

Investigation of Complex Formation of the Modifications of Hydrolytic Lignin with Metal Ions

MAQSUD JA. JUMANIYAZOV¹, AMANULLA F. KHODJAYEV² and BALTABAY D. DYUSEBEKOV²

¹*Urgench State University,
Ul. Kh. Alimjana 14, Urgench (Uzbekistan)*

²*Institute of General and Inorganic Chemistry, Academy of Sciences of Republic of Uzbekistan,
Ul. Kh. Abdullaeva 77a, Tashkent (Uzbekistan)*

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Abstract

Soluble modifications of lignin were obtained by means of alkaline and oxidative processing of nitro lignin. Using mono- and triethanolamine as alkaline reagents, we obtained lignin compounds of the type of quaternary ammonium salts. Complex compounds of zinc (II), iron (III), nickel (II) and copper (II) with nitroligninmono- and triethanolammonium were synthesized. The composition, structure and thermal stability of the new modifications of nitrolignin and its metal complexes were established with the help of IR spectroscopy, X-ray diffraction, chemical analysis and derivatography.

INTRODUCTION

Lignin is a large-scale waste product of hydrolysis and pulp and paper industry; it is stored mainly in dumps [1]. Lignin is used as a fuel, as a polymer product, and as the initial substrate to obtain valuable low-molecular chemical products [2, 3].

In order to broaden the application areas, various modifications of lignin were obtained [4, 5].

Methods of chemical modification of lignin include the following processes: transformation into partially soluble phenolate derivatives in reactions with various metal salts; nitration, chlorination, oxidation in alkaline medium by oxygen or hydrogen peroxide. Modified lignins are used as dispersing agents, emulsifying agents, stabilizers, complex forming ligands, etc. [5]. It was shown that sulpho- and chloro modifications of lignin form poorly soluble salts with the ions of some metals, which can be used to purify waste water from heavy metal

ions [6]. Water-soluble modifications of lignin are required for these purposes.

In the present work we report on the results of investigations dedicated to obtaining water-soluble modifications of nitrolignin and their interaction with the ions of some metals.

EXPERIMENTAL

Commercial nitrolignin of cotton husk, monoethanolamine (MEA) of «ch.» (pure) grade were used in experiments. Initial salts were sulphates of di- and trivalent metals. Phosphate nitrolignin (PNL) was obtained by treating nitrolignin with trisodium phosphate; silicate nitrolignin (SNL) and carbonate nitrolignin (CNL) were obtained by treating with sodium silicate and carbonate. Oxidized lignin called lioxide (LO) is obtained by oxidation of hydrolysis lignin with hydrogen peroxide; it is soluble in diluted alkaline solutions [7, 8]. By treating lioxide with the solution of sodium hydroxide,

TABLE 1

Results of elemental analysis of nitrolignin and its complexes isolated in the monoethanolamine-containing medium, %

No.	Compound	Carbon	Hydrogen	Nitrogen	Metal oxide
1	Nitrolignin	45.75	5.28	3.17	–
2	Zinc complex	34.5	5.6	6.6	22 (ZnO)
3	Iron (III) complex	39.3	7.1	10.4	29 (Fe ₂ O ₃)
4	Nickel complex	39.3	7.1	6.7	14 (NiO)
5	Copper (II) complex	39.0	6.3	5.8	16 (CuO)

the alkaline lioxide (ALO) was obtained; with trisodium phosphate – PLO, with sodium carbonate – CLO, sodium silicate – SLO.

Metal complexes of nitrolignin were synthesized as follows. Nitrolignin in the amount of 5 g is triturated in a mortar with 0.2 g of aluminium sulphate. While mixing, 5 ml of MEA is added drop by drop. The resulting mixture is fully transferred with distilled water into a glass with a volume of 200 ml, thoroughly mixed, filtered. Metal complexes are salted out from the filtrate with acetone, and dried at room temperature. Metal complexes of nitrolignin with metal ions, *i. e.* Fe³⁺, Ni²⁺, Cu²⁺, Zn²⁺, were obtained similarly.

The synthesized compounds were analyzed for nitrogen according to Dumas' procedure, for carbon using the modified microprocedure [9]. The results of elemental analysis of the commercial lignin, nitrolignin and its complexes are listed in Tables 1 and 2.

