Short communication

EPR characteristics of petrographically complex coal samples from durain and clarain

A.B. Więckowski*, W. Wojtowicz, B. Pilawa

Division of Experimental Physics, Institute of Physics, Faculty of Mathematics, Physics and Technology, Pedagogical University, Plac Słowiański 6, PL-65-069 Zielona Góra, Poland

Received 14 June 1999; received in revised form 30 September 1999; accepted 30 September 1999

Abstract

Electron paramagnetic resonance (EPR) spectroscopy was used to analyse properties of paramagnetic centres systems of the samples separated from two lithotypes of Polish coal (85.6 wt% C). The EPR spectra of the durain samples with a content of 2–22 vol.% exinite, 73–86 vol.% vitrinite and 5–17 vol.% inertinite, and the clarain samples with a content of 3–14 vol.% exinite, 65–90 vol.% vitrinite and 4–32 vol.% inertinite were compared. Three different groups of paramagnetic centres in each of the coal samples were found. The concentration of unpaired electrons and the parameters of the resonance absorption curves: linewidths and g-factor, were determined. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Coal; Lithotypes; Macerals; Electron paramagnetic resonance

1. Introduction

Multicomponent structure of electron paramagnetic resonance (EPR) spectra of coals [1–8] and macerals [7,9–14] was known. The lineshape and EPR parameters of the spectra depended on the degree of coalification and the type of macerals. The abundance of the broad and narrow lines in the total spectra strongly changed for samples with low and high carbon content.

Because of the relatively small differences in g-values of the individual groups of paramagnetic centres existing in coals, the deconvolution of the complex coal EPR spectra is difficult. The broad and narrow components of the EPR spectra of coal samples saturate at low and high microwave powers, respectively. The differences in microwave saturation of these EPR lines were helpful for separation of the components of the EPR spectra of coal and macerals [10]. The complex character of the coal spectrum is often visible for the higher microwave powers, when some components became partly saturated and the intensities of the others relatively increased. The analyses of multicomponent structure of EPR spectra of coals and macerals have been developed so far. The nature of paramagnetic centres in coal has been studied. The existence of thermally excited multiplet states in coal and macerals has also been searched.

There are a lot of papers about the influence of physical and chemical processes on the total amount of paramagnetic centres in coal and macerals or about the changes in their resultant EPR spectra. Separation of coal samples into density fractions is one of those processes. The role of the individual groups of paramagnetic centres of coal and changes of their physical behaviour (spin–spin and spin–lattice interactions, interactions with oxygen molecules) was not known so far.

The performed analysis pointed out that the EPR spectroscopy is a very useful technique for investigation of changes in the complex paramagnetic centres system of coal. This work also presented the difficulties of the EPR studies of coal and tried to explain how to conquer them.

The aim of the present work was to determine the number of different groups of paramagnetic centres existing in the coal samples with complex petrographic composition and to characterize their properties.

2. Experimental

Durain and clarain were hand-picked from Polish medium-rank coal of 85.6 wt% C. The coal contained 9 vol.% exinite, 77 vol.% vitrinite and 14 vol.% inertinite. The lithotypes were demineralized using an aqueous solution of HCl and HF at 50°C. The demineralized durain and clarain were centrifuged in toluene–CCl₄ mixtures, and the
samples with densities (g/cm$^3$): 1.24–1.28; 1.30–1.31; 1.30–1.32; 1.30–1.36; and 1.32–1.36 were obtained. The petrographic compositions of the separated samples are presented in Figs. 1 and 2.

The EPR spectra for the evacuated (0.01 Pa) samples were taken using a spectrometer at X-band (9.3 GHz) with magnetic modulation 100 kHz. The microwave frequency was recorded. The measurements were made at relatively low microwave power to avoid signal saturation. The lineshape of the spectra was numerically analysed by Opfermann’s algorithm [15]. The values of the root-mean-square (RMS) deviations ($S$) for the approximations of the experimental spectra by different superpositions of Gauss and Lorentz lines were determined. Those approximations, which gave the smallest RMS deviation, were assumed as the best results of curve fitting. The linewidths ($D_{pp}$), g-factor and abundance of the components of the total spectrum were evaluated.

Total concentration of paramagnetic centres in the samples was calculated as the value proportional to the area under the absorption curve. The area under the absorption curve was determined by double integration of the first-derivative EPR spectra. Ultramarine containing stable free radicals was used as the reference for the concentration of paramagnetic centres. The EPR signals of a ruby crystal permanently placed in the resonance cavity were taken for each sample to control experimental conditions and to avoid their influence on the obtained data. The percentages of the component lines in the total spectrum permitted us to determine the concentrations of paramagnetic centres responsible for the EPR components.

3. Results and discussion

As was expected, the numerical analysis of the lineshape of the EPR spectra of the clarain and durain samples indicated only a poor approximation for the fitting by single Gauss and Lorentz lines. The experimental spectra were sum of three lines ($S$: 0.06–0.10 cm) resulted from three different groups of paramagnetic centres. For example, the multicomponent structure of the resonance absorption curves of the samples with densities 1.24–1.28 g/cm$^3$ and 1.32–1.36 g/cm$^3$ are shown in Fig. 3 (durain samples) and Fig. 4 (clarain samples). Table 1 contains the total concentrations of paramagnetic centres, concentrations of paramagnetic centres responsible for the EPR components and parameters of the component lines: linewidths ($\Delta H_{pp}$) and g-factor, for the EPR spectra of the studied samples. The data in Table 1 concern with the best-fitted spectra (the lowest RMS values).

