HOKKAIDO UNIVERSITY

Instructions for use

Polarographic Reduction of Extracts of Coals
in Dimethylformamide

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Abstract

Polarographic reduction behaviour of the extracts of ten Japanese coals in dimethylformamide was examined with a dropping mercury electrode. For the extract solutions of almost identical concentrations (g/l), the current flowing at -1.0 V (vs. the mercury pool) is nearly the same irrespective of the carbon content of original coals whereas the current at -2.2 V increases remarkably with the rise of carbon content. The fact is interpreted by the concept that the content of carbonyl groups in these coals does not change very much with the degree of coalification while the concentration of polycyclic aromatic structures increases with it. This conclusion was further supported by a large scale electrolysis and the measurement of infrared spectra of the extracts. Based upon the experimental results, the possibility of predicting the structural features of coals from polarographic behaviour of the extract was stressed.

I. Introduction

The study of the structure of coal by means of electrochemical techniques has been developed over the last ten years. Hallum and Drushel[1] examined the polarographic behaviour of carbon black particles suspended in dimethylformamide (DMF) and proposed that the hydroquinone and quinone groups at the edges of polycyclic aromatic rings protrude from the average surface of the particle. They considered that two waves appearing in the anodic and cathodic polarograms are respectively related to the oxidation of the hydroquinone and the reduction of the quinone groups. Given and others[2],[3] obtained reduction polarograms for solvent extracts of coals in DMF over a potential range from 0 to -2.2 V against the mercury pool. It is suggested that the substances to be

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reduced between 0 and -1.0 V are mainly aromatic ketones (quinones) and the polycyclic aromatic structures can only be reduced in a range from -1.0 to -2.2 V. Their conclusion is based upon the knowledge of half wave potentials for simple aromatic hydrocarbons which are considered to be characteristic components of coals[4]~[6].

In the present investigation, polarographic reduction behaviour was examined for DMF extracts of ten kinds of coals mined in Hokkaido. A large scale electrolysis and measurement of infrared spetra were also carried out for these extracts.

II. Experimental

1. Preparation of the dimethylformamide extract of coal

The coal samples which analyses are shown in Table 1 were pulverized to pass a 200 mesh screen and 2.5 gram portion of each sample was suspended in

TABLE 1. Analyses of coals

Coal samples	C	H	N	S	O*
1 Tokachi lignite	61.5	5.7	1.0	—	31.8
2 Sohya coal	70.3	5.3	1.2	0.4	22.8
3 Sumiyoshi coal	75.5	6.1	1.2	—	17.2
4 Taiheiyo coal	76.7	6.4	0.7	—	16.2
5 Shakubetsu coal	77.6	5.8	1.9	0.6	14.1
6 Showa coal	79.6	6.2	1.8	0.2	12.2
7 Horonai coal	79.7	6.2	1.2	0.1	12.8
8 Bibai coal	80.0	6.0	1.7	0.1	11.5
9 Sunagawa coal	81.7	6.2	1.6	0.2	10.3
10 Yubari coal	84.0	6.4	0.8	—	8.8
Lignin	62.5	5.4	—	—	32.1

* Percentage of oxygen content was estimated by balance.

50 ml of DMF purified by double distillation. Extraction was made at room temperature by exposing to irradiation with 40 Kc/s ultrasonic waves for ten minutes, the insoluble residue being removed by filtraton. The concentrations of the extract solutions and yields of extraction (i e. the weight of extract divided by the weight of coal) are shown in Table 2. The analyses of the extracts indicated in this table are similar to those of the original coals. The amounts of extracts were always measured after removing the solvent by vacuum evaporation.

TABLE 2. Results of extraction and analyses of the extracts

Original coals	Extraction yield %	Concentration of extract %	C	H	N	O
1 Tokachi lignite	3.2	0.1356	70.2	8.7	—	21.1
2 Sohya coal	6.4	0.2710	72.4	6.9	1.8	18.9
3 Sumiyoshi coal	15.5	0.6488	73.5	6.6	1.0	18.9
4 Taiheiyo coal	14.0	0.6220	78.3	7.5	1.2	13.0
5 Shakubetsu coal	9.0	0.4078	77.1	6.6	1.4	14.9
6 Showa coal	13.0	0.5414	76.5	6.5	2.3	14.7
7 Horonai coal	12.7	0.5790	80.3	7.0	1.0	11.7
8 Bibai coal	11.7	0.5200	77.9	6.5	1.9	13.7
9 Sunagawa coal	15.6	0.7098	82.0	6.5	1.5	10.0
10 Yubari coal	7.3	0.3224	82.0	7.0	1.4	9.6