Thermal analysis was carried out using the Paulic-Paulic-Erday system derivatography with the heating rate of 10 °C/min and the weighed portion of 0.1 g under atmospheric conditions with permanent removal of the gas medium with a water-jet pump. The IR absorption spectra were recorded with UR-20 spectrometer (400–4000 cm⁻¹) in tablets with KBr.

RESULTS AND DISCUSSION

Lignin is an amorphous substance; nitrolignin and the products of its neutralization, as well as lioxide, are crystalline substances. The X-ray diffraction patterns of nitrolignin and its modified samples are shown in Fig. 1. One can see that these are individual substances possessing their own lattices. Therefore, the treatment of nitrolignin with alkaline reagents results not only in neutralization of the acidic

TABLE 2

Results of elemental analysis and decomposition temperature of lignin and its various modifications

No.	Compounds under investigation	Element content, %			Decomposition temperature, °C
		Carbon	Hydrogen	Nitrogen	
1	Lignin of cotton husk	62.41	6.87	–	
2	Nitrolignin, water-soluble part	32.08	3.09	4.29	100
3	The same, solid part	45.72	5.28	3.17	110
4	PNL	15.91	1.92	1.59	70
5	SNL	25.53	2.76	2.24	70
6	CNL	25.49	3.5	3.09	65
7	LO	49.55	6.43	–	90
8	PLO	19.28	3.20	–	97
9	SLO	63.39	10.45	–	100
10	ALO	28.44	4.62	–	105
11	CLO	14.81	4.99	–	–

