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**ORGANIC SOLVENTS AS PYRIDINE AND IMIDAZOLIUM BASED
IONIC LIQUID [Bmim]Cl AFFECTING FUNCTIONAL GROUPS AND
PARAMAGNETIC PROPERTIES OF LOW RANK NALAIKH COAL**

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This work considers experimental results of low rank Nalaikh coal dissolution in organic solvents as pyridine and imidazolium based ionic liquid of [Bmim]Cl. The low rank coal and its treated samples were therefore analyzed by Fourier transformation infrared and electron paramagnetic resonance spectroscopy. Different paramagnetic centers are good resolved in the electron paramagnetic resonance electron paramagnetic resonance spectra of the extraction samples.

Keywords: brown coal, pyridine, imidazolium based ionic liquid [Bmim] Cl, Fourier transformation infrared, electron paramagnetic resonance.

Introduction

Coal is the most abundant and approachable resource in Mongolia. The total coal resource is estimated about 175 billion tonnes and located in more than 200 coal occurrences in the country [1]. Consequently it is necessary to improve an effective and environmentally friendly utilization of coals for what the coal molecular structure must be well defined and understood. Coal is itself highly heterogeneous, macromolecular matrix and its concept of structures still not completely accurate. Simultaneously, coal insolubility priority gives numerous challenging for obtaining coal structural information.

Series of works [1-4] were referring about the significance for earning coal structural details in the coal and solvent interaction, particularly, when having an extraction in the result. Because extraction mechanism and its product reveal the molecular complexity of coal macro molecular matrix.

Among the solvents potential ones are a basic heterocyclic organic compound such as pyridine [1-6] and recently discovered as a coal colossal solvating product [7, 8], environmentally friendly room temperature imidazolium based ionic liquid such as 1-butyl-3-methylimidazolium chloride [Bmim]Cl.

In this work we are reporting experimental results of coal and solvent interaction that are studied by Fourier transformation infrared (FTIR) spectroscopy to obtain chemical information about the organic solids, in addition an electron paramagnetic resonance (EPR) spectroscopy which gives more physical information about coals. Here should be noted that various spectroscopy methods have been applied to investigate and to better understand of coal behaviors in these solvents, although there is a few EPR-spectroscopy research.

Experimental

Sample preparation. Nalaikh coal deposit is located approximately 40 km to the south-east of Ulaanbaatar, Central Mongolia. The basic geological structure is formed of a homoclinal structure tending north-west and dipping 8-10 degree south-west. Bearing bed is 280-350 m in thickness and contains 11 coal seams of which 5 seams are minable (I, II, III, IV and V) [9]. The sample analyzed in this work are taken from only one borehole, which means the sample cannot be representative for the whole deposit.

Pyridine, a basic heterocyclic organic compound (C_5H_5N) is from Sigma-Aldrich and used as received. Ionic liquid, 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) which was obtained from Sigma-Aldrich and used as received (solid in a room temperature). Methanol, the simplest alcohol methanol with the formula CH_3OH is used as received from Sigma-Aldrich.

Sample preparation for analysis was performed in accordance with standard procedures of coal chemistry: A piece of coal from each deposit was crushed initially and then milled to a size of 0.05 mm or less by using agate mortar in an argon flow glove box. At last, milled samples were kept in Schlenk flask under argon. The coal sample was analyzed by scanning electron microscope (SEM, JOEL) equipped with backscattered and secondary electron detectors coupled with energy dispersive X-ray spectrometry (EDS). The SEM-EDS provides detailed imaging information about the morphology and surface texture of individual particles, as well as an elemental composition of sample. In this study, backscattered electron imaging (BSE) which provides visual information based on gray-scale intensity between chemical phases and EDS were used to characterize heavy elements in the coal sample (Table). The elemental composition of coal sample is determined using characteristic X-ray spectrum up to 20 kV on the surface of the coals. The elemental analysis was performed in a "spot mode" in which the beam is localized on a single area manually chosen within the field of view. The location is represented on the provided SEM images by a "+". The EDS detector was capable of detecting elements with atomic number equal to or greater than six.

Table
Elemental analysis, as well as heavy element content, of Nalaikh coal

Elemental content, wt. %	C	O	Al	Si	Ca	S	Fe	Se	Mn	Mg
Nalaikh coal	68.08	21.24	1.28	3.27	3.66	0.38	1.11	-	0.43	0.46

Solubility of coal in pyridine: Nearly 1 g of Nalaikh coal sample was refluxed in 25 ml of pyridine for 24 hrs at under pressure of 10^{-2} Torr. Centrifugation was done for 1.5 hrs for each sample at 6000 RPM. Thus the extract was separated from the solid that a pyridine treated insoluble coal residue (labeled PTCR). The extract then dried by evaporating its pyridine until a soluble part of coal becomes a high viscosity substance. The substance of soluble part of coal then called a pyridine treated coal extract (labeled PTCE).

