

Interactions between Coal and Solvent during the Solvent Extraction of Coal in View of Free Radicals

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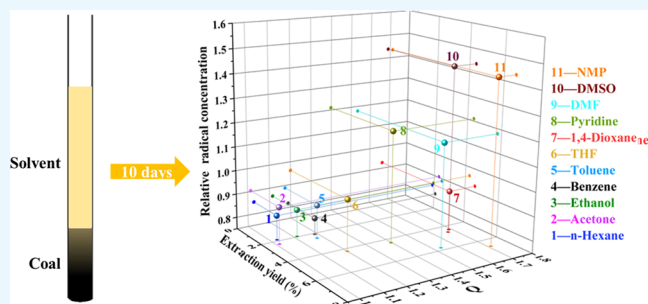
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ABSTRACT: In this study, variations in the free radical concentration, degree of swelling (Q), and extraction yield of Buertai coal (C%, 80.4%) in 11 solvents with different characteristics were determined to investigate the interaction between the coal and solvent, as well as the bond cleavage during solvent extraction. Derivative thermogravimetry (DTG) results for the residues and raw coal were compared to confirm whether the covalent bond breaks during solvent extraction. The free radical concentration decreases in certain solvents but increases in a few others. The relative free radical concentration, Q , and extraction yield are positively correlated. The charge-transfer capability of the solvent, and in particular its electron-donating capability, plays an essential role in influencing the interaction between the coal and solvent. The increase in the free radical concentration during solvent extraction can be attributed to (1) the formation or decomposition of charge-transfer complexes, (2) dissociation of charge-transfer complexes into radical ions, and (3) breakage of weak covalent bonds. DTG results show the occurrence of weak covalent bonds breakage at temperatures of 133.9–320.1 °C during solvent extraction due to the reduction of the bond energy caused by the formation of radical ions.



1. INTRODUCTION

Coal is an important fossil fuel with a complex structure consisting of a macromolecular phase connected by cross-links, forming a three-dimensional network and a small molecular phase.¹ The two phases are mainly connected by noncovalent bonding forces such as van der Waals forces, hydrogen bonds, π - π interactions, and charge-transfer interactions.^{2–5} The solvent extraction of coal is an important process to investigate the molecular structure of coal,⁶ extraction and refining of organic matter in coal,^{7–9} and pretreatment of coal.^{10–12}

Solvent properties play an important role in solvent extraction. The viscosity of solvents affects solvent penetration and extractive diffusion; for example, the extraction yield of CS₂/*N*-methyl pyrrolidone (NMP) is high because the addition of CS₂ reduces the viscosity of the NMP solvent, enabling the penetration and diffusion of the solvent.¹³ Chemical properties influence the interaction between coal and the solvent, resulting in different weakening effects on the cross-links in coal, thereby affecting the extraction yield and swelling. For example, the extraction yields of Buertai (BET) coal (C%: 80.4%) in *n*-hexane, toluene, tetralin, tetrahydrofuran (THF), and NMP solutions at room temperature are 0.7, 1.2, 1.2, 1.9, and 6%, respectively,¹⁴ and the degrees of swelling of Illinois No. 6 coal (C%: 80.6%) at 20 °C after 10 days of storage in methanol, ethanol, 1-propanol, 1-butanol, *n*-propylamine, *n*-butylamine, and *n*-hexylamine are 1.23, 1.24, 1.36, 1.34, 2.45, 2.64, and 3.19, respectively.¹⁵

When a solvent penetrates coal, the interaction between the solvent and coal molecules would negatively affect the interactions among the coal molecules, causing changes in the three-dimensional structure of coal.^{11,16} Most researchers believe that covalent bonds break only at 300 °C or above because of their relatively higher energy. Therefore, many phenomena such as swelling and an increase in the extraction yield at elevated temperatures are primarily attributed to the breakage of noncovalent bonds,^{17–20} which possess lower energy. Mathews et al.¹⁵ extensively summarized the literature and noted that the higher extraction yields (>20%) could be attributed to hydrogen bond breakage rather than covalent bond breakage in coal. However, they noted that the influence of covalent bond breakage on the increase in the solvent extraction yield at temperatures higher than 350 °C remained unclear. Chen et al.¹⁸ proposed that the swelling of coal was mainly induced by the breakage of noncovalent bonds, such as hydrogen bonds and bonds held together by van der Waals forces. Zhang et al.²¹ reported that the dissolution behavior of

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low-molecular-weight compounds in coal is essentially determined by the strength of noncovalent interactions between such compounds and the macromolecular structure of coal.

