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COMPLEXATION OF CAFFEIC AND FERULIC ACIDS BY TRANSITION-METAL IONS

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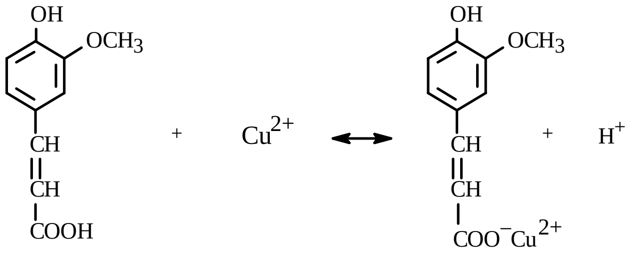
Potentiometric titration and IR and UV spectroscopies are used to study complexation of caffeic and ferulic acids by metal ions. Caffeic and ferulic acids, which occur in lignin, are shown to react with metal ions mainly through an ionic mechanism. However, coordination bonding is also possible depending on the nature of the ligand and metal ion and the ratio of starting components. The strongest complex forms between caffeic acid and $CuCl_2$ (2:1 ratio).

Key words: complexation, IR spectroscopy, caffeic acid, ferulic acid.

The polyfunctionality of the lignin macromolecule complicates the determination of its chemical reactivity. Low-molecular-weight model compounds should be used to study the chemical reactions of the lignin functional groups. The phenylpropane structure mimics the lignin structural unit [1]. Therefore, alkylaryl compounds, in particular, natural caffeic and ferulic acids, can be used as models.

We investigated the reaction of caffeic and ferulic acids with a series of di- and trivalent metal ions (Ni^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+}, Al^{3+}). Such reactions are interesting for elucidating the mechanism of action of lignin as a sorbent for metal ions in various media [2-4].

One widely used and readily available method for studying complexation processes is potentiometric titration [5]. We obtained potentiometric-titration curves for caffeic and ferulic acids with and without metals (Ni^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+}, Al^{3+}) present (Fig. 1). It can be seen that the acid—base equilibrium in all instances shifts in the presence of the metal ions. This appears as a shift of the titration curves as the content of $M^{2+,3+}$ in solution increases. Potentiometric-titration curves in the presence of metal salts are located below those of caffeic and ferulic acids. This indicates that these acids react with the metal ions through an electrostatic mechanism. Therefore, an ionic mechanism of reaction of the acids with the metals that is accompanied by release of protons can be represented as follows (using ferulic acid and Cu^{2+} as an example):



The potentiometric-titration curves in Fig. 1 indicate that the electrostatic reaction ferulic acid—$Me^{2+,3+}$ and caffeic acid—$Me^{2+,3+}$ to form complexes occurs in weakly acidic, neutral, and weakly basic solutions.

Coordination reactions in addition to the ionic ones are also probable because ferulic and caffeic acids contain not only carboxylic but also reactive phenolic groups. We performed IR and UV spectroscopic investigations.

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TABLE 1. Vibrational Frequencies of Functional Groups of Caffeic and Ferulic Acids and Their Complexes with $CuCl_2$ and $AlCl_3$

Compound	ν_{COO^-}, cm^{-1}	$\nu_{C\text{-}OH}$, cm^{-1}	ν_{OH}, cm^{-1}
1. Caffeic acid	-	1279 m	3435, 3237
2. Ferulic acid	-	1279st	3439
3. Na-salt of caffeic acid	1457s*	1130w	3421
4. Na-salt of ferulic acid	1370s	1250m	2800-3600
5. Caf:Cu^{2+}: 2:1	1396s	1055st	3154
6. Caf:Cu^{2+}: 1:1	1397s	1149, 1114st	3421
7. Caf:Cu^{2+}: 1:2	1396s	1104st	3253
8. Fer:Cu^{2+}: 2:1	1400s	1090st	3366
9. Fer:Cu^{2+}: 1:1	1407s	1152, 1125st	3422
10. Fer:Cu^{2+}: 1:2	1407s	1122st	3465
11. Caf:Al^{3+}: 3:1	1436s	1268st	3422
12. Caf:Al^{3+}: 1:1	1457s	-	3332
13. Caf:Al^{3+}: 1:2	1471s	-	2500-3500
14. Fer:Al^{3+}: 3:1	1434s	1278m	3438
15. Fer:Al^{3+}: 1:1	1435s	1279m	2500-3500
16. Fer:Al^{3+}: 1:2	1435s	1280m	3364

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*Absorption band (ab) of carboxylate antisymmetric stretching vibration overlaps ab of aromatic ring vibrations; st - strong ab; m - medium ab; w - weak ab.