2. Preparation of sample for polarographic measurement

For polarographic measurements, the concentration of extracts was ajusted to 0.125 (w/v) % by adding a suitable amount of DMF. The solution contained 0.15 M tetrabutylammoniumiodide (TBAI) as the supporting electrolyte. The dropping mercury electrode had a drop time of 4.48 seconds and the amount of dropping mercury was 0.815 mg/s on open circuit. Measurement was carried out at 20°C by means of a Model PA 201 Yanagimoto Polarograph after bubbling nitrogen for some time through the solution placed in a simple cylindrical cell. The potential was measured against the mercury pool anode in a potential range from 0 to -2.4 V.

3. Large scale electrolysis of DMF extract of coal

The DMF solutions of extracts containing 0.15 M TBAI were reduced for 1 hr in nitrogen atmosphere in large scale electrolysis. The volume of the DMF solutions in the cathodic compartment was 50 ml and the concentration of the extract ranged from 0.15 to 0.4 %. The electrolytic cell used is schematically shown in Fig. 1. It is provided with a stirred mercury pool cathode (area 5.74 cm^2) and a platinized platinum anode. The anodic and cathodic compartments are separated by a cellophane diaphragm preliminarily perforated. A saturated silver chloride electrode was used as the reference, the tip of the Luggin capillary was plugged by 3% agar-agar containing some TBAI. Cathodic polarization was made at a constant potential of -2.46 V against the silver chloride electrode by the aid of an electronic potentiostat (Nichiya, Model HL–1). This potential corresponds to the potential of -2.0 V against the mercury pool on open circuit. Before and after the electrolysis, cathodic reduction polarograms were obtained with the same
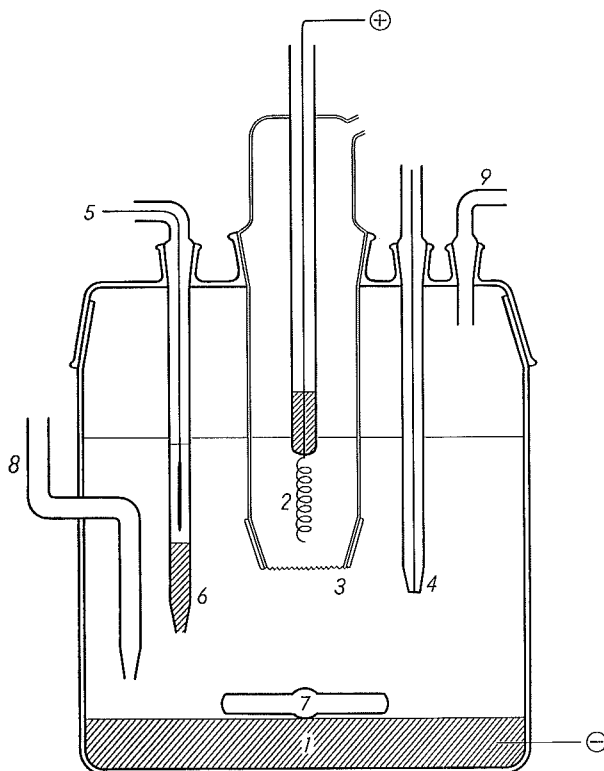
Fig. 1. Electrolytic cell

1. mercury pool cathode.   2. platinized platinum anode.
3. cellophane diaphragm with holes. 4. dropping mercury
electrode.   5. saturated silver/silver chloride electrode.
6. agar plug. 7. stirrer. 8. gas inlet. 9. gas outlet.

dropping mercury electrode described above (see Fig. 1).

4. Measurement of infrared spectra

Infrared spectra was obtained for the extracts before and after the above electrolysis.   The procedure is as follows: The solvent was removed from the solution by vacuum evaporation.   The residue thus obtained was stirred together with methylalcohol, collected on a filter and washed again with methylalcohol. After drying overnight in a vacuum, a 2～3 mg portion of the residue was ground with 250～350 mg of KBr to prepare KBr disks.   Measurement was carried out in the usual manner with a Model EPI–2 Hitachi spectrophotometer.