However, some studies have shown that covalent bonds break at low temperatures. Lv et al.²² found that the oxidation of Yanshan petroleum coke with sodium hypochlorite at 30 °C can produce various arene carboxylic acids and that $O_2^{\bullet-}$ plays an essential role in the depolymerization of condensed aromatic moieties. Yi et al.²³ reported that a Se–N covalent bond with an estimated bond energy of 46.11 kcal mol⁻¹ could be dynamically cleaved by heating or treatment with stronger electron-donating pyridine derivatives. Kozłowski et al.²⁴ reported the breakage of the C–C bond in the reduction reaction of a K/liquid ammonia system. Xiong et al.²⁵ indicated that H₂O₂ breaks the bridge bonds and side chains connected to aromatic clusters during the oxidation of coal with H₂O₂ at 60 °C. Our previous studies found that the free radical concentrations of the three coals increased during solvent extraction with NMP.¹⁴ The increase is likely due to the breakage of weak covalent bonds, as covalent bond breakage always generates free radicals. However, aspects such as the mechanism for the breakage of weak covalent bonds during solvent extraction and further elucidation explaining the increase in the free radical concentration during solvent extraction remain to be addressed.

To overcome these challenges, it is important to first understand the interaction between the solvent and coal during solvent extraction. Therefore, in this study, 11 solvents with different properties were used for the solvent extraction of BET coal. The changes in the free radical concentrations, degree of swelling (*Q*), and extraction yields were determined to investigate the interaction between the solvents and coal, as well as the bond cleavage in coal. To confirm the occurrence of covalent bond cleavage during solvent extraction, the derivative thermogravimetry (DTG) results for the residues after solvent extraction were acquired and compared with that of raw coal.

2. RESULTS AND DISCUSSION

2.1. Changes in the Free Radical Concentration and *Q* during Solvent Extraction.

Based on testing, the solvents contained no free radicals, and none were produced after storage at room temperature. The BET coal inherently possesses many free radicals, the concentrations of which remain unchanged after a while. Interestingly, we found that when solvents were added to the BET coal, its free radical concentration changed over time, even at room temperature (Figure 1). The variation in the free radical concentration was different for different solvents. According to Figure 1, the changes in the free radical concentration of the BET coal can be approximately classified into three stages during solvent extraction. For *n*-hexane, benzene, and toluene, the free radical concentrations decrease gradually over time; for ethanol, 1,4-dioxane, THF, and acetone, the free radical concentrations decrease first and then increase slightly after 10 h of solvent extraction but are lower than the original values; for DMF, dimethyl sulfoxide (DMSO), pyridine, and NMP, the free radical concentrations increase gradually up to 30% over time.

The decrease in the free radical concentration can be attributed to the combination of free radicals.^{14,26} In the coal structure, small and medium-sized molecules are embedded in the macromolecular network of coal *via* noncovalent bonds. During solvent extraction, the interactions between the coal

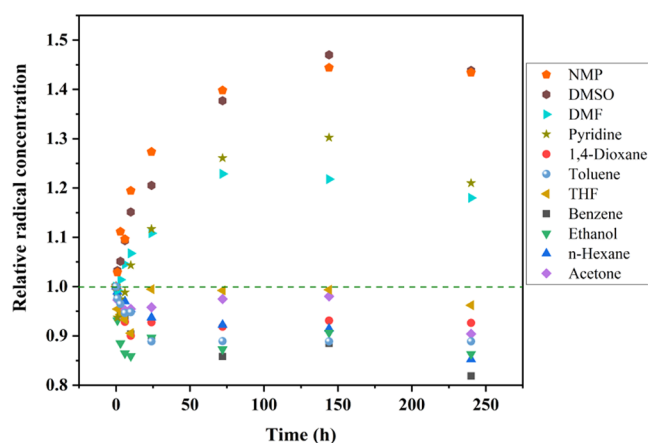


Figure 1. Variation in the free radical concentration during solvent extraction.

and solvent inhibit those between the small molecules and the macromolecular network structure. When the small molecules separate from the macromolecular network of coal, the radicals on the small molecules and the macromolecular network of coal are exposed, enabling their binding.

