUDY OF SURFACE LAYERS ON COAL

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ABSTRACT

An infrared reflection-absorption spectroscopy (IRAS) technique has been developed to study the structure of adsorbed surfactant layers on coal. Owing to the optical properties of coal, negative as well as positive absorption bands are observed in the recorded spectra which depend on the angle of incidence (θ) and the polarization of the incident radiation. Theoretical calculations make it possible to predict the changes in absorbance with θ and polarization. These changes are a function of the optical properties of the coal and the adsorption layer. The application of the IRAS method to studies of the adsorption layer is presented for several systems, i.e., adsorption of sodium laurate and a nonionic surfactant on coal. In addition, the oxidation layer produced during low-temperature oxidation of coal has been investigated. The results obtained indicate that the IRAS method has an enormous potential for use in determining the structure of an adsorption layer on coal after different treatments.

INTRODUCTION

Systematic studies of coal structure have been carried out in recent years. Since coal is a mixture of various organic and inorganic compounds which are non-crystalline and mostly insoluble, the standard analytical methods of structural determination are of little use. Thus, spectroscopic techniques such as transmission infrared (1,2) and NMR (3,4) are usually applied to characterize the structure of coal and its derivative products.

In most coal cleaning processes, such as froth flotation, the coal surface properties play an important role. Diffuse reflectance (DR) (5,6) and attenuated total reflection (ATR) (7,8) in infrared, and x-ray photoelectron spectroscopy (XPS) (9) are very surface-sensitive techniques and, hence, have been used to study the coal surface. Nevertheless, the study of the surface structure of coal is very difficult because the recorded spectra are the summation of the spectra of heterogeneous bulk coal and those of the surface layers.

In the present paper, the structure of surface layers on coal has been studied using the infrared reflection-absorption spectroscopy (IRAS) technique. To date most of the IRAS studies have been done to study metals surfaces (10-13) which strongly reflect the incident beam. Coal, on the other hand, shows low reflectivity relative to metals, and interpretation of the recorded spectra in terms of an oriented surface structure is more complicated. However, the theoretical analysis presented in this paper makes it possible to predict the changes in the absorbance of polarized light, which makes it easier to interpret the recorded spectra. Moreover, as shown in this work, the IRAS method provides a means of distinguishing the spectrum of the thin surface layer from that of the substrate, and provides a means of examining the flat surface of a large coal slab directly after treatment.

EXPERIMENTAL

Preparation of Thin Layer

Coal slabs 10x30 mm in size were cut by means of a diamond wheel using water as the cooling medium. The coal sample was from a Pittsburgh seam in West Virginia. Each specimen was wet-polished with emery paper (No. 600 and 1200) and washed in water in an ultrasonic bath.

For the study of adsorbed layers, the samples were immersed into 100 ml of 2×10^{-4} M solution of nonylphenolpolyethyleneglycol ether with a pH of 7.2 ± 0.2 for 5 minutes or 12 hours, and for 1 hour in 100 ml of 10^{-3} M sodium laurate with a pH of 6.0 ± 0.2 . After adsorption, the samples were removed from solution, dried at room temperature and placed into the FTIR spectrometer to record the spectra.

Low-temperature oxidation of the coal specimens was carried out at 125°C in air for a period of 24 hours. The oxidized sample was examined spectrometrically and then treated with barium hydroxide (0.05 M) to change the surface carboxyl groups to ionic form. The spectrum of the sample was recorded again after this treatment.

The reagents used were nonylphenolpolyethyleneglycol ether (Tergitol NP-9), a nonionic surfactant obtained from Union Carbide Corporation, with an average of 9 ethylene glycol groups per molecule. The sodium laurate was obtained from Pfaltz and Bauer, Inc. Both reagents were used as received with no further purification. Double distilled water produced in an all-glass still was used in all the experiments.

Measurement

The infrared spectra were recorded on a Perkin-Elmer Model 1710 FTIR spectrometer with an MCT detector using an external reflection attachment (Spectra Tech, Inc) with a single reflection. A wire grid polarizer (Harrick Scientific Company) was placed before the sample and provided polarization selection. The spectra were taken at 4 cm^{-1} resolution by co-adding 64 scans in the $4000\text{--}500 \text{ cm}^{-1}$ region. The unit of intensity is given in terms of $-\log(R/R_0)$, where R and R_0 are the reflectivities of the samples after different treatment and freshly exposed coal, respectively. The transmission spectra of lauric acid and coal in KBr pellets, and chloroform solution of Tergitol NP-9 were prepared and measured in the standard way.