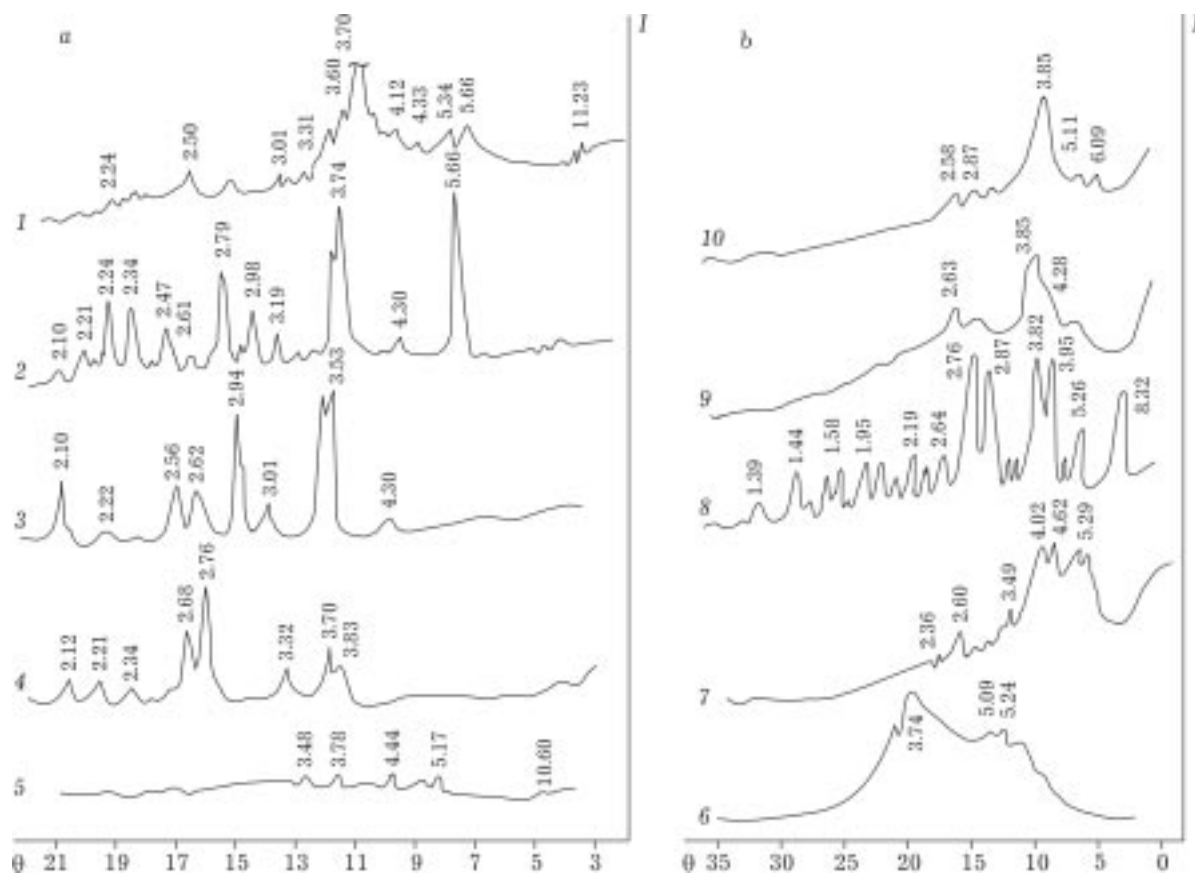


Fig. 1. X-ray diffraction patterns of nitrolignin (1), 2-nitrolignin obtained from the liquid phase (2), ANL (3), PNL (4), CNL (5), LO (6), ALO (7), PLO (8), CLO (9), SLO (10).

functional groups but also in complex interaction between components.

Nitrolignin, both the synthesized sample and commercially available one, starts to decompose at 100–110 °C, which is exhibited at the heating curve (DTA) as an endoeffect (Fig. 2). Within the temperature range of 150–700 °C, a complicated process of carbonization and combustion of NL accompanied by several exoeffects takes place. In this process, 96 % of the substance gets burnt. It should be noted that the commercial NL and the sample synthesized by us exhibit identical derivatograms.

Nitrolignin and lioxide also have identical heating curves. Exoeffects within two temperature regions are observed in the derivatograms of lioxide and its modifications (Fig. 3). Temperature of start of decomposition increases from lioxide (95 °C) to CLO (100 °C). Two groups of exoeffects are observed in DTA curves: within the range 300–430 and 510–850 °C. For heating above 300 °C, the smallest

mass loss is characteristic of PLO, and the largest for lioxide.

Analysis of the temperature curves of heating shows that detachment of water molecules is observed in nitrolignin, starting from 70 to 210 °C; at higher temperatures, combustion of the organic part of nitrolignin occurs with the complete mass loss.

In the derivatograms of nitrolignin metal complexes obtained in the presence of monoethanolamine, we observe endothermic effects with water loss at 70–230 °C and exothermal effects connected with the combustion of the organic part, starting from 295 to 850 °C, while at higher temperature oxidation of metals with oxygen occurs. Mass loss is 80 to 90 %. According to the temperature of the start of decomposition, thermal stability of the metal complexes increases in the row: Fe < Zn < Ni < Al < Cu.

Investigation of thermal behaviour of the synthesized complexes in the presence of triethanolamine showed that dehydration occurs