An increase in free radical concentration always means the generation of free radicals caused by the breakage of the covalent bond.²⁷ However, typically, covalent bond cleavage is not considered during solvent extraction. Therefore, it is difficult to understand the reason for the increase in the radical concentration during solvent extraction; the same will be discussed later.

By observing the changes in the free radical concentration during solvent extraction, we found that the coal swelled in the sample tube. The *Q* values of the coal samples were subsequently determined and calculated. Figure 2 shows that

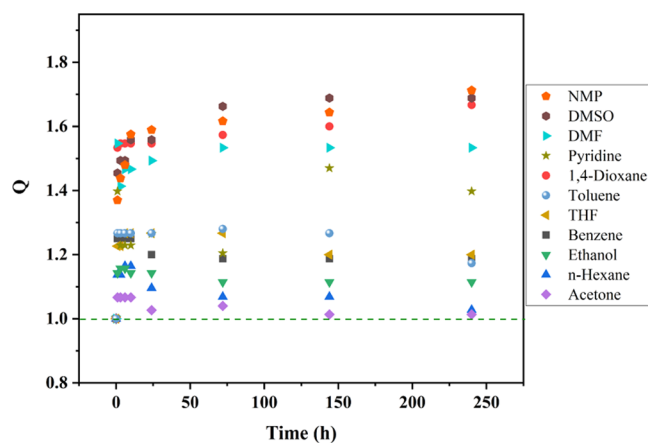


Figure 2. Changes in *Q* during solvent extraction.

the coal samples swell significantly in NMP, DMSO, 1,4-dioxane, DMF, and pyridine; swell moderately in toluene, THF, benzene, and ethanol; and swell slightly in acetone and *n*-hexane. *Q* increases with time for solvents such as NMP, DMSO, 1,4-dioxane, and DMF, but decreases with time for the other solvents. It is generally considered that during solvent extraction, the solvents penetrate the coal, break the noncovalent bonds, and reduce the cross-linking density of the coal.²⁸ Consequently, the structure of the coal is fully stretched and relaxed, leading to the swelling of the coal.¹⁶ This can be