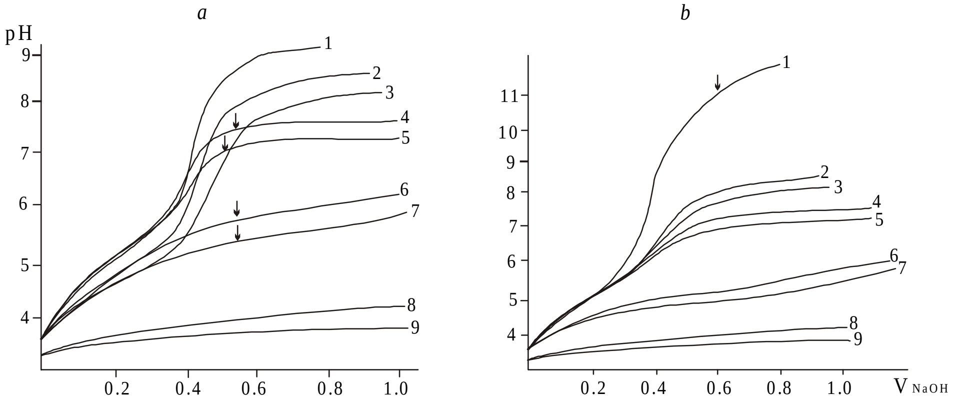

Fig. 1. Potentiometric titration curves of ferulic (a) and caffeic (b) acids; [ferulic and caffeic acids]:[metal ion] = (1), (Co^{2+}) = 1:1 (2), (Co^{2+}) = 1:2 (3), (Zn^{2+}) = 1:1 (4), (Zn^{2+}) = 1:2 (5), (Cu^{2+}) = 1:1 (6), (Cu^{2+}) = 1:2 (7), (Al^{3+}) = 1:1 (8), (Al^{3+}) = 1:2 (9). Ferulic acid = 0.01 M.

Changes in the IR spectra caused by entrance of the ligand into the coordination sphere are widely used to study the mechanism of complexation of carboxylic acids because the carboxyl stretching frequency is very sensitive to a change of metal atom nature [6]. Therefore, it seemed interesting to investigate the mechanism of reaction of caffeic and ferulic acids, which are natural acids, with $CuCl_2$ and $AlCl_3$ by IR and UV spectroscopy. Copper ions form stronger complexes than Zn^{2+} and Ni^{2+} whereas $AlCl_3$ is known [7-9] to have vacant *p*-orbitals that are good acceptors and reacts with acids and ketones to form $C{=}O{\rightarrow}M$ coordination bonds. Data for the principal characteristic stretching frequencies of carboxyls (ν_{COOH}), carboxylates (ν_{COO^-}), and hydroxyls (ν_{OH}) are given in Table 1 and Fig. 2.

TABLE 2. Stability Constants of Ferulic and Caffeic Complexes with Cu^{2+} and Zn^{2+}

Compound	K_{st}, (M^{-1})	Compound	K_{st}, (M^{-1})
Fer:Cu^{2+}		Fer:Zn^{2+}	
2:1	$8.4 \cdot 10^5$	2:1	$1.64 \cdot 10^5$
1:1	$1.03 \cdot 10^3$	1:1	$2.72 \cdot 10^2$
1:2	$4.55 \cdot 10^4$	1:2	$8.95 \cdot 10^3$
Fer:Cu^{2+}		Caf:Zn^{2+}	
2:1	$6.7 \cdot 10^6$	2:1	$7.6 \cdot 10^5$
1:1	$2.38 \cdot 10^3$	1:1	$3.3 \cdot 10^2$
1:2	$9.55 \cdot 10^4$	1:2	$4.1 \cdot 10^4$

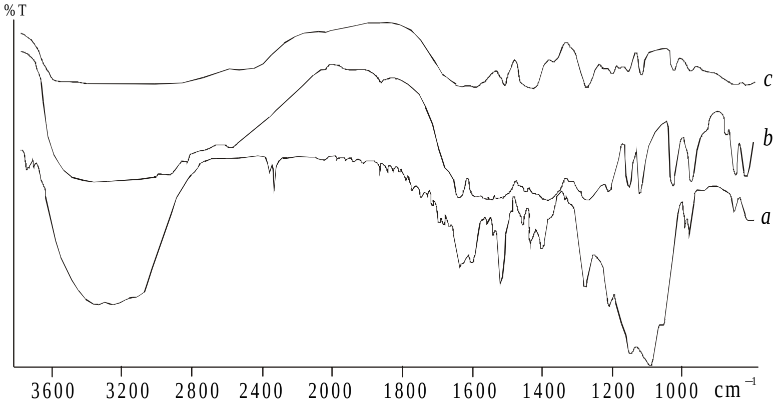

Fig. 2. IR spectra: Fer:Cu^{2+}, 2:1 (**8**) (a), Na-salt of ferulic acid (**4**) (b), Fer:Al^{3+}, 1:1 (**15**) (c).