III.   Results

1. Polarographic measurement

Cathodic reduction polarograms for the extracts of coals in DMF (0.125 %) are shown in Fig. 2. The current increases rather continuously with the lowering potential and no distinct waves were recognized. The steep rise of current beyond
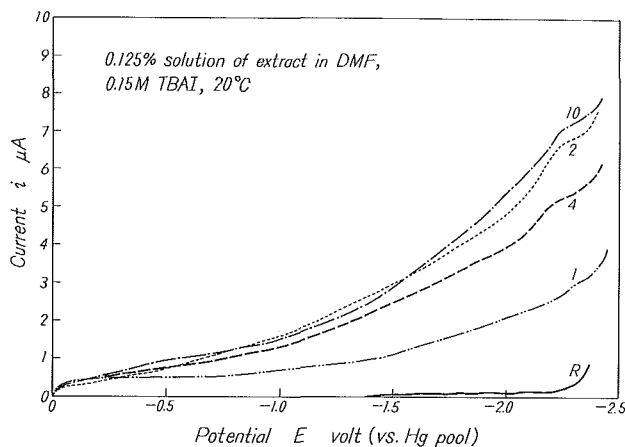

Fig. 2. Polarograms for the extract solutions of identical concentration.
  1. Tokachi lignite. 2. Sohya coal. 4. Taiheiyo coal.
  10. Yubari coal. R. Residual current observed for solvent.

-2.3 V is considered to correspond to the commencement of the decomposition of TBAI to produce hydrogen. The change of the polarograms with the concentration of the extract was checked for Horonai coal (Fig. 3). It was ascertained
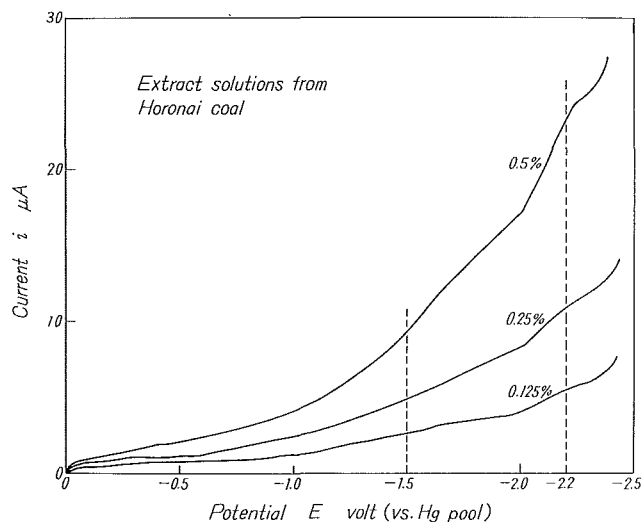

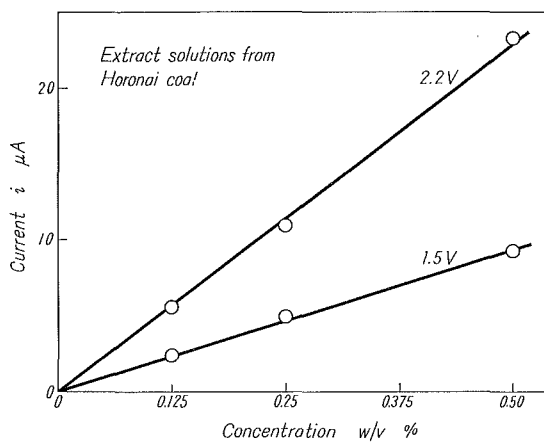Fig. 3. Change of polarogram with the concentration of extract.

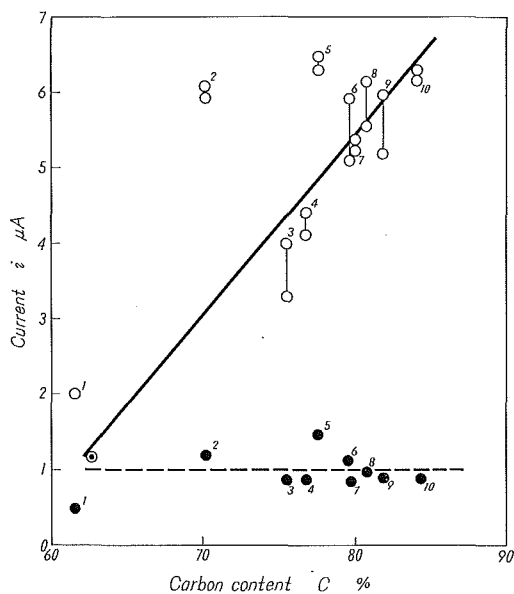**Fig. 4.** Change of current with the concentration of extract.