The experimental spectra were best approximated by a
superposition of broad Gauss ($\Delta H_{pp}$: 0.86–0.90 mT); broad Lorentz 1 ($\Delta H_{pp}$: 0.46–0.58 mT); and narrow Lorentz 2 ($\Delta H_{pp}$: 0.11–0.14 mT) lines (Table 1). Paramagnetic centres responsible for the broad components are located on structures consisting of a few aromatic rings [3,7–14,16]. Dipolar interactions of unpaired electrons broaden their EPR signals. Paramagnetic centres of large aromatic structures are responsible for the narrow lines [3,7–14,16]. The last group of paramagnetic centres mainly contains delocalized $\pi$-electrons with strong exchange interactions narrowing the EPR signals. Our earlier studies of coal, macerals and their pyridine extraction products indicated that the other assignments of the narrow and broad EPR lines cannot be assumed as correct. Because of the paramagnetic centres with narrow lines occurred not only in inertinites, but also in exinites and vitrinites [7,9–14], the opinions about the assignment of narrow and broad lines to individual macerals [2] was rejected. The assignment of narrow and broad lines to the macromolecular and molecular phase of coal [1] was not confirmed, because narrow lines were detected in both parts of the coal substance [7,11].

The $g$-values of range 2.0028–2.0029 were obtained for unpaired electrons with narrow Lorentz lines (Table 1). The $g$-factors of range 2.0030–2.0032 were measured for unpaired electrons with broad Gauss and Lorentz lines (Table 1). The $g$-values increase for unpaired electrons localized at heteroatoms (N, O, S) compared to unpaired electrons localized at carbon atoms [6]. It can be then concluded that some free radicals with unpaired electrons localized at nitrogen or oxygen atoms existed in both of the two groups of paramagnetic centres with broad (Gauss and Lorentz) lines. Nitrogen and oxygen free radicals were also detected for low- and medium-rank coals [7,17], but they did not exist in anthracites [18] which are almost free of N and O atoms.

Total concentration of paramagnetic centres increased with increasing of density of the durain and clarain samples (Table 1). The highest contents of paramagnetic centres with the broad Lorentz lines ($3.8–6.8 \times 10^{18}$ spin/g) in the studied samples were measured, whereas they were considerably lower for paramagnetic centres with broad Gauss ($2.4–3.2 \times 10^{18}$ spin/g) and narrow Lorentz ($0.2–0.6 \times 10^{18}$ spin/g) lines. These effects were expected, because vitrinite was the main petrographic constituent of all the analysed samples (Figs. 1 and 2) and the highest contents of paramagnetic centres with the broad Lorentz lines were measured for the studied coal [10]. The highest concentrations of paramagnetic centres with the narrow Lorentz lines were previously measured for its inertinite [10]. The amount of paramagnetic centres responsible for the narrow Lorentz lines of the spectra recorded in this work increased in the samples with the highest content of inertinite (Figs. 3 and 4, Table 1).
The performed EPR analysis of complex coal samples indicated the correlation between the paramagnetic centres behaviour and the petrographic composition of the samples. The complex character of paramagnetic centres systems of the two studied lithotypes was confirmed.

### Table 1

<table>
<thead>
<tr>
<th>Density of the sample (g/cm³)</th>
<th>$N \times 10^{18}$ (spin/g)</th>
<th>Gauss</th>
<th>Lorentz 1</th>
<th>Lorentz 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$N_G \times 10^{18}$ (spin/g)</td>
<td>$\Delta H_{pp} \pm 0.02$ (mT)</td>
<td>$g \pm 0.0002$</td>
<td>$N_L \times 10^{18}$ (spin/g)</td>
</tr>
<tr>
<td>Durain</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.24–1.28</td>
<td>6.4</td>
<td>2.4</td>
<td>0.89</td>
<td>2.0031</td>
</tr>
<tr>
<td>1.30–1.31</td>
<td>7.8</td>
<td>2.5</td>
<td>0.88</td>
<td>2.0031</td>
</tr>
<tr>
<td>1.30–1.32</td>
<td>8.0</td>
<td>2.9</td>
<td>0.86</td>
<td>2.0030</td>
</tr>
<tr>
<td>1.30–1.36</td>
<td>9.2</td>
<td>2.9</td>
<td>0.90</td>
<td>2.0032</td>
</tr>
<tr>
<td>1.30–1.36</td>
<td>9.6</td>
<td>2.5</td>
<td>0.86</td>
<td>2.0031</td>
</tr>
<tr>
<td>Clarain</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.24–1.28</td>
<td>8.7</td>
<td>2.4</td>
<td>0.89</td>
<td>2.0031</td>
</tr>
<tr>
<td>1.30–1.31</td>
<td>8.5</td>
<td>2.9</td>
<td>0.88</td>
<td>2.0031</td>
</tr>
<tr>
<td>1.30–1.32</td>
<td>8.8</td>
<td>3.2</td>
<td>0.88</td>
<td>2.0030</td>
</tr>
<tr>
<td>1.32–1.36</td>
<td>10.2</td>
<td>2.8</td>
<td>0.88</td>
<td>2.0030</td>
</tr>
</tbody>
</table>
centres systems of durain and clarain, as for their poor macerals [7,10], similar properties were observed.

Acknowledgements

The authors are very grateful to Dr Z. Chruściel and co-workers at the Central Mining Institute in Katowice for petrographic analysis. Wiesława Cyran, MSc, is thanked for technical assistance.

References