

Synthesis and Ion-Exchange Properties of Amine Derivatives of Oxidized Coals

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Abstract

Chemical modification of oxidized and weathered coals from the Shubarkol field (Kazakhstan) is studied. Coals are shown to be fit for the synthesis of amine derivatives *via* their interaction with amines (diamines) in the presence of acidic catalysts. Physical and chemical analysis data support the suggested synthesis scheme. Conductometric analysis method is developed for determining the functional composition of the oxidized coal modification products. It is demonstrated that nitrogen introduction into the coals improves their complexing ability and makes them polyampholyte. Sorption capacity of amine derivatives as pH function is shown to be a parabola with minimum at pH 4–5. This fact confirms the polyampholyte nature of these agents. Amino modified coals may be used for demineralization of mine waters and as extracting agents for metal ions precipitation from hydrometallurgy wastewaters.

INTRODUCTION

Humic acids (HA) of coals are known to be subacid cation exchangers. When nitrogen atoms being more inclined to donor-acceptor bonding with metal ions than oxygen ones are introduced into these coals, the latter become more complexing and polyampholyte.

One of our HA amination method includes preliminary electrochemical chlorination stage. Then chlorine atoms are substituted by the amino groups [1]. Carbonyl groups present in HA allow the simpler direct amination. This way is proved to be possible for the coals from the Kyzyl-Kiya field [2].

This work aims at the modification of naturally oxidized coals from the Shubarkol field (Central Kazakhstan) *via* their direct amination. Synthesized amine derivatives are studied with regard to their poly ampholyte properties.

EXPERIMENTAL

Humic acids being extracted with alkali from the oxidized coals of the Shubarkol field have

the following characteristics: yield (with respect to dry mass) – 70 %, nitrogen content – 1.02 %, carboxyl groups content – 3.5 mg-eq/g, phenol group content – 2.0 mg-eq/g, reduced viscosity of 1 % solution – 0.07 dl/g.

Monovinyl ether of monoethanol amine (VEEA) was distilled at boiling point 50 °C/15 mm, $n_d^{20} = 1.4382$, $d_4^{20} = 0.909$.

Coal amination was performed in water at 70–95 °C for 1–2 h in the presence of acetic acid or sodium acetate. Thus synthesized mixture was treated by the water solution of acid. Sediment was filtered off and then dried.

Acid groups number in the product was determined by the conductometry in titration of alkali or ammonia solutions by sulphuric acid. Amino groups were determined *via* the hydrochloric acid solution titration by the alkali. The carbonyl groups content was determined *via* the formation of oximes [3].

Static exchange capacity (SEC) of heavy and transition metal ions (copper sulphate, nickel chloride, ferric chloride, calcium chloride) was studied under static condition at the ambient temperature, (ion exchanger) : (salt solution)

ratio being 1 : 100. Starting metal salt concentration was 0.05 mol/l, contact time was 24 h. Initial and equilibrium concentrations of metal cations were determined by the complexometric titration [4, 5].

Exchange capacity (EC) at various pH was determined by potentiometric method [6] (for certain samples). Weighted samples of H-form ion exchanger (0.1 g) were put into flasks and covered with the same amount of 0.2 M NaCl solution. Thus prepared samples were titrated by the 0.1 M NaOH (0–5 ml) with a step of 0.5 ml. Solution pH was determined 3 days after titration procedure was completed. Separately sodium chloride solution was titrated by the 0.1 M NaOH solution. EC was determined for each pH value by the difference of abscissas of the points lying on the two plots, pH value being the same. For the acid range plots building 0.1 M HCl solution was used instead of alkali, and above described titration procedure was repeated.

Desalinization of the mine water samples from the Karaganda field (mineralization 4.5 g/l) was carried out by amine derivatives under static conditions at the room temperature, amine derivative: mine water ratio being 1 : 50. Sodium and potassium cations (1500 mg/l) dominate in the mine water, which also contains the cations of magnesium, calcium, copper and iron in small amounts. Anions content (SO_4^{2-} , Cl^- , HCO_3^-) was 3000 mg/l. Mineral salts content and specific electrical conductance of samples were determined using conductometer 2020.

ESR spectra were registered using spectrometer 1306 equipped with dispersion observation device. Nitroxyl served as intensity and bandwidth standard.

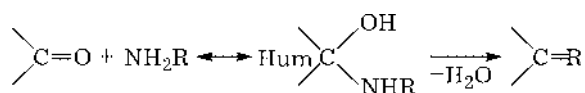
Thermal analysis was performed using NETZSCH STA 409 PC/PG.

IR spectra were registered in KBr tablets using spectrometer UR-20.

RESULTS AND DISCUSSION

Aliphatic amines were used to obtain amine derivatives: VEEA, diethylamine (DEA) and ethylenediamine (EDA). Medium acidity maintenance in the range of pH 5–6 was a key condition for the amine derivatives synthesis. Sodium acetate or acetic acid were used for the purpose, since their presence suppressed the salts yielding reaction of humic acids with amines.