Calculation of Reflection-Absorbance

Figure 1 shows a model of the three-phase system investigated and the interaction of an electromagnetic wave with the system. The optical properties of each phase are characterized by the complex refractive index $\hat{n}_j = n_j + ik_j$, where n_j is the real refractive index and k_j is the absorption constant. The thin film has a thickness, d_2 .

The theoretical calculation of the intensity of an absorption band in the reflection spectra is described in several papers (14-17). In this paper, a recently reported (17) theoretical analysis was used. The calculation was made for the following data: for ambient (air) $n_1 = 1.0$ and $k_1 = 0$; for the adsorption layer of lauric acid, $n_2 = 1.5$ and $k_2' = 0.3$ at 1705 cm^{-1} ; and for the adsorption layer of a nonionic surfactant, $n_2 = 1.5$ and $k_2'' = 0.38$ at 1103 cm^{-1} . The thickness of the adsorbed monolayer was assumed to be 5×10^{-9} m.

The optical constants of coal were calculated to be $n_3 = 2.05$ and $k_3 = 0.02$ at 1800 cm^{-1} . These latter data were obtained on the basis of transmission spectra of KBr pellets of coal and measurements of the ratio of reflectivities of p- and s-polarization at different angles of incidence. These particular optical data for the three phases are only approximations of the real values and were chosen to simulate the optical properties of adsorption layers on coal.

RESULTS AND DISCUSSION

Adsorption of Nonylphenolpolyethyleneglycol Ether on Coal

The infrared transmission spectra of the coal and nonionic surfactant used in this study are shown in Figures 2 and 3, respectively. Figure 4 shows the reflection spectra of the thin surface film of Tergitol NP-9 on the coal after 12 hours of treatment time in a $2 \times 10^{-4}\text{ M}$ solution. Since the absorbance was measured in terms of $-\log(R/R_0)$, any spectrum recorded showed the effect of the treatment. It should also be noted that no spectrum is recorded after only 5 minutes of treatment, indicating slow adsorption kinetics. It is shown that the intensity of the absorption bands vary with the polarization and the angle of incidence. The negative absorption bands observed in the recorded spectra are not unique for the system studied in the present work. Others were theoretically predicted (14,18) for low-absorption substrates and observed experimentally for water (16) and cuprous sulfide (17) substrates.

In order to explain the changes in IRAS spectra observed, theoretical calculation of the absorbance for the system has been carried out, and the results are shown in Figure 5. The solid lines represent the changes of absorbance (A) at 1100 cm^{-1} , as a function of the angle of incidence for both s-polarization (A_{\perp}) and p-polarization (A_{\parallel}). This calculation was performed for an isotropic layer of the nonionic surfactant. The experimental points obtained after 12 hours of adsorption from the $2 \times 10^{-4}\text{ M}$ solution are shown as circles and crosses for s- and p-polarization, respectively. In general, a reasonable agreement between the experimental results and the theoretically predicted values is observed. For s-polarization, negative absorption bands are predicted and, in fact, only negative bands are observed. For s-polarization which has electric field components which are only parallel to the interface plane (Figure 1), only those molecular groups that have transition moment components parallel to the substrate surface can interact with the incidence radiation, allowing absorption to be observed. The difference between the relative intensity ratios of the observed bands in IRAS (Figure 4, s-polarization) and transmission spectra (Figure 3) indicates that adsorbed molecules are oriented on the surface of coal.

The same conclusion can be obtained from the spectroscopic results for p-polarization. An intense absorption band is observed at 1103 cm^{-1} for p-polarization and at an 80-degree angle of incidence, while the calculated values of absorbance, A , under these conditions is close to zero (Figure 5). This discrepancy can be explained by consideration of the two components, $E_{\parallel x}$ and $E_{\parallel z}$, of p-polarization of the incident beam (Figure 1). The theoretical calculation of the $A_{\parallel x}$ and $A_{\parallel z}$ components has been done in the same way as reported recently (17), and the results are shown in Figure 5 as dashed lines. According to this calculation, an intense positive absorption band should be obtained at an angle of incidence of 80 degrees for molecular groups which have transition moments parallel to the surface of the substrate. Since the absorption band at 1103 cm^{-1} can be assigned to (C-O-C) stretching, the presence of this intense absorption band in the recorded spectra indicate that the polyethylene glycol part of the adsorbed molecule is positioned parallel

to the surface of the coal. However, the nonylphenol unit of the adsorbed molecule is inclined to the plane of substrate.