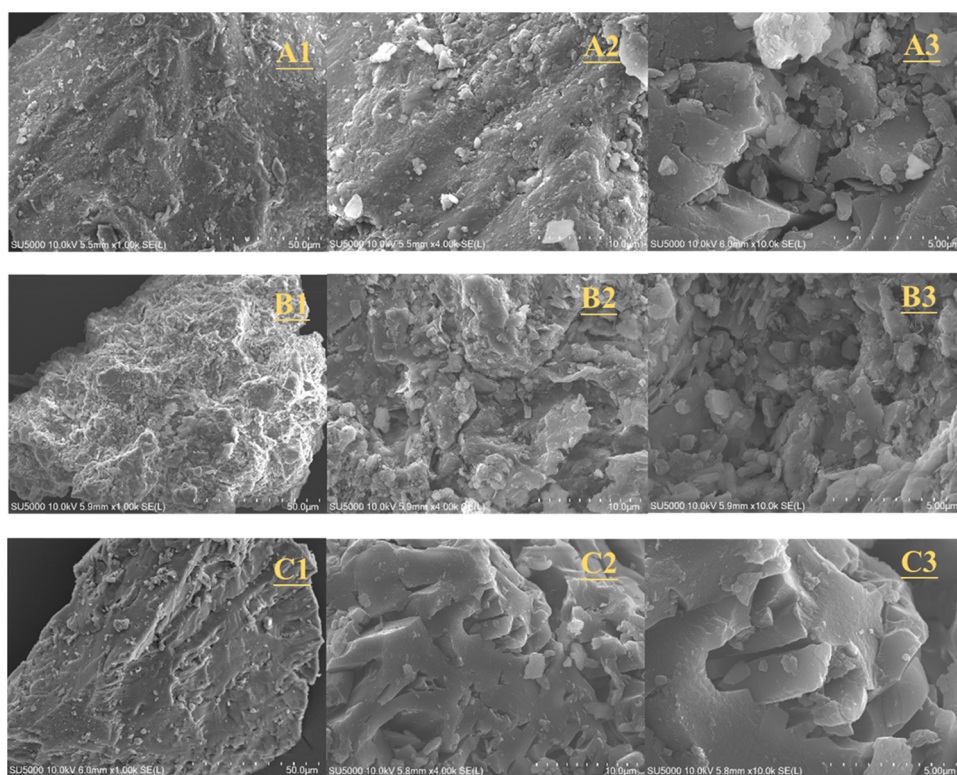


Figure 3. SEM images of (A) coal and residues (B) after NMP extraction and (C) after THF extraction: (1) $\times 1.0k$; (2) $\times 4.0k$; and (3) $\times 10.0k$.

verified by the scanning electron microscopy (SEM) images of the residues (Figure 3). According to Figure 3, the residue after NMP extraction has a looser structure and more debris than the raw coal.

The decrease in Q in this experiment was unusual. Two possible reasons could explain this phenomenon. The first is that the amount of solvent penetrating the coal structure is lower than the amount of coal dissolved in the solvent during solvent extraction, which leads to the collapse of the coal structure. According to the SEM images of the residue after THF extraction (Figure 3), the residue has more gaps, but the lumpy part is denser in structure compared with the raw coal, which confirms the above speculation. The collapse of the coal structure further led to the combination of free radicals during solvent extraction, especially in the macromolecular network of coal. The second reason is the settling of pulverized coal over time because the experiment was carried out in a closed glass tube, and it was impossible to perform centrifugation before measuring the height.

The extraction yields were also detected and compared with the experimental results shown in Figures 1 and 2. Solvents with a high Q , such as NMP and DMF, were found to possess a high relative radical concentration and high extraction yield. Therefore, we correlated the data for Q , the extraction yield, and relative free radical concentration on the 10th day of solvent extraction (Figure 4). From Figure 4, we found that solvents with a high Q always exhibit an increased free radical concentration and high extraction yield. This phenomenon indicates that solvent extraction is not merely a simple physical process. It is inevitably accompanied by the destruction of some kind of force in the coal molecule. Simultaneously, solvent properties are an essential factor affecting the extraction process.

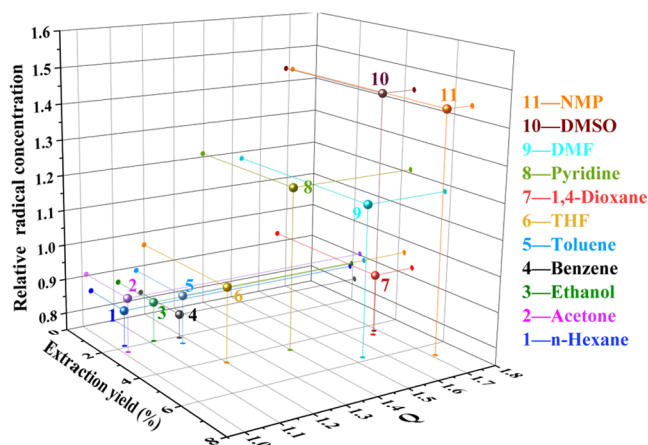


Figure 4. Relationships among the relative radical concentration, Q , and extraction yield on the 10th day of solvent extraction.

2.2. Effect of Solvent Properties. According to previous reports, solvent properties such as solubility,²⁹ viscosity, polarity,³⁰ electron-donating capacity, and electron-accepting capacity³¹ possibly affect the interaction between the coal and solvent during solvent extraction. The effects of these solvent properties on the variation in the radical concentration and swelling were also studied. Since the solvent properties have similar effects on the radical concentration and swelling, we discuss only one of them in this paper.