Fig. 5. Change of polarographic current with the carbon content of original coals.
concentration of extract : 0.125 w/v %.
●⋯cathode potential at −1.0 V.
○⋯cathode potential at −2.2 V.
☉⋯data obtained at −2.2 V for lignin extract.
The numbers express the data obtained for the extracts from
different original coals shown table 1 and 2.

that the current increases almost linearly with the concentration at any potential from 0 to −2.2 V, as can be seen in Fig. 4. This means that the extract is certainly reduced and there are no appreciable side reactions. An attempt was made to plot the current against the carbon content (wt %) of original coals for potentials at −1.0 and −2.2 V (Fig. 5). It was found that the current scarcely changes with the carbon content at −1.0 V, whereas it increases remarkably at −2.2 V. The current observed for a DMF solution of lignin (0.125 %) at −2.2 V is also indicated in this figure. Scattering of the data for the respective coals may be due to the use of different batches of extract solutions. It is interesting that the current is extraordinarily large for Sohya and Shakubetsu coals which have higher aromaticity. The characteristic features of these results do not change if the plots were made against the carbon content of extracts.

2. Large scale electrolysis

The successive procedures and the results obtained for Showa and Shakubetsu coals are as follows:
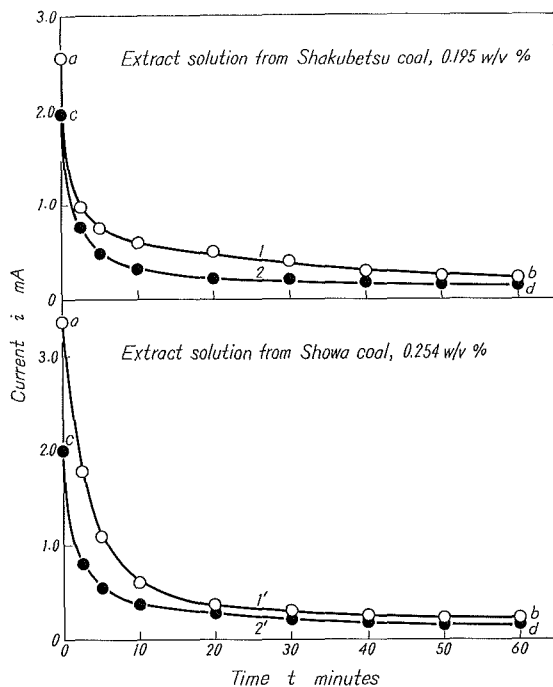

Fig. 6. Change of current with time of electrolysis at constant potential of −2.2 V (vs. the mercury pool).

The numbers attached to the curves: see text.

A) The change of current with time was followed for 1 hr in nitrogen atmosphere after applying a constant cathode potential of -2.0 V (Fig. 6 curves 1 and 1').

B) Reoxidation of the extract was made for 30 minutes by bubbling air through the solution. The procedure A was repeated after replacing air with nitrogen (Fig. 6 curves 2 and 2').