Thin Layer of Lauric Acid on Coal

The adsorption was performed from 10^{-3} M solution of sodium laurate at pH 6.0 ± 0.2 . Under these conditions, the reagent exists in solution as lauric acid ($pK=4.7$). It was found that a significant part of surfactant was deposited on the coal surface from a thin film of solution during drying of the sample.

The reflection spectra of the thin film of lauric acid on coal are shown in Figure 6. Theoretical calculations performed for the coal-lauric acid system (Figure 7) allow an explanation of the results obtained in a similar way as was discussed for the non-ionic surfactant. Generally good agreement is observed between the experimental data and the theoretical analysis. This agreement also suggests that the lauric acid molecules in the thin layer on the surface of coal are randomly oriented. Data presented in Figure 7 was calculated for a thin layer of 50 \AA . Since the experimental intensities for the absorption bands are nearly 5 times higher than those calculated, the thickness of the lauric acid could be considered to be as thick as 250 \AA . The real thickness of the lauric acid layer is probably much thinner. Various reasons for the discrepancy between real and theoretically calculated values have been discussed recently (17).

Low-Temperature Oxidation of Coal

During the oxidation, the following changes in the reflection spectra (Figure 8) are observed: the bands at 1700 , 1555 and 1180 cm^{-1} appear and the intensity of the band at 1440 cm^{-1} decreases. These results indicate that the oxidation products, such as carbonyl and carboxyl groups (band at 1700 cm^{-1}), ionized $-\text{COO}^-$ groups (band at 1550 cm^{-1}) and C-O groups in ether, alcohol or phenyl (band at 1180 cm^{-1}), are formed while the aliphatic groups (band at 1440 cm^{-1}) present in the coal are oxidized.

The band at 1700 cm^{-1} is markedly distorted due to the anomalous dispersion of the refractive index of the oxidation products. Notably, band shape distortion when using the reflection method has also been reported (19).

For p-polarization at a 70-degree angle of incidence, positive absorption bands in the spectrum are observed. However, for the other measurement conditions, i.e., different angles and polarization, only negative absorbances are recorded (Figure 8). Hence, for oxidized coal samples, the negative and positive absorption bands appeared at the same angle of incidence and polarization as was found for the adsorption layer from solution (Figures 4 and 6).

The barium hydroxide-treated oxidized coal sample shows intense absorption bands at 1550 and 1400 cm^{-1} (Figure 9). These bands can be assigned to asymmetric and symmetric stretching vibrations of the COO group, respectively. A notably strong increase in the intensities of these bands is due to the change of the $-\text{COOH}$ groups to the ionized $-\text{COO}^-$ form.

A significant increase in the intensity of the band at 1555 cm^{-1} after oxidation (Figure 8) relative to the band at 1440 cm^{-1} could indicate that the ionic groups $-\text{COO}^-$ which are formed during the oxidation process are oriented with both of the oxygen atoms oriented toward the ambient (air).

CONCLUSIONS

The infrared reflection-absorption spectroscopy (IRAS) method has been developed for characterizing the surface layer on coal. The absorbance is shown to be a function of the optical properties of the coal and the surface layer, as well as of the angle of incidence and the polarization of the incident beam.

The results obtained show that the IRAS method makes it possible to determine both the chemical nature and the structure of the adsorbed layers on the coal substrate.

