

Groups of Paramagnetic Centres in Reduced and Methylated Low Rank Coal

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Low rank Illinois No. 6 coal was studied by electron paramagnetic resonance EPR spectroscopy. The parameters of EPR spectra (spectroscopic splitting factors g , linewidths ΔB_{pp} , concentrations of paramagnetic centres N) were measured for raw and chemically treated coal (demineralized, reduced and methylated samples). The multi-component structure of experimental spectra of this coal was proved. Two groups of paramagnetic centres responsible for broad Lorentzian 1 and narrow Lorentzian 2 lines exist in studied samples. Paramagnetic centres connected with component lines revealed different behaviour during chemical treatments.

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1. Introduction

The electron paramagnetic resonance (EPR) spectroscopy is a very useful method for study of coal. The source of EPR signal of coal are unpaired electrons localized on carbon, oxygen and nitrogen atoms [1–4]. Coal presents a complex system of paramagnetic centres. The EPR spectrum of coal is a superposition of a few component EPR lines with Gaussian and/or Lorentzian shapes [3, 4]. Gaussian and Lorentzian lines are connected with particular group of paramagnetic centres. The resultant EPR spectrum of coal looks like a single line because atoms with unpaired electrons indicate very closely values of spin–orbit coupling constant λ [5]. It indicates that the values of spectroscopic splitting factor g for each component lines are almost the same. Numerical deconvolution of experimental EPR spectrum is used for showing the number and shapes of component lines. The intensity of component lines depends on the type of coal (low, medium and high rank coal) [3, 4], on chemical treatment (e.g. demineralization) [6, 7]. The intensity of EPR signal is proportional to the concentration of paramagnetic centres. The relaxation processes (spin–spin, spin–lattice) were studied by EPR method for different groups of paramagnetic centres in coal [3, 4, 6, 7]. Relaxation processes are responsible for saturation (or not saturation) of component lines with microwave power used during EPR experiments.

The aim of this work was to determine the changes in different groups of paramagnetic centres in American low

rank Illinois No. 6 coal with a carbon content 74.1 wt% after reduction and methylation. The effects of two types of methylation on paramagnetic centres in coal were compared.

2. Experimental

2.1. Samples

For EPR study low rank Illinois No. 6 coal with a carbon content of 74.1 wt% was used. The coal was demineralized by the Radmacher and Mohrhauer method [8] using hydrochloric and hydrofluoric acids. The reduction of coal was carried out in the potassium/liquid ammonia (K/NH₃) system using ethyl alcohol as a protonating agent. The reduction was made once or twice. Reductive alkylation of coal in the potassium/liquid ammonia system [9] and non-reductive alkylation of coal proposed by Liotta [10] were performed. Methyl iodide (iodomethane) was used as an alkylating (methylating) agent. All studied samples with elemental analysis are listed in Table I.

TABLE I

Elemental analyses of the studied coal samples (wt% daf).

Sample of coal	Ash	C	H	H/C	N	S _{org}
raw	10.7	71.9	4.5	0.746	1.3	3.0
demineralized	0.6	74.1	5.2	0.836	1.4	3.0
reduced 1×	7.4	75.0	5.8	0.950	1.5	
reduced 2×	6.9	74.6	6.4	1.050	1.6	
methylated in K/NH ₃ system	0.5	73.4	5.9	0.942	1.9	
methylated by Liotta method	0.2	75.1	5.8	0.936	1.6	

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2.2. EPR measurements

EPR measurements were performed for the evacuated coal samples (10^{-4} Torr) using an X-band (9.3 GHz) EPR spectrometer with modulation of magnetic field 100 kHz (Radiopan, Poznań, Poland). EPR spectra were recorded at low microwave power (≈ 0.7 mW) to avoid microwave saturation. The shapes of the coal EPR spectra recorded at higher microwave power (≈ 70 mW) were also compared. The number of component lines in the EPR spectra and their shapes were numerically determined. Peak-to-peak linewidths ΔB_{pp} , spectroscopic splitting factors g and integral intensities of the component EPR lines were measured. g -factors were calculated from the EPR condition

$$g = h\nu/\beta B_r,$$

where g — spectroscopic splitting factor, h — the Planck constant (6.626069×10^{-34} J s), ν — microwave frequency [GHz], β — the Bohr magneton (9.274009×10^{-24} J T $^{-1}$), B_r — magnetic resonance field [mT].