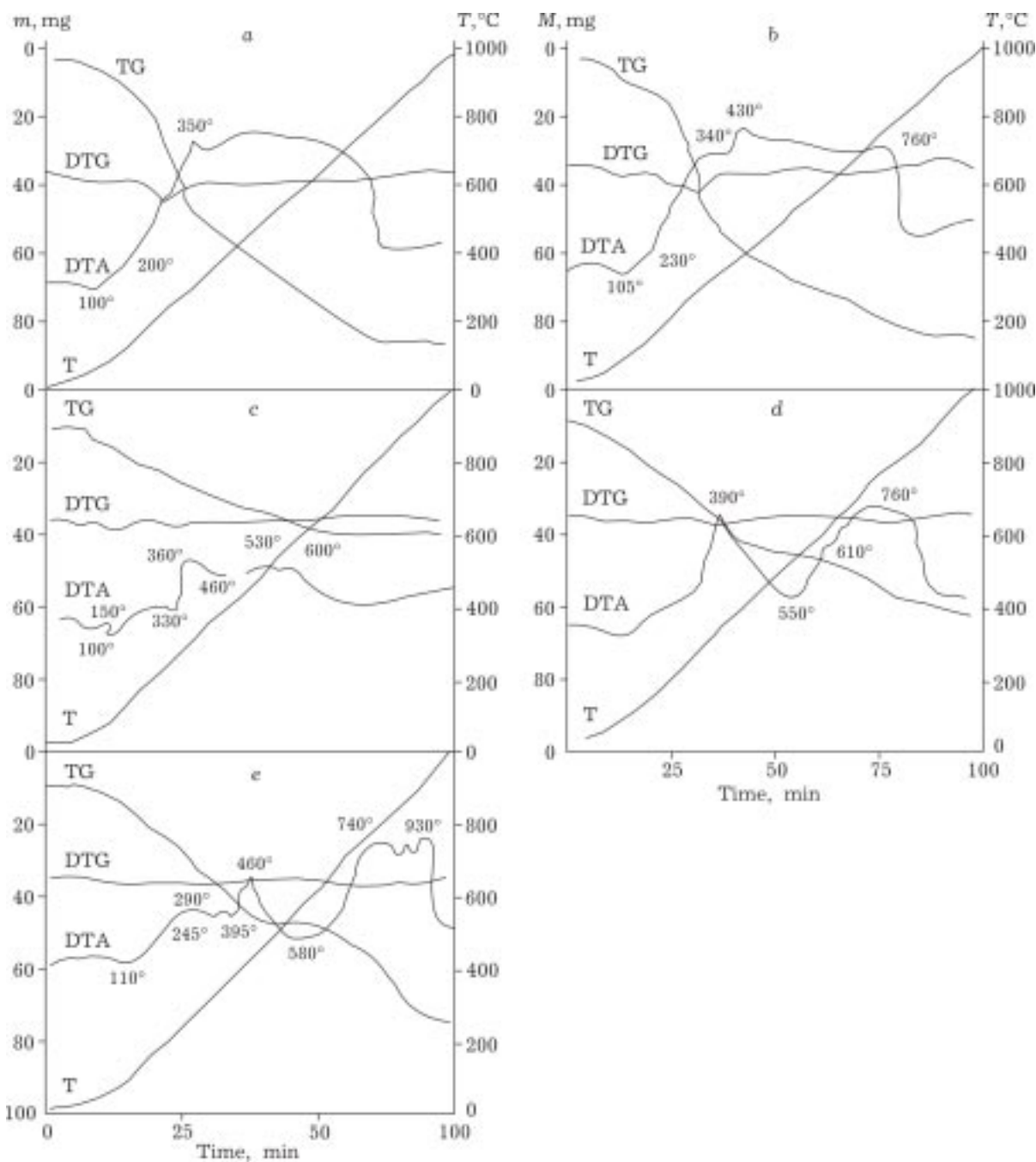


Fig. 2. Derivatograms of NL (a), ANL (b), PNL (c), SNL (d), CNL (e).

at 80–140 °C, decomposition of the organic part at 195–870 °C, which is accompanied by exoeffects. Thermal stability of triethanolamine-containing complexes increases in the row: Fe < Cu < Al < Ni < Zn. The final products of thermolysis are the oxides of the corresponding metals.

A broad band is observed in the IR spectrum of the modified nitrolignin in the region

3100–3500 cm^{-1} , which is due to the vibrations of OH groups participating in inter- and intramolecular hydrogen bonds. Within the region 2800–3000 cm^{-1} , the bands of stretching vibrations of the C–H bonds of alkyl radicals were detected. The vibrations of aromatic rings are likely to give bands 1000–1100 cm^{-1} , as well as the bands with the frequencies near 1615 cm^{-1} and an inflexion at 1585 cm^{-1} . The absorption