REFERENCES

1. Painter, P. C., Starsinic, M. and Coleman, M. M., 1985. in Fourier Transform Infrared Spectroscopy, Vol. 4 (J. R. Ferraro and L. J. Basile, Eds.), Academic Press, New York, p. 169 and references therein.
2. Gethner, J. S., 1987. Appl. Spectrosc., 41:50.
3. Fredericks, P. M., Warbrooke, P. and Wilson, M. A., 1983. Org. Geochem., 5:89.
4. Painter, P. C., Kuchn, D. W., Starsinic, M., Davis, A., Havens, J. R. and Koenig, J. L., 1983. Fuel, 62:103.
5. Fuller, M. P., Hamadeh, I. M., Griffiths, P. R. and Lowenhaupt, D. E., 1982. Fuel, 61:529.
6. Smyrl, N. R. and Fuller, E. L., 1987. Appl. Spectrosc., 41:1023.
7. Mielczarski, J. A., Denca, A. and Strojek, J. W., 1986. Appl. Spectrosc., 40:998.
8. Bubnowskaia, L. M., Popov, W. K. and Rusianova, 1982. Koks i chemia, 5:9.
9. Perry, D. L. and Grint, A., 1983. Fuel, 62:1024.
10. Golden, W. G., 1985. in Fourier Transform Infrared Spectroscopy, Vol. 4 (J. R. Ferraro and L. J. Basile, Eds.), Academic Press, New York, Chapter 8.
11. Swalen, J. D. and Rubolt, J. F., 1985. in Fourier Transform Infrared Spectroscopy, Vol. 4 (J. R. Ferraro and L. J. Basile, Eds.), Academic Press, New York, Chapter 7.
12. Mielczarski, J. A. and Leppinen, J., 1987. Surface Science, 187:526.
13. Liedberg, B., Carlsson, C. and Lundstrom, I. J., 1987. Coll. Inter. Science, 120:64.
14. McIntyre, J. D. E., 1973. in Advances in Electrochemistry and Electrochemical Engineering, Vol. 9 (R. M. Muller, Ed.), Wiley Interscience, New York, Chapter 2.
15. Allara, D. L., Baca, A. and Pryde, C. A., 1978. Macromolecules, 11:1215.
16. Dluhy, R. A., 1986. J. Phys. Chem., 90:1373.
17. Mielczarski, J. A. and Yoon, R. H., 1988. J. Phys. Chem.; submitted.
18. Hansen, W. N., 1970. Symp. Faraday Soc., 4:27.
19. Porter, M. D., Bright, T. B., Allara, D. L. and Kuwana, T., 1986. Anal. Chem., 58:2461.

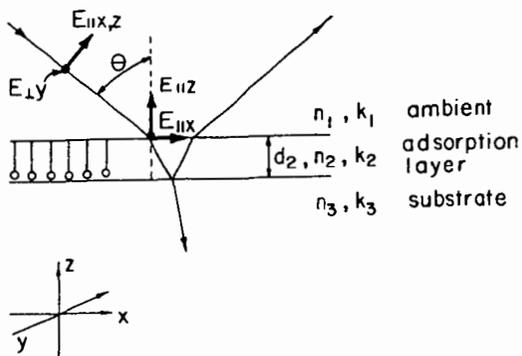


Figure 1. Electric field vectors in a three-phase system. Parallel (p) ($E_{\parallel z}$, $E_{\parallel x}$) and perpendicular (s) ($E_{\perp y}$) components are shown for incident radiation.

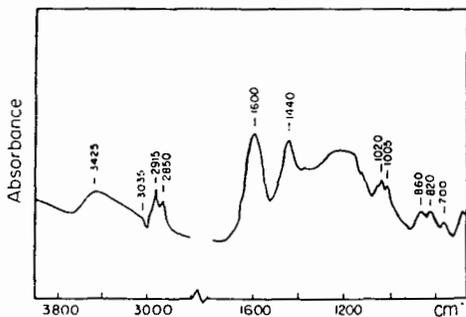


Figure 2. Transmission spectrum of Pittsburgh seam coal.

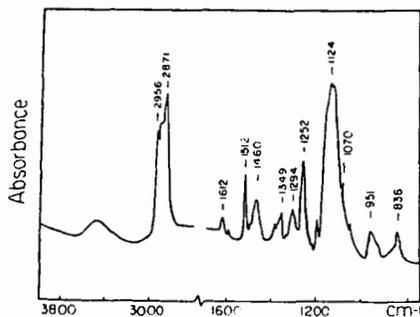


Figure 3. Transmission spectrum of nonylphenolpolyethyleneglycol ether.

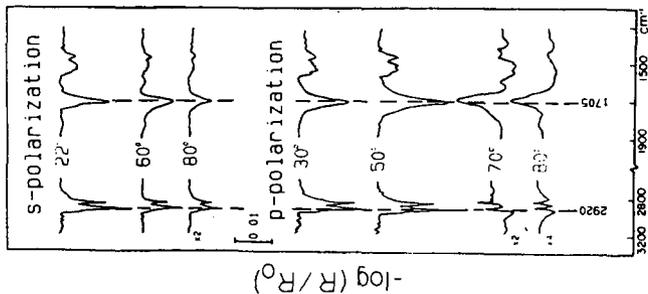


Figure 6. IRAS spectra of lauric acid layer on coal recorded at various angles of incidence with s- and p-polarization.