Similarly, the solid, insoluble coal residue was then washed by methanol followed the isolation from methanol by evaporating. Finally, was dried under nitrogen by evaporating.

Solubility of coal in [Bmim]Cl: Approximately 1 gram of Nalaikh coal is placed in a contact with 10 g of [Bmim]Cl. A mixture was placed and capped in a two necked flask and then heated to 100°C for 48 hrs under pressure of 10^{-2} Torr and stirring, with assistance of a magnetic stir. This condition was comparatively well enough for dissolving sufficient amount of coal.

The suspension cannot be filtered using conventional filters because of its quick reconversion to solid state at room temperature, therefore we kept high temperature of suspension while centrifuging it for 6 min at 4000 RPM. After first centrifugation we could manage to separate supernatant solution from the insoluble part of coal. The supernatant then called an ionic liquid treated coal extract (labeled ILTCE) was kept under nitrogen gas in an oil bath heated up to 100°C. A methanol (approximately 70 ml) was poured to the insoluble part of coal several times and stayed in oil bath heated at 60°C for 1 hour stirring until the whole ionic liquid dissolved. After for 12 hrs staying fixed, a supernatant was removed by sucking with pipette, and a residue then was dried just by open flask nitrogen blowing in an oil bath heated up to 60°C with stirring. Dry insoluble coal part then was called an ionic liquid treated insoluble coal residue (labelled ILTCR).

Fourier Transformation Infrared (FTIR) spectroscopy: Functional groups of the samples were detected by the In situ Fourier Transform Infrared (FTIR) Nicolet Avatar 330 Spectrometer, in transmittance mode. Raw coal sample was firstly dried in an oven at 110°C for 72 hrs and prepared by grinding with KBr (optimized mass ratio of coal to KBr was 1:50) using a mortar. Thus, every pellet scanned from 250 times ranged from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} .

Electron paramagnetic resonance (EPR) spectroscopy: The continuous wave EPR spectra were obtained at room temperature (~300 K) on the samples sealed firstly under argon flow glove box in glass pipettes. A Bruker EMx6/1 X-Band spectrometer with a rectangular cavity was used operating at a frequency of 9.8 GHz, with a 100 KHz modulation frequency, 0.1 mT modulation amplitude and ≤ 50 mW microwave power (50 mW at 6 dB attenuation). Modulation amplitude and time constant of EPR

registration were chosen from well-known requirements for undistorted registration of first derivative resonance absorption signal by magnetic induction.

EPR spectra of the studied coals were registered as a first derivative of the microwave absorption versus applied magnetic field. The parameters of the EPR spectra: g-factor, linewidth and integral intensity were evaluated. g-factor was determined as $g = hv/\beta H_r$, where h is the Planck constant, β the Bohr magneton, v the microwave frequency, and H_r is the resonance magnetic induction. The linewidth was determined as the difference of field positions of maximum and minimum of the first derivative EPR spectrum. The integral intensity is the distance between maximum and minimum of the first derivative EPR spectrum.

The XRD (Shimadzu MAXima_X XRD-700) measurements of the melted and crystallized samples were carried out at the 2θ -range from 5 to 70° with Cu-K α radiation.

Results and discussion

FTIR spectroscopy: Analytical data on the coal is provided by FTIR spectroscopy result (fig.1 raw coal, residue and extraction products). The coal insoluble residue spectra would yield the changes in basic absorption bands in coal (fig. 1 a) spectrum ILTCR. The main changes are in the FTIR spectrum intensity.