Basing on experimental data and data presented in [2] we may suggest the following scheme of coal and HA amination yielding Schiff's bases:



Amines may be also added to non-saturated bonds of humic acids forming donor-acceptor complexes.

Functional and elemental analysis, conductometry and IR spectroscopy data confirm the above given scheme.

During the coal and HA amination carbonyl and acid groups decrease in number, while nitrogen content increases. Carbonyl groups number decreases proportionally to the content of amino groups (Table 1). Amine content in the coal and HA does not exceed 12 %, and its type has no essential effect on the process performance and product composition.

TABLE 1
Characteristics of aminated humic acids

Sample	Yield, %	Nitrogen content, mass %	Content, mg-eq/g			Amine content, mass %	pK _a
			COOH + OH	C=O	NH		
Coal	–	1.20	2.72	2.04	–	–	9.72
Coal-DEA	85.2	2.06	2.50	1.52	0.74	4.48	10.04
Coal-EDA	80.0	4.26	2.20		3.64	6.80	11.32
HA		1.02	5.50	2.32	–	–	5.71
HA-VEEA	78.4	2.19	4.50	1.64	0.92	7.71	–
HA-DEA	80.3	2.98	5.45	1.93	1.41	9.8	6.04
HA-EDA	66.1	6.54	4.40	1.82	2.03	11.8	–

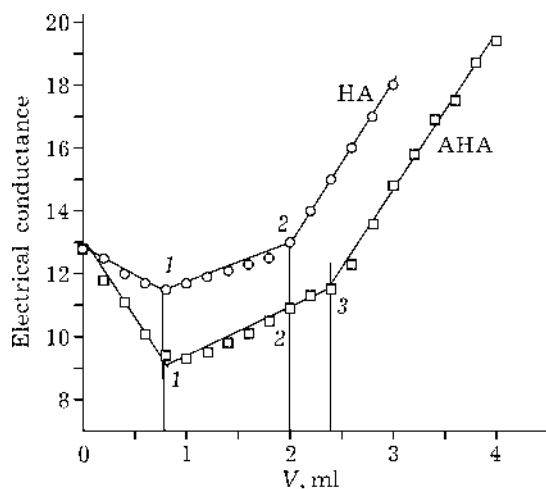


Fig. 1. Conductometric titration plots obtained at humic samples titration.

In Fig. 1 one may see the plots showing the titration of alkali HA solution and its DEA derivative (AHA) by the 0.25 M H_2SO_4 . These plots allow the estimation of acid and amine groups content. Since the places of first plot bending coincide for the two samples, the sum of acid groups remains the same. This fact also confirms the above suggested reaction scheme.

The second parts of HA and AHA plots (see Fig. 1) differ by their length and correspond to acid groups release from the salts under the acid effect (to point 2) and then due to the basic AHA groups neutralization (to point 3). After the second equivalence point further titration by acid causes a linear increase of the hydrogen ions concentration. One may judge about the content of amino groups in AHA by the difference of second bends on the HA and AHA plots (points 2 and 3).

Comparing the IR spectra of amine derivatives and starting compounds one may see that at amino groups introduction carbonyl groups band intensity ($1700-1720\text{ cm}^{-1}$) decreases, and intensity of amino groups oscillation band ($1550-1640\text{ cm}^{-1}$) increases. Valence oscillations of secondary amine groups appear at $3300-3340\text{ cm}^{-1}$, methylene groups appear around $2920-2850\text{ cm}^{-1}$. A wide and intensive band at $3400-3200\text{ cm}^{-1}$ is provided by the NH and OH groups of humic derivatives linked by the hydrogen bonds.

The SEC study of amine derivatives with respect to sodium, copper, nickel, calcium and iron ions show that SEC depends on the sub-

TABLE 2

Ion exchange properties of aminated coal and HA (pH 5)

Sample	SEC, mg-eq/g				
	NaOH	Ni ²⁺	Cu ²⁺	Fe ³⁺	Ca ³⁺
Coal	5.12	0.30	0.75	4.05	—
Coal-DEA	0.80	1.22	3.90	2.04	
Coal-EDA	5.80	0.60	2.30	3.95	2.13
HA	5.73	0.95	2.25	3.35	0.94
HA-DEA	6.22	0.70	2.20	3.85	1.20
HA-EDA	6.03	0.90	2.30	4.10	1.10

strate, on the added amine and on the complex forming reagent (Table 2). There is a tendency of adsorption capacity increase in a series: coal \leq aminocoal \leq humic acid \leq aminohumic acid. A higher sorption of metal ions by the amine derivatives in comparison to the non-modified analogs is provided by the complex formation ability of the introduced nitrogen atoms. By their SEC new ion exchangers based on oxidized coals may be classified as weak and moderate acid cation exchangers.

Sample SEC comparison with respect to NaOH and metal ions shows that ion exchange properties of adsorbents are not developed to full extent. Nickel ion adsorption at pH 4–5 is 14–30 %, calcium adsorption is 18–22 %, copper adsorption is 26–52 %, and iron adsorption is 67–85 %.