The results in Figure 5 show that the free radical concentrations approximately increase with the solubility parameters, viscosity, solution dielectric constant, electron donor number (DN), electron acceptor number (AN), and the DN-AN of the solvents, except for ethanol. The solubility parameters reflect the solubility of coal in solvents and follow

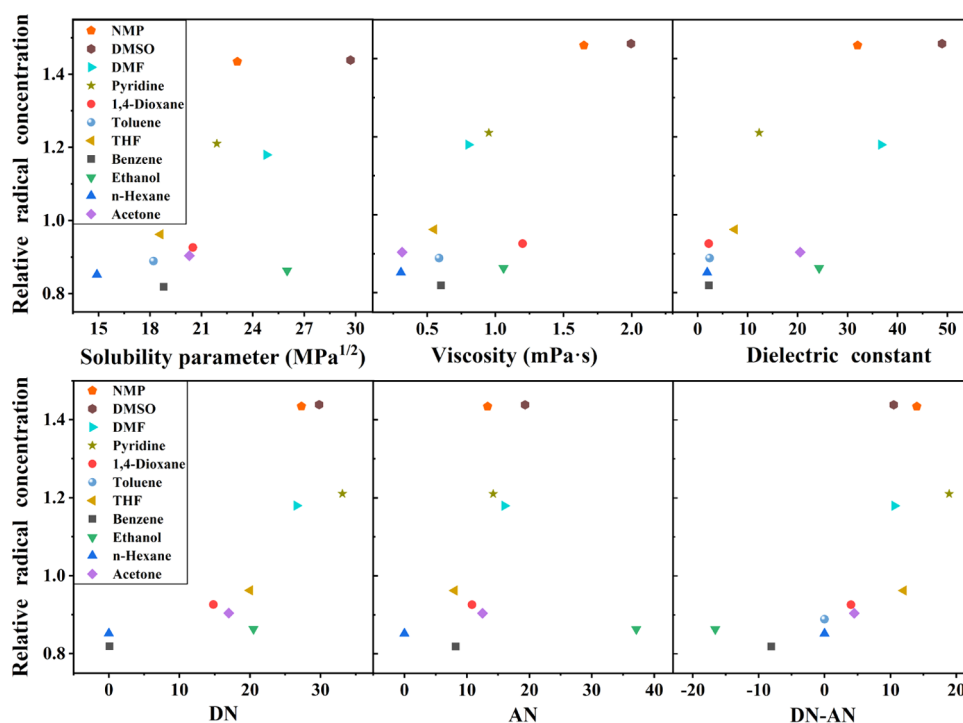


Figure 5. Relationships between solvent properties and free radical concentration.

the rule of “like dissolves like”. The solubility parameter of coal is $\sim 25 \text{ MPa}^{1/2}$,^{32,32} which is closest to that of DMF, among all solvents; however, the free radical concentration of coal is not the highest in the DMF solution. Physically, the viscosity of the solvent affects solvent penetration and extractive diffusion, and high viscosity is unfavorable for the extraction process; however, the free radical concentration increases with the viscosity. These phenomena indicate that the solvent extraction of coal is a physical process accompanied by chemical changes. The dielectric constant reflects the polarity of a solvent. The higher the polarity of a solvent, the easier it is to acquire or lose electrons. The DN, AN, and DN-AN are parameters that directly reflect the capability of the solvents to donate and accept electrons.

In Figure 5, the free radical concentration exhibits the best regularity with the data for DN and DN-AN. Thus, we can conclude that solvent extraction is mainly affected by the charge-transfer capability. For ethanol, the solubility and AN are high, whereas the polarity and DN are low, and hence, the radical concentration of the coal is low. These results indicate that the electron-donating capability plays an essential role in influencing the interaction between coal and solvent. Bodzek et al.³³ revealed that a higher extraction yield is obtained for a solvent with higher electron-donating ability, and the extraction can be regarded as a substitution reaction between the electron-donating solvent molecules substituted with electron-donating fragments of coal. Szeliga et al.³⁴ reported that the swelling of coal was strongly correlated with the electron-donating ability of the solvent. These observations are consistent with the results of the present study.