In both short (4000-2500 cm⁻¹) and long wave (2000-400 cm⁻¹) zones an intensity increase is significant for the case of ionic liquid as a solvent. This grandiose intensity increase is on a broad band around 3400 cm⁻¹ due to O-H and N-H stretching of various intermolecular hydrogen bonded groups like phenols and alcohol. The area is included either a stretching of CH_x group (2800-3100 cm⁻¹) of 2951, 2920 and 2850 cm⁻¹. Bands at 2920 and 2850 cm⁻¹ are from stretching (symmetrical and asymmetrical) vibrations of aliphatic group CH₂ and CH₃ relatively and an aromatic hydrogen around 3030 cm⁻¹. The absorption bands were well resolved due to the intensity increment in the area of 1500-400 cm⁻¹. In this area there are the bending of CH₂ and CH₃ groups [10, 11] at 1490, 1440 and 1385 cm⁻¹ whose intensity correlates preferentially with the intensity of bands from carbonate minerals in the area of 1300-900 cm⁻¹. Despite, the bands near 1400 cm⁻¹ are contributes to the presence of minerals [12], the identification of minerals such as clay minerals in the current area remains very difficult because of their complicated and non-constant composition and also because band positions can vary owing to isomorphous replacements. Furthermore, the notably overlapped absorptions at 1267, 1160, 1090 and 1020 cm⁻¹ were strengthened through solving processing. These absorptions are suchlike previous ones assigned to the mineral fractions in the coal matrix. Precisely, a presence of the bands of 1160 and 1040 cm⁻¹ calls the band near 694 cm⁻¹ is resulting from quartz [12] and 1260 cm⁻¹ is due to the aromatic ethers.

The prominent intensive absorptions in the short-wave zone are at 870, 800 and 750 cm⁻¹ from isolated out-of-plane deformational vibration (890-850 cm⁻¹) or two-adjacent (830-815 cm⁻¹) or three-adjacent (800-775 cm⁻¹) of sp²-hybrid bonded aromatic CH-groups. The strongly overlapped absorptions at 750 and 800 cm⁻¹ are an evident of different kinds of quartz in the coal [13]. Besides, there are the intense absorptions at 600, 530 and 460 cm⁻¹. The probable assignments to these bands are e.g. Si-O bending or

stretch, Si-O-Al deformation, Al-OH stretches and OH translations [14] by agree with element content, particularly true to Nalaikh coal.

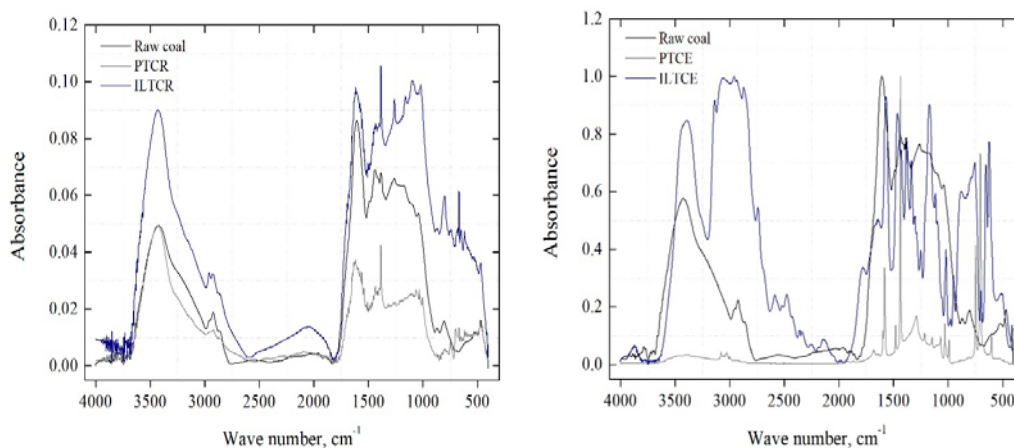


Fig. 1. FTIR spectra of Nalaikh raw coal and solvent treated samples

In the case of the ionic liquid treatment, solely an intensity of the broad band at 1600 cm^{-1} , from the carbonyl group (carbonyl absorption from in aromatic ring characterized by sp^2 -carbon or conjugated hydrogen bonded carbonyl groups, or due to donor and acceptor interaction between aromatic carbon macromolecules), is barely unchanged.

In opposite way of a trend in the intensity of the spectrum when the insoluble residue of Nalaikh coal and pyridine as a solvent interaction was received (fig. 1 a) spectrum PTCR. In this case an unchanged peak intensity was at 3400 cm^{-1} . The result above provides Nalaikh coal can be cleaned well by using and solving in pyridine as a solvent. Coal extraction products of both solvents were yielded sufficient amount and the FTIR spectra contain many intense absorptions from the solvent used, particularly, in the long-wave zones (fig. 1 b) spectra of PTCE and ILTCE. However, it should be noted that the ionic liquid is still a powerful solvent in the meaning of solving insoluble material like coal in the area of $3000\text{-}2800\text{ cm}^{-1}$.

EPR spectroscopy: Singlet, symmetric EPR spectra were registered for the studied Nalaikh coal in as received form and pyridine treated residue samples (fig. 2 a) spectra of raw coal and PTCR.