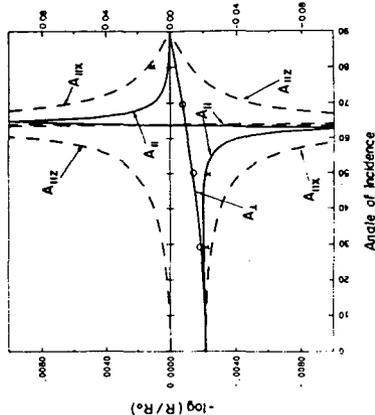


Figure 5. Calculated absorbance for hypothetical layer of nonylphenolpolyethylene glycol ether ($n_2 = 1.5$, $k_2 = 0.36$, $\lambda = 9.09$, $d_2 = 5 \times 10^{-9}$ m) on coal ($n_3 = 2.05$, $k_3 = 0.02$) (solid and dashed lines). Experimental results (note different absorbance scales) shown as circles for s-polarization and as crosses for p-polarization.

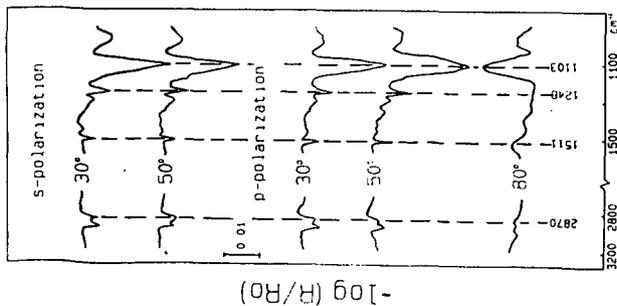


Figure 4. IRAS spectra of the adsorbed layer of nonylphenolpolyethylene glycol ether on coal recorded at various angles of incidence with s- and p-polarization.

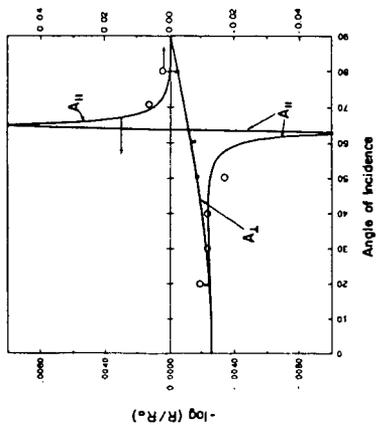


Figure 7. Calculated absorbance for hypothetical layer of lauric acid ($n_2 = 1.5$, $k_2 = 0.3$, $\lambda = 5.85$, $d_2 = 5 \times 10^{-9}$ m) on coal ($n_3 = 2.05$, $k_3 = 0.02$) (solid lines). Experimental results (note different absorbance scales) shown as circles for s-polarization and as crosses for p-polarization.

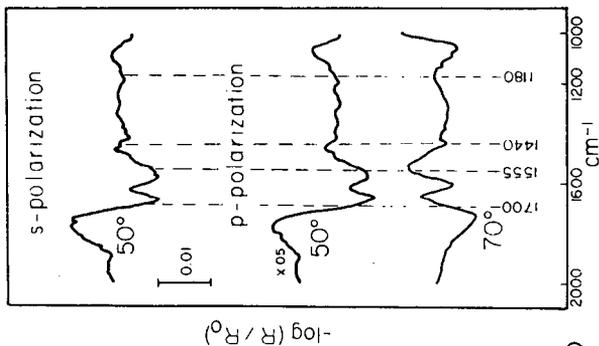


Figure 8. IRAS spectra of low-temperature oxidized coal recorded at different angles of incidence for s- and p-polarization.

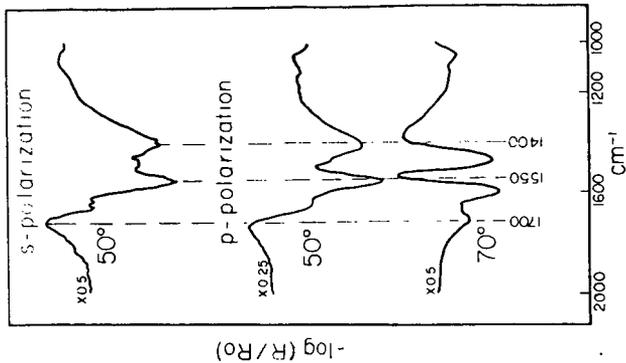


Figure 9. IRAS spectra of barium hydroxide treated oxidized coal recorded at different angles of incidence for s- and p-polarization.