2.3. Reasons for the Increase in Radical Concentration. The decrease in the free radical concentration during solvent extraction is easy to understand, as explained in the preceding section. However, an increase in the same is complex and difficult to understand. Analysis of the variation in the free radical concentrations during solvent extraction helps

enhance our understanding of the interaction between the coal and solvent. Therefore, in this section, we attempt to elucidate why the free radical concentration increases during solvent extraction.

2.3.1. Formation or Decomposition of Charge-Transfer Complexes. As shown in Figure 5, the free radical concentration increases with the DN and DN-AN of the solvents. Charge transfer is among the predominant routes for noncovalent coal-coal interactions in the BET coal.^{2,35} When solvents with electron-donating and electron-accepting capabilities are added to the coal, the interactions between the solvents and the coal may inhibit those among the coal molecules, forming new charge-transfer complexes that replace the coal-coal complexes.³⁶ The substituted fragments of coal can be molecules with or without free radicals. Further, the formation or decomposition of charge-transfer complexes may release radicals, leading to an increase in the radical concentration.

Oxygen adsorption is also a charge-transfer process.³⁷ Oxygen is an electron acceptor and can combine with an electron-donating group (molecules or radicals) in the coal to form coal-oxygen complexes.^{38,39} Dack et al.³⁹ reported that free radicals responsible for the narrow signal in brown coal electron spin resonance (ESR) spectra interact reversibly with atmospheric oxygen because of the formation of coal-oxygen complexes during coal oxidation. To analyze the change in the free radical concentration during charge transfer, we can investigate such a change during the adsorption or desorption of oxygen by coal.

Because coal samples may be repeatedly exposed to oxygen during mining, transportation, and laboratory storage, we used fresh semicoke produced by pyrolysis at 600°C to investigate the change in the free radical concentration during oxygen absorption and desorption by in situ ESR. The oxygen absorption was performed by exposing the sample tube with semicoke to air, and deoxygenation was achieved by purging

the sample tube containing semicoke (which was oxygenated) with nitrogen. The results are shown in Figure 6. The free

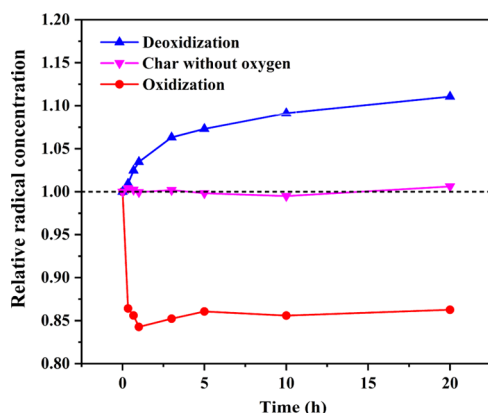
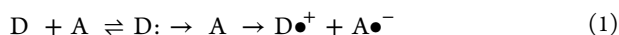


Figure 6. Variation in the free radical concentration during oxygen absorption and desorption.

radical concentration of semicoke decreases after oxygen absorption and increases after deoxidation but changes slightly when sealed in the tube without oxygen. Bradbury et al.⁴⁰ and Xiang et al.⁴¹ also showed that the radical concentration of chars decreased considerably by oxygen adsorption but increased by nitrogen purging. These phenomena can be attributed to the formation and decomposition of coal–oxygen complexes,^{39,42,43} similar to the formation and decomposition of charge-transfer complexes in the solvent extraction of coal.

2.3.2. Dissociation of the Charge-Transfer Complexes. The newly formed charge-transfer complexes may also dissociate into radical cations and radical anions under certain conditions,^{44,45} as shown in formula 1



where D is the electron donor, A is the electron acceptor, and D:→A is the charge-transfer complex. Some small radical ions are annihilated by the coupling reaction, but some with high steric hindrance may exist stably in the system, leading to an increase in the radical concentration. Miyajima⁴⁶ found that when iodine was introduced into coal tar pitch (CTP) at room temperature, charge-transfer complexes were formed, and the radical concentration of the CTP increased. Further, hyperfine sublevel correlation spectroscopy detected a radical cation with a relatively high molecular weight. Therefore, the dissociation of the charge-transfer complexes can lead to an increase in the radical concentration.