Total concentration of paramagnetic centres N_t in the samples and concentrations of paramagnetic centres responsible for the individual EPR lines N were determined according to the formula [11]:

$$N = n_u[(W_u A_u)/P_u][P/(W A m)],$$

where n_u — number of paramagnetic centres in ultramarine (used as the reference), W , W_u — the receiver gains for the sample and ultramarine, A , A_u — the amplitudes of the ruby signal for the sample and ultramarine (ruby crystal was used as the interior reference), P , P_u — the areas under the absorption curves for the sample and ultramarine (obtained by double integration of the first derivative EPR spectra), m — the mass of the sample.

3. Results and discussion

The EPR spectra of studied samples recorded at low and high microwave power (0.7 and 70 mW) are presented in Figs. 1–6. The multicomponent character of the EPR spectrum is visible for low microwave power. This effect was also seen earlier for other

coals [7, 12]. The deconvolution of recorded EPR spectra was made. Parameters of the component lines of EPR spectra are shown in Table II. EPR spectra of the studied coal samples are superposition of two Lorentzian lines (Lorentzian 1, Lorentzian 2). g -factor for Lorentzian 1 lines is in the range 2.0032–2.0035. Values of g -factors marginally decreased after chemical treatment for Lorentzian 1 lines (Table II). g -factor for Lorentzian 2 lines is smaller (2.0028–2.0030) (Table II). The direction of the changes of g -factor values is contrary to that for Lorentzian 1 lines. Different linewidths were obtained for these two EPR components. The linewidths of the broad Lorentzian 1 lines were in the range of 0.46–0.55 mT. The linewidths of 0.07–0.09 mT were measured for the narrow Lorentzian 2 lines. The narrowing of EPR component lines is caused by exchange (and superexchange) and the broadening of EPR lines is a result of dipole-dipole interactions in the system of paramagnetic centres [6, 7, 11]. Paramagnetic centres belonging to coal units consisting of a few aromatic rings are responsible for the broad lines. Paramagnetic centres belonging to large coal structures consisting of condensed aromatic rings are responsible for the narrow lines (delocalized π electrons) [2, 9, 13]. The linewidths of both Lorentzian 1 and Lorentzian 2 components of the EPR spectra of coal change slightly during the performed processes. Different groups of paramagnetic centres in coal behave differently during EPR measurements at the same values of microwave power [4, 9]. The broad Lorentzian 1 lines saturate with microwave power earlier than the narrow Lorentzian 2 lines. The slow relaxation spin-lattice processes are characteristic for Lorentzian 1 lines and fast for Lorentzian 2 lines.

Paramagnetic centres with broad Lorentzian 1 lines dominate (85–96%) in all of the studied low rank coal samples (Table II). This group of paramagnetic centres was the most active during reduction and methylation. The role of paramagnetic centres with narrow Lorentzian 2 lines in reduction and methylation of coal

TABLE II

Parameters of the component lines of the EPR spectra: linewidth (ΔB_{pp}), g -factor, and concentrations (N) of paramagnetic centres in the studied coal samples.

Sample of coal	N_T [$\times 10^{-17}$ spin/g]	ΔB_{pp} ± 0.02 [mT]	g ± 0.0002	N [$\times 10^{-17}$ spin/g]	ΔB_{pp} ± 0.02 [mT]	g ± 0.0002	N [$\times 10^{-17}$ spin/g]
raw	10.9	0.55	2.0035	10.7	0.08	2.0030	0.2
demineralized	11.8	0.51	2.0034	11.6	0.07	2.0030	0.2
reduced 1 \times	6.2	0.51	2.0033	6.0	0.08	2.0029	0.2
reduced 2 \times	3.5	0.51	2.0033	3.3	0.08	2.0028	0.2
methyated in K/NH $_3$ system	7.9	0.55	2.0033	7.6	0.09	2.0029	0.3
methyated by Liotta method	5.8	0.46	2.0032	5.5	0.09	2.0028	0.3

is negligible (Table II). The highest concentration of paramagnetic centres (total and for Lorentzian 1 line) is characteristic for demineralized coal (is higher than for raw coal). Reduction of coal strongly lowers the concentration of paramagnetic centres with broad Lorentzian 1 lines in the sample. The concentrations of paramagnetic centres with Lorentzian 1 lines for twice reduced coal were lower than those for once reduced coal. Methylation of reduced coal in potassium/liquid ammonia system considerably increases concentrations of paramagnetic centres with broad lines (Lorentzian 1). This effect was not so strong for coal non-reductively methylated by the Liotta method. It can be then concluded that the more effective method of alkylation of coal is the methylation in the potassium/liquid ammonia system.

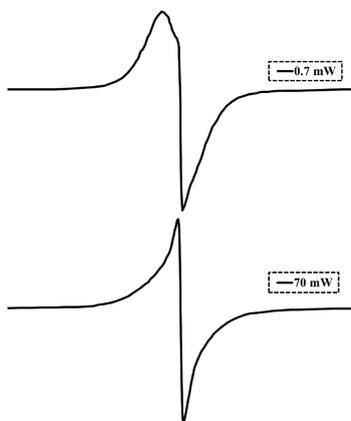


Fig. 1. EPR spectra of raw coal.