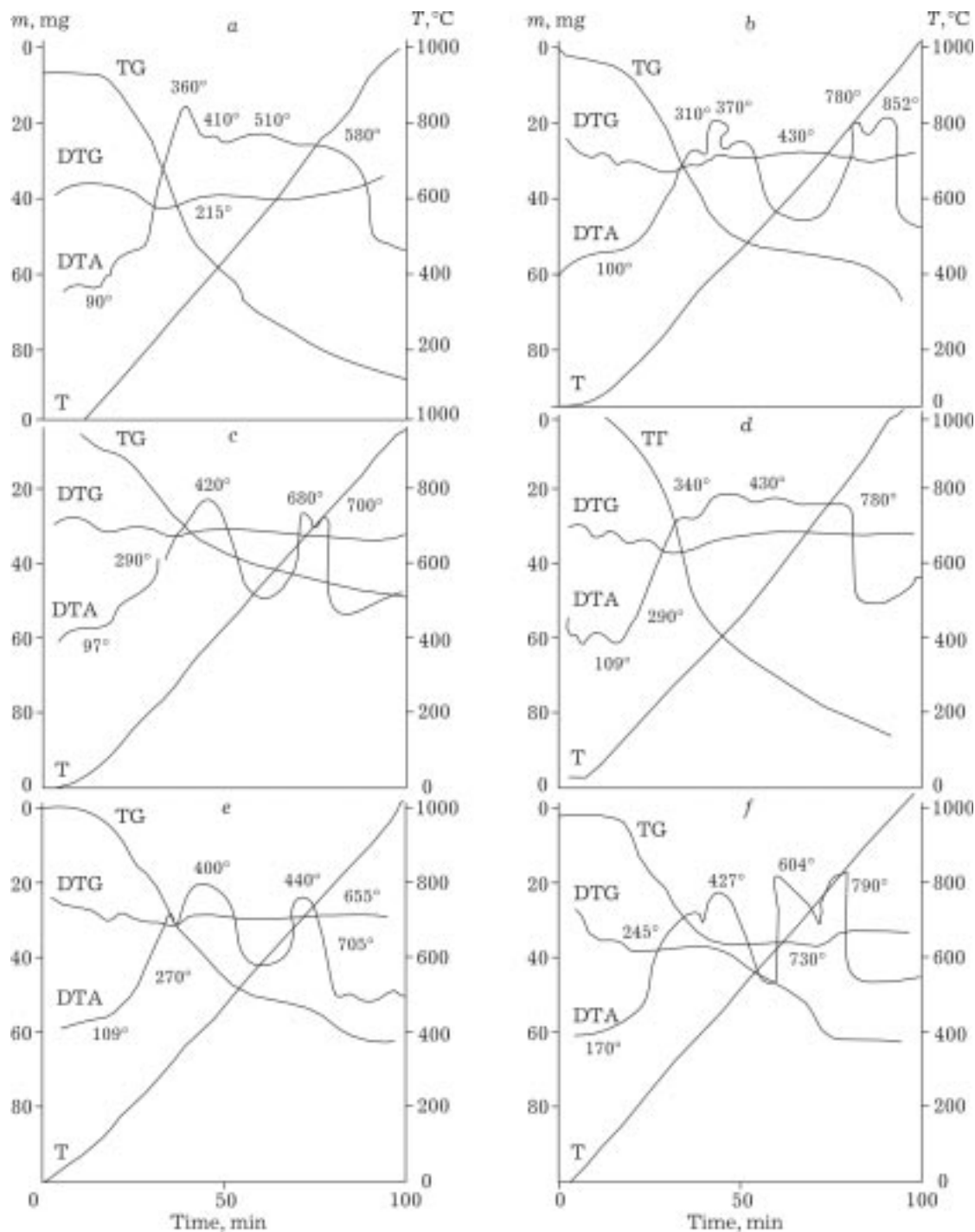


Fig. 3. Derivatograms of LO (a), CLO (b), PLO (c), ALO (d), SLO (e), LDSVK (f).

band of the C=O bond of non-ionized carbonyl group is exhibited near 1715 cm^{-1} . Along with the above-indicated bands, the spectrum of NL contains the bands at $1630\text{--}1640\text{ cm}^{-1}$ ($\nu_{\text{as}}(\text{NO}_2)$) and 1330 cm^{-1} ($\nu_{\text{s}}(\text{NO}_2)$) [10, 11].

In the IR spectra of SNL and CNL, broad bands $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ are observed in

the region $1600\text{--}1400\text{ cm}^{-1}$. A band at about 1115 cm^{-1} is likely to be attributed to the vibrations of SiO_3^{2-} group. In addition, vibrational frequencies at about 1170, 1090, 970, 878 cm^{-1} are observed in the spectrum of PNL, which are due to the presence of $\gamma(\text{PO}_4)$, $\nu_{\text{as}}(\text{PO}_2)$ and $\nu_{\text{s}}(\text{PO}_2)$ [12].