The parameters of the EPR spectra are as following:

- EPR line width is 7.43 Gs for the raw coal and 6.94 Gs for pyridine treated residue.

- g-factor is 2.0069 for both samples. This g-factor value is relatively high comparing those of free radical, therefore, it could be associated to the oxygen content.

Coal free radicals as integral intensities of the EPR signals were detected and quantified using the approximation: (the derivative amplitude $\cdot \Delta H_{pp} / 2$) / sample mass. An intensity of the EPR spectra is decreasing in the solvent treatment. It is clear that the

free radicals amount strictly depends linearly on the carbon (direct proportion) and oxygen (inverse proportion) contents in coal.

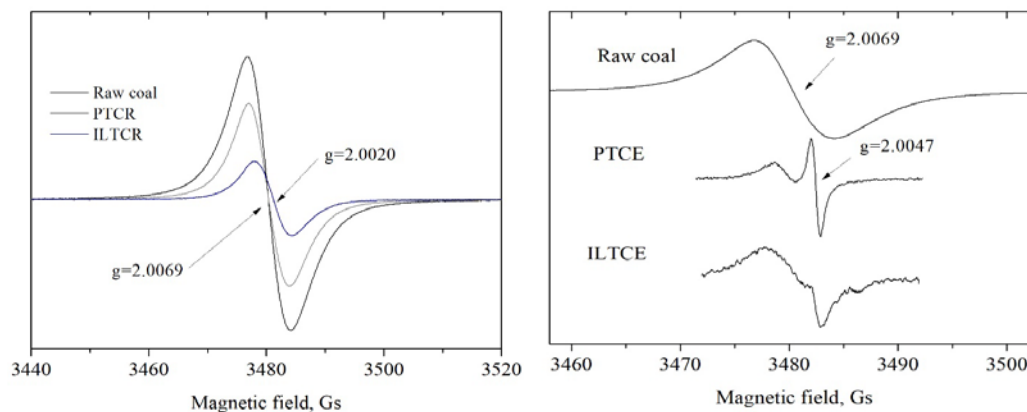


Fig. 2. EPR spectra of Nalaikh raw coal and solvent treated samples

For the ionic liquid treated case the EPR spectrum is asymmetric with g-factor of 2.0020 (fig. 2 a) spectrum ILTCR. Asymmetry indicates a complex character of coal EPR spectrum. But the variation of g-factor can be associated with free radicals of different nature in the samples. Accordingly, it might be non-identical paramagnetic species, which are differently located in an exterior magnetic field or presence of crystal field, in the sample [15-17].

For the ionic liquid treated case the EPR spectrum is asymmetric with g-factor of 2.0020 (fig. 2 a) spectrum ILTCR. Asymmetry indicates a complex character of coal EPR spectrum. But the variation of g-factor can be associated with free radicals of different nature in the samples. Accordingly, it might be non-identical paramagnetic species, which are differently located in an exterior magnetic field or presence of crystal field, in the sample [15-17].

Thereafter, this differentiation in the paramagnetic centers is provided well resolved spectra from extraction products (fig. 2 b) spectra of PTCE and ILTCE. In fig. 2, it is clearly shown well resolved EPR spectra for the extraction products. The central narrow line has g-factor of 2.0047 which is overlapped with the initial broad coal line.

Conclusion

Organic solvents such as pyridine and imidazolium based ionic liquid as [Bmim]Cl anion were applied for the solubility of low rank Nalaikh coal. Extraction products could have received for the both solvents. FTIR spectroscopy shows a well productivity of the extraction using the ionic liquid. However [Bmim]Cl solvent treated residue was less promising by the intensity increase. Pyridine cleans coal well.

Coal free radical quantification via EPR spectrum intensity indicates a significant decrease due to the solvent treatment. An asymmetry of the residue EPR spectrum is evidenced a strong solubility quality of the used ionic liquid than the ordinary solvent

like pyridine. Different paramagnetic centers are good resolved in the EPR spectra of the extraction samples.