2.3.3. Breakage of Weak Covalent Bonds. The formation of radical ions after charge transfer can significantly relax chemical bonds.^{47–49} This relaxation is beneficial to the breakage of chemical bonds and can lead to the swelling of the coal. Pruitt⁵⁰ and Xue⁵¹ reported that the bond energy is significantly reduced after the formation of free radical cations or anions through charge transfer. For example, the bond dissociation energies of C–H, C–H^{•+}, and C–H^{•-} in xanthene are 75, 41, and less than 43 kcal mol⁻¹, respectively. The decrease in the bond energy assists covalent bond breakage during solvent extraction.

To verify the occurrence of covalent bond cleavage during solvent extraction, DTG plots of the BET coal were compared with those of the residue after 10 days of solvent extraction, and the results are shown in Figure 7. Compared with the raw

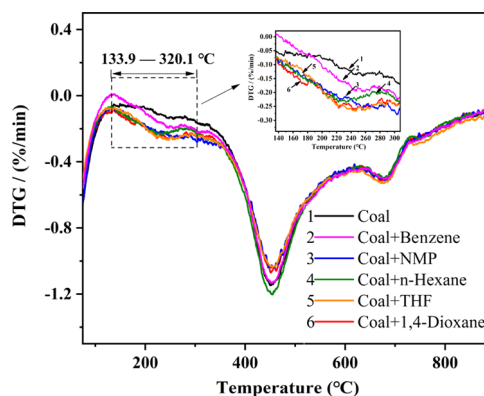


Figure 7. DTG curves of raw coal and residues.

coal, all residues showed a prominent weight loss at temperatures of 133.9–320.1 °C. Note that the weight loss at 133.9–320.1 °C did not represent the weight loss of the solvents because the solvents were removed. In our previous study,¹⁴ we found that the free radical concentrations increased with time at 85 °C using THF as the solvent and increased with the time and temperature when using NMP. The increase in the radical concentration, combined with the weight loss shown in Figure 7, indicates the occurrence of covalent bond breakage at temperatures of 133.9–320.1 °C or even lower during solvent extraction. The breakage of covalent bonds during solvent extraction is related to the formation of radical ions during charge transfer.

2.4. Mechanism for Increase in Radical Concentration. According to the above analysis, the mechanistic diagram describing free radical production during solvent extraction has been proposed, as shown in Figure 8. In Figure 8, Process ①

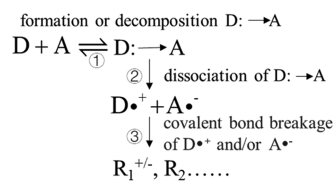


Figure 8. Mechanistic diagram of the free radical production during solvent extraction. R: radicals.

refers to the formation or decomposition of the charge-transfer complex; Process ② refers to dissociation of the charge-transfer complex into radical ions; and Process ③ refers to covalent bond breakage of the radical ions because the formation of the radical ions reduces the energy of the bond. Processes ①, ②, and ③ all lead to an increase in radical concentration.

3. CONCLUSIONS

In this study, the BET coal (C%, 80.4%) was extracted using 11 solvents with different characteristics to analyze the interactions between the coal and solvents with respect to the free radicals. The trend in the variation of the free radical concentration of coal differed for the different solvents: in hexane, benzene, and toluene, the free radical concentration gradually decreased; in ethanol, 1,4-dioxane, THF, and acetone, the free radical concentration first decreased and then slightly increased after 10 h of solvent extraction; in DMF, DMSO, pyridine, and NMP, the free radical concentration gradually increased. The decrease in the radical concentration

Table 1. Proximate and Ultimate Analysis Results for the BET Coal^a

M_{ad}	proximate analysis (wt/%)			ultimate analysis (wt/%)				
	A_{ad}	V_{ad}	FC_{ad}	C_{daf}	H_{daf}	O_{daf}^*	N_{daf}	$S_{t,daf}$
9.67	16.21	27.44	46.68	79.29	3.95	15.08	1.19	0.49

^aNote: M: moisture; A: ash; V: volatile; FC: fixed carbon; ad: air dry; daf: dry and ash-free; t: total; *: difference.