It is seen in Fig. 6 that the current decreases rapidly in the initial period but the rate of decrease becomes smaller as the time elapsed. It is also recognized that the currents for curves 2 and 2' are smaller than those for curves 1 and 1'. The current is almost constant after 40 minutes and does not show a tendency of reaching zero. This fact can be explained because the degree of reduction of the extract estimated from the amount of charge passed should not be more than 5% even at 60 minutes. Before and after the electrolytic procedures A and B, cathodic reduction polarograms were obtained in nitrogen atmosphere (Fig. 7). Symbols a, b, c and d attached to the curves express the time at which measurements were made (see Fig. 6). The size of current for Curve b obtained after
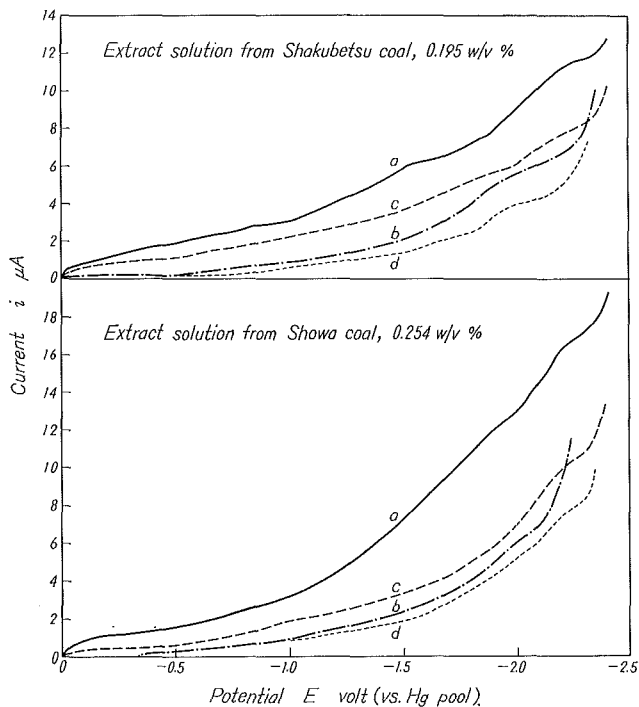
Fig. 7. Polarograms obtained for the extracts before and after electrolysis.
Symbols attached to the curves : see text.

the procedure *A* is much smaller than that for Curve *a* obtained before this procedure. This is of course due to the reduction of the extract during electrolysis. The current recovers to some extent on reoxidizing the extract with air. This is shown by Curve *c* in Fig. 7. The size of current for Curve *d* obtained after the procedure *B* is somewhat smaller than that for Curve *c*. This may be explained by the concept that, by the repetition of reduction and oxidation, the chemical structure of the extract changes to one which is easier to be reduced electrolytically.

4. Infrared spectra

The infrared spectra of the extracts of coals were measured before and after the above procedure *A*, a typical result of which is shown in Fig. 8. The absorbance per gram of the extract was estimated by the base line method[7] for various wave lengths at which characteristic absorption bands are observed (Table 3). It is seen that the change of spectra before and after the electrolysis is similar to each other for all of the extract samples. It is seen for most of the extracts that the absorption at 1600 cm^{-1} decreases while the absorption at 1100 cm^{-1} increases correspondingly. This is explained by the assumption that carbonyl radicals have been reduced to form hydroxyl radicals. Further, as can be seen, the absorption at 1600 cm^{-1}, 1260 cm^{-1} and 820 cm^{-1} decreases whereas absorption at
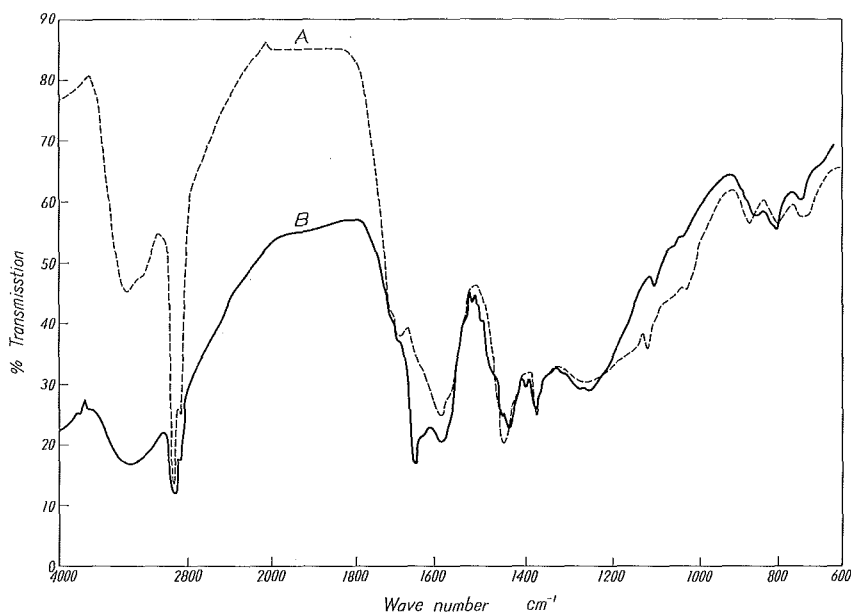

Fig. 8. Typical change of infrared spectra of the extract before and after electrolysis.