TABLE 3

Vibrational frequencies determined from the IR spectra of nitrolignin, monoethanolamine and their metal complexes, cm^{-1}

MEA	NL	NL-MEA					Attribution
		ZnSO ₄	Al ₂ (SO ₄) ₃	Fe(NO ₃) ₃	NiSO ₄	CuSO ₄	
3350	3400, 3360	3400, 3320	3400, 3380	3400	3400	3400	$\nu(\text{OH})$
3200	3280	3280	–	–	–	2930	$\nu(\text{NH}_3^+)$
2930	2940	2930	2940	2930	2930	2930	$\nu(\text{CH})$
2865	2865	–	–	–	–	–	
–	1720	–	–	–	–	–	$\nu(\text{CO})$
–	1635	1610	1610	1620	1600	1620	$\nu_{\text{as}}(\text{COO})$ $\delta(\text{NH}_3^+)$
–	1550	1550	–	1590	–	1580	$\nu_{\text{as}}(\text{NO}_2)$,
–	1515	–	1470	1450	1450	1460	$\nu_{\text{s}}(\text{COO})$
–	1350	1370	1370	1370	–	1370	$\nu_{\text{as}}(\text{NO}_2)$
1175, 1165	1180	1170	1175	1180	1185	1170	$\nu(\text{arom. ring})$, $\delta(\text{OH})$
1085	1075	1085	1090	1085	1085	1080	$\nu(\text{C-N})$
1035	1045	1020	1030	1030	1030	1030	$\delta(\text{CO})$
870	–	820	–	840	–	820	$\delta(\text{COO})$, $\delta(\text{NH})$
–	–	450	420	440	445	450	$\nu(\text{Me-O})$

The basic vibrational frequencies determined from the IR spectra of monoethanolamine, nitrolignin and their metal complexes are listed in Table 3.

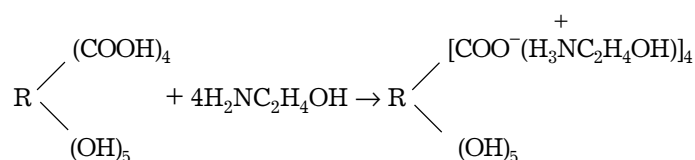
It follows from the data of IR spectroscopic analysis that the interaction of nitrolignin with MEA results in the addition of the proton of carboxylic group to the nitrogen of the amine group of MEA with the formation of nitroligninmonoethanolammonium (Scheme 1).

In the case of excess MEA, complex compounds are formed in the presence of metal ions (Scheme 2).

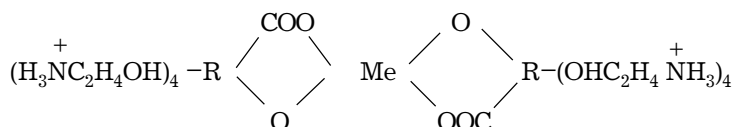
It cannot be excluded that the complexes can be polynuclear due to the bridging groups; they have polymeric structure, which is confirmed by their solubility inorganic solvents.

The absorption bands related to the ionized amino group (~ 3200 , 1600 cm^{-1}) and ionized carboxylic group (~ 1620 , 1460 cm^{-1}) are detected in the presence of mono- and triethanolamine in the IR spectra of the isolated metal complexes.

On the basis of the data of elemental analysis, IR spectroscopy, X-ray phase analysis and thermographic examination, the following com-



Scheme 1.



Scheme 2.

position was proposed for the complexes isolated from the systems nitrolignin – triethanolamine – metal ions:

$1/2 \text{ NL} \cdot 2\text{TEA} \cdot \text{Me} \cdot x\text{H}_2\text{O}$, in the case of TEA
in excess $\text{NL} \cdot 4\text{TEA} \cdot 2\text{Me} \cdot x\text{H}_2\text{O}$.

CONCLUSION

By means of alkaline processing of hydrolysis lignin, we obtained new modifications of nitrolignin, isolated their complex compounds with metal ions. The composition and structure of the obtained compounds were proposed on the basis of the data of physicochemical analysis. We assume that the modified derivatives of nitrolignin can be used to purify waste water containing various metal ions. The isolated metal complexes are inhibitors of metal corrosion in salt solutions or dryers for the manufacture of corrosion-resistant coatings.

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