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References

1. Bat-Orshikh E., Insung L., Delegiin B.-E., Luvsanchultem J. Mongolian coal-bearing basins: Geological settings, coal characteristics, distribution, and resources // *International Journal of Coal Geology*. — 2009. — V. 80, № 2. — P. 87-104.
2. Tognotti L., Petarca L., D'Alessio A., Benedetti E. Low temperature air oxidation of coal and its pyridine extraction products: Fourier transform infrared studies // *Fuel*. — 1991. — V. 70. — P. 1059-1064.
3. Frank R.M., John S.Z., Lee A.P. Extractions and reactions of coals below 100°C: 1. Solubilities of coals in pyridine and amines // *Fuel*. — 1988. — V. 67, № 5. — P. 595-599.
4. Petrakis L., Grandy D.W. Formation and behaviour of coal free radicals in pyrolysis and liquefaction conditions // *Nature*. — 1981. — V. 289. — P. 476-477.
5. Larsen J.W., Baskar A.J. Hydrogen bonds from a subbituminous coal to sorbed solvents. An infrared study // *Energy Fuels*. — 1987. — V. 1, № 2. — P. 230-232.
6. Ndaji F.E., Thomas K.M. The kinetics of coal solvent swelling using pyridine as solvent // *Fuel*. — 1993. — V. 72, № 11. — P. 1525-1530.
7. Painter P., Pulati N., Cetiner R., Sobkowiak M., Mitchell G. M. Dissolution and Dispersion of Coal in Ionic Liquids // *Energy Fuels*. — 2010. — V. 24. — P. 1848-1853.
8. Yi Li, Xiangping Zhang, Shiyao Lai, Haifeng Dong, Xuelian Chen, Xiaoliang Wang, Yi Nie, Ying Sheng, Suojiang Zhang. Ionic liquids to extract valuable components from direct coal liquefaction residues // *Fuel*. — 2012. — V. 94. — P. 617-619.
9. Khurelkhuu P. The final technical report of a pre-feasibility study on methane recovery and utilization in the Nalaikh mine area, Mongolia // *Mongolian Nature and Environment Consortium*. — 2010
10. Dayer J.R. Application of absorption spectroscopy on organic compounds. — M.: Chemistry, 1970. — 164 p.
11. Dick D.P., Mangrich A.S., Menezes S.M.C., Pereira B.F., Betania F. Chemical and spectroscopical characterization of humic acids from two south Brazilian coals of different ranks // *J. of the Brazilian Chemical Society*. — 2002. — V. 13, № 2. — P. 177-182.
12. van der Marel H. W., Beutelspacher H. Atlas of infrared spectroscopy of clay minerals and their admixtures. — Amsterdam: Elsevier, 1976. — 396 p.
13. Gómez-Serrano V., Fernández-González M.C., Rojas-Cervantes M.L., Alexandre-Franco M.F., Macías-García A. Carbonization and demineralization of coals: A study by means of FT-IR spectroscopy // *Bulletin of Materials Science*. — 2003. — V. 26, № 7. — P. 721-732.
14. Frost R., Vassallo A.M. The dehydroxylation of the kaolinite clay minerals using infrared emission spectroscopy // *Clays and Clay Minerals*. — 1996. — V. 44, № 5. — P. 635-651.
15. Retcofsky H.L., Stark J.M., Friedel R.A. Electron spin resonance in American coals // *Anal. Chem*. — 1968. — V. 40, № 11. — P. 1699-1704.
16. Berveno V.P. Separation of the compound EPR spectra of bituminous coals to broad and narrow components // *Solid Fuel Chemistry*. — 1982. — V. 1. — P. 57-58
17. Doetschman D.C., Mustafi D.E. p.r. and spin echo study of bituminous coal radicals // *Fuel*. — 1985. — V. 65. — P. 684-693.

ОРГАНИЧЕСКИЕ РАСТВОРИТЕЛИ ТАКИЕ КАК ПИРИДИН
И ИМИДАЗОЛИЧЕСКАЯ ИОННАЯ ЖИДКОСТЬ [Bmim]Cl
ВЛИЯЮЩИЕ НА ФУНКЦИОНАЛЬНЫЕ ГРУППЫ
И ПАРАМАГНИТНЫЕ СВОЙСТВА БУРОГО УГЛЯ НАЛАЙХА

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Работа посвящена рассмотрению результатов растворения бурого угля Налайха в органических растворителях, таких как пиридин и имидазолическая ионная жидкость [Bmim]Cl. Бурый уголь Налайха и полученные образцы после растворителя изучались методами инфракрасной спектроскопии с Фурье преобразованием и электронного парамагнитного резонанса. Показано, что различные парамагнитные центры хорошо разрешены в спектрах ЭПР в изученных образцах.

Ключевые слова: бурый уголь, пиридин, имидазол, ионная жидкость, парамагнитные свойства, инфракрасная спектроскопия с Фурье преобразованием, электронный парамагнитный резонанс.