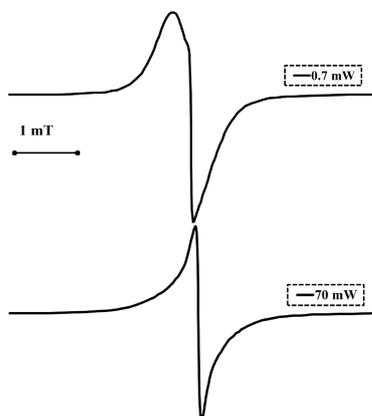


Fig. 2. EPR spectra of demineralised coal.

Chemical processes influence on the chemical structure of coal [14–16]. The modification of chemical structures of coal leads to quenching of some groups of paramagnetic centres. The demineralization of coal leads to a considerable change in the amount of ash (Table I) [14–16]. Both way of methylation (in the K/NH_3 system and the Liotta method) cause increase of hydrogen, nitrogen and carbon content (Table I). The increase of hydrogen is caused by hydrogenation of aromatic structures by

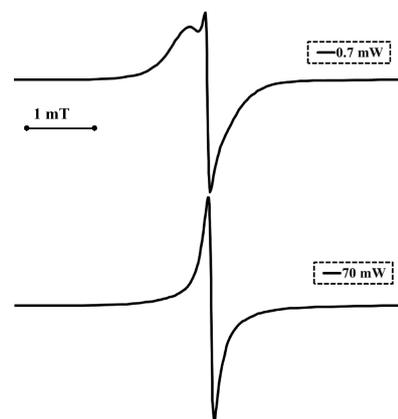


Fig. 3. EPR spectra of 1 time reduced demineralised coal.

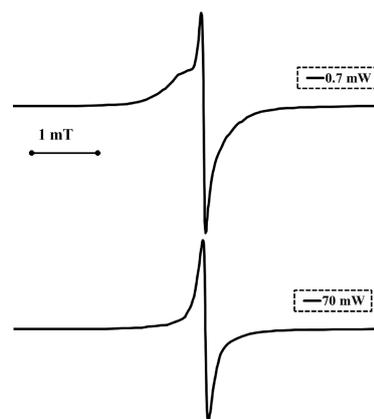


Fig. 4. EPR spectra of 2 times reduced demineralised coal.

the way of formation of hydroaromatic systems [17, 18]. The adsorption of ammonia takes place during reduction [16] and the content of nitrogen increases. The original sulphur compounds in coal are diluted by introduction of methyl substitutes which leads to the decline of sulphur content [19, 20]. Similar effects in changes of

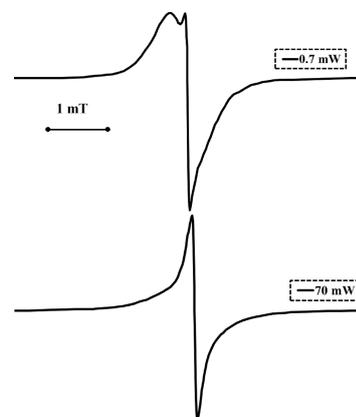


Fig. 5. EPR spectra of coal methylated in the potassium/liquid ammonia system.

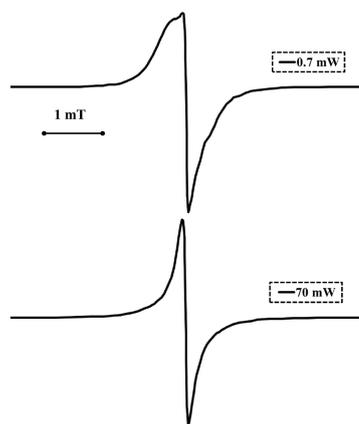


Fig. 6. EPR spectra of coal methylated by Liotta method.

content of elements after demineralization and methylation was observed also for other coals (Mequinenza, Zofiówka) [14–16]. The correlation between total concentration N_t and concentration of paramagnetic centres with Lorentzian 1, 2 lines N versus H/C ratio are presented in Figs. 7, 8. Higher concentration of paramagnetic centres in coal is observed for lower H/C ratio [6, 12, 21]. Paramagnetic centres connected with Lorentzian 2 lines are not sensitive to chemical treatment used in this work.