The IR spectra of caffeic (**1**) and ferulic (**2**) acids and their corresponding $CuCl_2$ and $AlCl_3$ complexes (**5-16**) show a broad absorption band at 1390-1470 cm^{-1} that is due to symmetric (s) stretching of the carboxylate ion (COO^-). The presence of the characteristic carboxylate stretching frequency (Table 1) indicates that the metal–carboxyl bond, regardless of the ligand nature and metal:ligand ratio, is primarily ionic [10, 11].

A distinguishing feature of the spectra of the $CuCl_2$ complexes with caffeic and ferulic acids (**5-10**) compared with those of the sodium salts and $AlCl_3$ complexes is the appearance of a strong broad band at 1000-1280 cm^{-1} (Fig. 2a, -b, -c). Based on studies of IR spectra of copper salts of dicarboxylic acids [13], phenylglycolates [14], and condensation products of pyruvic acid [15], the observed absorption band can be assigned to C–OH vibrations with a coordination bond between the phenol hydroxyl and Cu^{2+} ($HO \rightarrow M$). The lowest frequencies of 1055 and 1090 cm^{-1} are observed in spectra of complexes of caffeic and ferulic acids with $CuCl_2$ with a 2:1 ratio (**5**, **8**) compared with the ratio for complexes (**6-7**) and (**9**, **10**). The rather large shift of band maxima to low frequencies for the C–OH stretches and OH bonds in spectra of caffeic and ferulic acids with $CuCl_2$ (**5**, **8**) relative to ν(C–OH) and ν(OH) of compounds **6**, **7**, **9**, **10** can be explained by the formation of a stronger complex at a 2:1 ligand:metal ratio.

The results of the spectroscopic studies were confirmed by calculations. A precipitate forms at a certain moment during titration of the studied solutions, as shown in the figures. Apparently this precipitate is a complex because the hydroxides of the corresponding metals do not precipitate under the given conditions. The amount of free metal ions in solution was determined using atomic absorption. The results were used to calculate the stability constants of the caffeic and ferulic complexes of metal ions at various ligand:metal ratios (Table 2).

Complexes with a 2:1 ligand:metal ratio are the most stable for both caffeic and ferulic acids. The different values of the stability constants for the complexes with different metals is reflected in the quantitative shift of the potentiometric-titration curves. The largest shift occurs for Cu^{2+} and then Zn^{2+} compared with the other divalent metal ions (under otherwise equal conditions). These results agree with the calculated K_{st} values.

It should be noted that complexes of caffeic and ferulic acids with $AlCl_3$ are mainly ionic (Table 1). However, $AlCl_3$, being a Lewis acid, can also form a $C{=}O \rightarrow M$ coordination bond, as was shown during a study of the IR spectra of ethylacetate and ethylformate complexes [16, 17]. Assignment of frequencies to C═O→M bonds in the $AlCl_3$ complex with caffeic and ferulic acids is difficult owing to absorption of the aromatic ring at 1500-1600 cm^{-1}. Therefore, we studied electronic absorption spectra of $AlCl_3$ complexes with caffeic and ferulic acids in the visible region. A maximum at 600 nm is observed only for the complex of $AlCl_3$ with caffeic acid at a 3:1 ratio and is assigned to absorption of a charge-transfer complex [18].

Thus, the study of complexation of caffeic and ferulic acids with metal ions in solution and the analysis of the IR and UV spectra of the resulting complexes indicate that the interaction of these acids, which act as ligands, with metal ions is mainly ionic.

However, coordination bonds are also possible depending on the nature of the ligand and the metal ion. The strongest complex forms with caffeic and ferulic acids and $CuCl_2$ at a 2:1 ratio.

EXPERIMENTAL

Titration was performed using a pH-340 potentiometer with a glass reference electrode and AgCl working electrode. The accuracy of the measurements is 0.005 pH units. The temperature was 20ºC. The acid concentration in all measurements was 0.01 M.

Atomic absorption analysis was performed by the standard method on a Perkin—Elmer 3030 V (Sweden) atomic absorption spectrometer at 217 nm with a deuterium corrector of propane—air background.

IR spectra were recorded on a Perkin—Elmer 2000 Fourier-IR spectrometer. Samples were prepared as KBr pellets. Aqueous solutions of acids and their salts were used on a Perkin—Elmer Lambda-16 UV spectrometer in 1-cm quartz cuvettes.

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