Table 2. Properties of the Solvents^{52,53}

Name	Formula	Solubility parameters (MPa ^{1/2})	Viscosity (25 °C, mPa·s)	Dielectric constant (25 °C)		
				DN ^{52, 53}	AN ^{52, 53}	
n-Hexane		14.9	0.296	1.90	0.0	8.2
Benzene		18.8	0.606	2.27	0.1	10.8
Toluene		18.2	0.548	2.38	--	0.0
Ethanol		26.0	1.057	24.30	20.5	37.1
1,4-Dioxane		20.5	1.211	2.21	14.8	12.5
THF		18.6	0.465	7.39	20.0	8.0
Acetone		20.3	0.308	20.50	17.0	16.0
DMF		24.8	0.843	36.71	26.6	19.3
DMSO		29.7	1.968	48.90	29.8	14.2
Pyridine		21.9	0.898	12.30	33.1	13.3
NMP		23.1	1.650	32.00	27.3	14.0

in coal can be attributed to the binding reaction of free radicals; however, the increase in the radical concentration is a relatively complex mechanism. The relative free radical concentration, Q , and extraction yield were positively correlated. The charge-transfer capability, particularly the electron-donating capability of the solvent, influences the interaction between the coal and solvent. The increase in the free radical concentration during solvent extraction can be attributed to (1) the formation or decomposition of charge-transfer complexes, (2) dissociation of charge-transfer complexes into radical ions, and (3) breakage of weak covalent bonds at temperatures of 133.9–320.1 °C or even lower during solvent extraction due to the reduction of the bond energy

caused by the formation of radical ions. These findings are essential for a better understanding of the solvent extraction process, the choice of solvents for the extraction or pretreatment of coal, and the enhancement of the extraction yield.

4. EXPERIMENTAL SECTION

4.1. Materials. The coal used in this study was the BET coal. Its proximate analysis (following the China National Standard GB/T 212-2008) and ultimate analysis results are shown in Table 1. The coal was ground and sieved to a size of 0.106–0.125 mm and dried at 110 °C under a vacuum for 6 h before the extraction experiments.

The solvents used were benzene, toluene, *n*-hexane, 1,4-dioxane, ethanol, acetone, THF, DMF, dimethyl sulfoxide (DMSO), pyridine, and NMP. These solvents were of analytical reagent grade, and their properties are shown in Table 2.

4.2. Radical and Swelling Analysis during Extraction.

A coal sample (5 mg) and solvent (60 μ L) were loaded in a glass capillary (2 mm in diameter) and sealed after purging with N₂ for a few minutes. The glass capillary-loaded samples were then inserted into a sample tube for ESR measurements (E-Scan, Bruker). The ESR measurements were performed at regular intervals at 25 °C. Blank experiments were also performed. The radical concentration data are represented as a percentage with respect to the initial value before extraction to avoid small differences in the sample loading.

The heights of the coal samples were also recorded after each radical measurement, and the *Q* of the coal samples was calculated by

$$Q = h_t/h_0 \quad (2)$$

where h_t is the height of the coal sample at time t and h_0 is the initial height of the coal sample.

4.3. Determination of the Extraction Yield. The extraction experiments were carried out in a closed tube to ensure consistency with the aforementioned experiments. The coal sample (50 mg) and solvent (0.6 mL) were added to the tube, following which the tube was sealed and stored at room temperature for 10 days. Subsequently, the slurry was filtered, and the residue was washed with ethanol and water and dried at 75 °C for 6 h under a vacuum. Finally, the residue was weighed, and its mass was labeled as m_{residue} . The extraction yield was determined by

$$\text{extraction yield} = \frac{m_{\text{coal}} - m_{\text{residue}}}{m_{\text{coal}}(1 - A_{\text{ad}} - M_{\text{ad}})} \quad (3)$$

where m_{coal} is the mass of the coal material dried at 110 °C for 6 h.

4.4. Analysis of the residues. The morphology of the residues was evaluated by SEM (SU8010), and the thermal weight loss of the residues was analyzed by thermogravimetry (TG) using a thermogravimetric analyzer (STA449F3; NETZSCH).

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Notes

The authors declare no competing financial interest.

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