TABLE 3.　Absorption intensities (absorbance/gr) of infrared spectra of the extracts before and after electrolysis

Characteristic frequencies of radicals		2910 -C-H(al)	1600 C=O C=C(ar)	1460 -CH₂-	1380 -CH₃	1260 -C-O-C- (ar)	1100 C-OH	1060 -C-O-C- (al)	820 cm⁻¹ C-H(ar)
1 Tokachi lignite	B	614	218	173	98	45	56	17	15
	A	—	—	—	—	—	—	—	—
2 Sohya coal	B	389	321	154	67	95	33	3	26
	A	528	141	183	93	20	45	14	15
3 Sumiyoshi coal	B	291	251	148	51	84	16	7	59
	A	538	161	183	87	18	60	11	29
4 Taiheiyo coal	B	450	256	176	67	72	24	6	55
	A	426	216	183	66	32	53	12	34
5 Shakubetsu coal	B	234	295	128	57	95	24	10	56
	A	322	171	174	72	14	20	16	29
6 Showa coal	B	252	270	137	70	87	27	12	58
	A	393	198	86	65	28	34	13	31
7 Horonai coal	B	405	244	173	60	87	17	—	52
	A	379	214	208	40	32	64	26	31
8 Bibai coal	B	284	309	159	60	87	23	18	75
	A	374	150	175	86	14	32	17	23
9 Sunagawa coal	B	285	228	183	58	41	20	21	69
	A	—	—	—	—	—	—	—	—
10 Yubari coal	B	319	216	159	51	64	19	14	73
	A	354	201	—	78	17	44	8	46

2910 cm^{-1} and 1060 cm^{-1} increases.　This probably means that aromatic structures are reduced to aliphatic ones.　It should be noted here that the extract after electrolytic reduction suffers some reoxidation by air during preparations of the KBr disks.　Accordingly, the actual degree of reduction just after electrolysis is much greater than that estimated by the infrared spectra.

IV.　Discussion

Since the reduction current was proportional to the concentration of extract at any cathode potential (Fig. 4), it is clear that the extract contains a number of active groups which can be reduced below the respective characteristic potentials. In connection with this, Given[2],[3] observed two to four distinct polarographic reduction waves for solvent extracts of English coals and reported their half wave potentials.　However, in our observation, the current increased smoothly with the lowering of the potential and no clearly defined waves were recognized.　This means that the extract is a mixture of many different materials with half wave potentials changing almost continuously.

It seems resonable to adopt Given's concept that half wave potentials for the reduction of the carbonyl structures and the polycyclic aromatic structures are in ranges of $0 \sim -1.0$ and $-1.0 \sim -2.3$ V (vs. the mercury pool), respectively. We checked this concept with a preliminary oximation experiment in which the extract was oximated in the usual manner before the polarogram was measured. The current was observed to decrease mainly in a range from 0 to-1.0 V, suggesting that only carbonyl groups can be reduced in this potential range. Reducibility of polycyclic aromatic structures in the lower potential range was quite evident from the measurement of infrared absorption spectra.

As shown in Fig. 5, the polarographic current at -1.0 V is nearly constant irrespective of the carbon content of the original coals. This suggests that the content of carbonyl radicals does not change very much with the change of the carbon content. It is interesting that Takeya and others have reached a similar conclusion from the chemical analysis of many different kinds of coals[7]. Further, the fact that the current flowing at -2.0 V increases with the rise of carbon content of the original coals can be explained by the well known concept that the degree of condensation of polycyclic aromatic rings increases with the increasing rank of coal[8)~13)]. As a matter of fact, Bergman[14] has reported from the measurement of the half wave potentials of several series of polycyclic aromatic hydrocarbons that the cathodic reduction becomes easier with the rise of degree of condensation. A large current observed for the extracts of Sohya and Shakubetsu coals can be interpreted by assuming a extraordinarily high degree of aromaticity of these coals. This assumption is in good agreement with the conclusion obtained by Takeya et al. from the measurement of nuclear mangnetic resonance spectra[13].

In concluding the discussion, it should be emphasized that there is a very good possibility of predicting the structural features of coals by the measurement of polarographic reduction behaviour of the extracts in organic solvents.

Acknowledgment

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