Humic acid and coal exchange capacity dependence on pH is shown in Fig. 2. As pH increases, cation exchange capacity of humic compounds grows, thus determining their application field. For aminohumic acid EC dependence on pH is a parabola with minimum at pH 4–5, proving that it is polyampholyte. Static

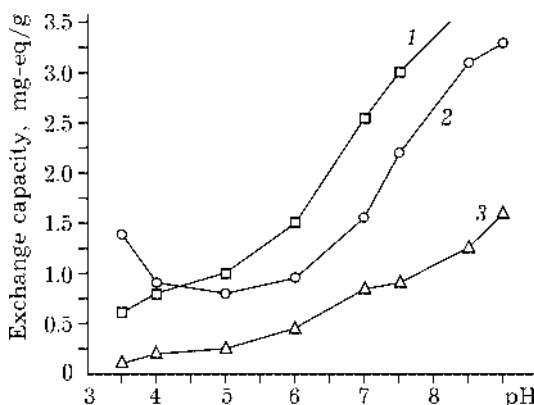


Fig. 2. Exchange capacity of humic acid (1), aminohumic acid (2) and coal (3) versus pH.

TABLE 3

Aminocoal effect on mine water mineralization

Sample	Contact time	χ , mS/cm	Mineralization		Cations		Anions	
			g/l	Purification degree, %	g/l	Cation removal, %	g/l	Anion removal, %
Water		8.63	4.50	–	1.50	–	3.00	–
Aminocoal	10 min	6.40	3.34	25.78	0.34	77.33	–	–
	1 day	3.24	1.69	62.45	–	–	1.69	43.67

exchange capacity increases with pH growth from 5 to 9, and at pH decrease from 5 to 3, while SEC by HCL for amine derivatives varies from 2.5 to 4.0 mg-eq/g.

New HA amine derivatives may be used for the sorption of metal ions in acid and alkali media. One may see the corresponding laboratory testing in demineralization of mine waters in Table 3. Apparently, water mineralization decreases as the time of its contact with aminocoal increases. At pH 5–9 cations are adsorbed (approximately by 77 %), then, when the main portion of cations is removed, and solution becomes acidic, anions are adsorbed (approximately by 44 %). The total daily decrease of mineralization degree attains 62.4 %. Therefore, amine derivatives may be efficiently used for the simultaneous removal of cations and anions to provide enough deep purification of mine water from mineral salts.

We have shown that at pH > 8 amine derivatives may be applied as extracting reagents precipitating metal ions from the water solutions of their salts (Table 4). Extraction degree in this case attains 78–91 % depending on the volume ratio of metal salt solution and extracting reagent. Aminohumic acids provide acceptable extraction degree, but are less efficient if compared to non-modified humic acids. There-

TABLE 4

Extracting properties of HA and its amine derivatives ($[Cu^{2+}] = 0.04$ mol/l, extracting reagent concentration 0.5 %, pH 8)

Copper salt : humic reagent, vol. parts	Cu ²⁺ extraction degree, %	
	HA	HA-DEA
1 : 1	62.5	61.2
1 : 2	81.2	70.0
1 : 3	87.5	83.7
1 : 4	89.3	91.2

fore, a more sophisticated structure of aminated humic acids aggravates the access of metal ions to adsorbent active sites. However, aminated coals and humic acids may be used in various acidity media. Moreover, they may be easily obtained from the coal mining wastes by a rather simple technology.

Aminated humic acids have 3 times more paramagnetic centers than non-aminated ones. This improves their complexing properties. As for aminated coals, their oxidation stability is higher by 50–80 °C than that of non-aminated ones.

CONCLUSION

Therefore, new amine derivatives were obtained by oxidized coals and humic acids interaction with amines. These compounds were investigated with regard to their ion-exchange and polyamolyte properties. Amine derivatives were found to be rather efficient extracting and precipitating reagents applicable for demineralization of mine wastewaters and hydrometallurgy effluents.

REFERENCES

- 1 G. A. Mustafina, Z. G. Akkulova, I. N. Ryabova, Zh. B. Rakhimberlinova, Mezhdunar. nauch.-prakt. konf. "Sostoyaniye i perspektivy razvitiya uglekhemii" (Thesises), Karaganda, 2004, p. 156.
- 2 N. I. Nazarova, N. K. Alybakova, Ugli Kirgizii i sostav ikh guminovykh kislot, Ilim, Frunze, 1976.
- 3 S. Siggia, G. J. Hana, Kolichestvenny organicheskiy analiz po funktsionalnym gruppam (Russian translation), Khimiya, Moscow, 1983.
- 4 G. S. Libinson, Fiziko-khimicheskiye svoystva karboksilnykh kationitov, Nauka, Moscow, 1969.
- 5 G. Shvarzenbach, F. Flashka, Kompleksonometricheskoye titrovaniye (Russian translation), Khimiya, Moscow, 1970.
- 6 O. N. Grigorov, I. F. Karpova, Z. P. Kozmina *et al.*, Rukovodstvo k prakticheskim rabotam po kolloidnoy khimii, Khimiya, Leningrad, 1964.