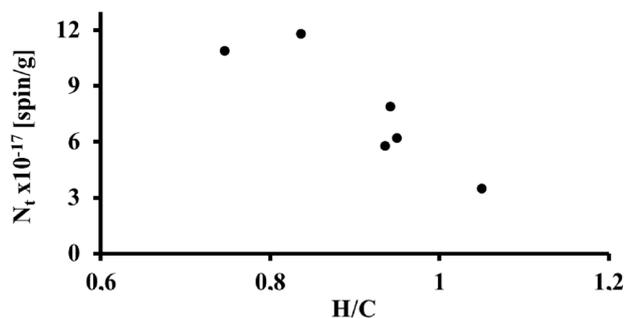


Fig. 7. Correlation between total concentration of paramagnetic centres and H/C of the studied coal samples.

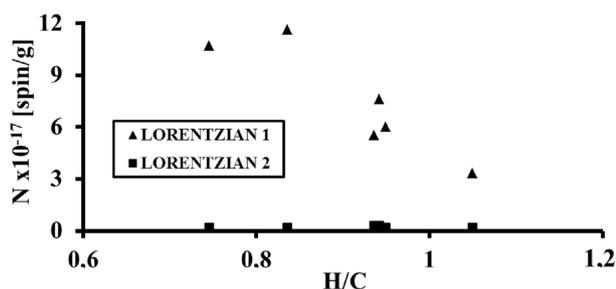


Fig. 8. Correlations between concentrations of paramagnetic centres with Lorentzian 1, 2 lines and H/C of the studied coal samples.

4. Conclusions

Two groups of paramagnetic centres exist in the studied coal samples. They are responsible for broad (0.46–0.55 mT) and narrow (0.07–0.09 mT) Lorentzian lines in the EPR spectra. g -factors indicate that unpaired electrons are localized mainly on carbon atoms in the samples. Paramagnetic centres with broad lines play the most important role during reduction and methylation of coal. The changes in concentration of paramagnetic centres for Lorentzian 1 lines are considerable. Paramagnetic centres giving Lorentzian 2 lines are not active during reduction and methylation. The more effective method of alkylation of coal is the methylation in the potassium/liquid ammonia system.

References

- [1] A. Marzec, *Fuel Process. Technol.* **77–78**, 25 (2002).
- [2] O. Ito, H. Seki, M. Iino, *Bull. Chem. Soc. Jpn.* **60**, 2967 (1987).
- [3] B. Pilawa, A.B. Więckowski, B. Trzebicka, *Radiat. Phys. Chem.* **45**, 899 (1995).
- [4] A.B. Więckowski, W. Wojtowicz, B. Pilawa, *Fuel* **79**, 1137 (2000).
- [5] J.E. Wertz, J.R. Bolton, *Electron Spin Resonance. Elementary Theory and Practical Applications*, McGraw-Hill, New York 1972.
- [6] B. Pilawa, A.B. Więckowski, H. Wachowska, M. Kozłowski, *Fuel* **77**, 1561 (1998).
- [7] B. Pilawa, A.B. Więckowski, H. Wachowska, M. Kozłowski, *Appl. Magn. Reson.* **24**, 73 (2003).
- [8] W. Radmacher, O. Mohrhauser, *Brennst. Chem.* **37**, 353 (1965).
- [9] H. Wachowska, A. Andrzejak, M. Kozłowski, *Fuel Process. Technol.* **19**, 215 (1988).
- [10] R. Liotta, *Fuel* **58**, 724 (1979).
- [11] B. Pilawa, A.B. Więckowski, S. Duber, *Erdol Kohle Erdgas P.* **43**, 240 (1990).
- [12] B. Pilawa, A.B. Więckowski, R. Pietrzak, H. Wachowska, *Centr. Eur. J. Chem.* **5**, 330 (2007).
- [13] S.W. Dack, M.D. Hobday, T.D. Smith, J.R. Pilbrow, *Fuel* **64**, 219 (1985).
- [14] M. Kozłowski, H. Wachowska, J. Yperman, *Fuel* **82**, 1041 (2003).
- [15] M. Kozłowski, H. Wachowska, J. Yperman, *Fuel* **82**, 1149 (2003).
- [16] M. Kozłowski, H. Wachowska, *Fuel* **78**, 1875 (1999).
- [17] R.G. Harvey, *Synthesis* **4**, 161 (1970).
- [18] P.W. Rabideau, E.G. Burkholder, *J. Org. Chem.* **43**, 4283 (1978).
- [19] H. Wachowska, M. Kozłowski, *Fuel* **74**, 1319 (1995).
- [20] H. Wachowska, M. Kozłowski, *Fuel* **74**, 1398 (1995).
- [21] D.P. Dick, A.S. Mangrich, S.M.C. Menezes, B.F. Pereira, *J. Braz. Chem. Soc.* **13**, 177 (2002).