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Complexion of Nonionic Macromolecules with 3rd Metal Ions of the Transition Series

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ABSTRACT

The article discusses the formation of complexes between transition metal ions and a copolymer of crotonaldehyde with N-vinylpyrrolidone. Complexation of copolymers with metal ions in solutions has been studied by methods of IR-UV spectroscopy, sedimentation, diffusion and viscosimetry. Coordination of the metal with the copolymer occurs through the oxygen atom of the cycloamide and aldehyde groups.

KEY WORDS: macroligand, polymer metallocomplexes, partial specific volume, diffusion constants, thermodynamic segment, lactam cycle.

INTRODUCTION

Polymermetallic complexes have physicochemical properties that differ significantly from the initial components [1-4]. Studies of high-molecular compounds are increasingly closely aligned with the study of biopolymers and modeling of biological systems, where complexing polymers as model systems are of particular interest [5-8]. Among the known metals, microelements-metals of the transition series are especially important, participating in various bioprocesses (photosynthesis, absorption and transport of oxygen, metalloenzymatic catalysis, etc.) [9-15]. Metal ions are able to bind with many high molecular weight compounds of a non-ionic nature.

Unlike low-molecular metal complexes with various compounds (amino acids, cyclic amides, aromatic acid amides, etc.), which exhibit biological activity, polymer metal complexes have a number of advantages:

- the toxicity of the metal ion is sharply reduced;
- the biologically active properties of the metal ion are enhanced by increasing the stability of the metal complex;
- there is a prolongation effect of the drug;
- biologically active properties of the polymer ligand are enhanced.

The coordination of polymer ligands with metal ions (Me) enhances the biologically active properties of both the metal and the polymer ligand, and the toxicity of the metal sharply decreases.

EXPERIMENTAL PART

Coordination compounds of copolymers with 3d metal ions of the transition series: cobalt (2+), nickel (2+), copper (2+), manganese (2+) and zinc (2+) were obtained by mixing one percent solutions of copolymers in acetone mixtures: dioxane; acetone: ethanol; acetone: dichloroethane; acetone: methylene chloride in a 2:1 ratio (by volume) with saturated solutions of

metal chlorides in an appropriate solvent with vigorous stirring. The formed flocculent precipitate was filtered off and washed with a solvent until a negative reaction to metal ion in the washing liquids. Synthesis The complexes were dried in vacuum at 10 mm. Hg at room temperature to constant weight. The metal content in the complexes was determined by the procedures [9-10]. based on the use of the complexometric titration method in the presence of macroligands

RESULTS AND ITS DISCUSSION

Copolymers based on crotonic aldehyde-vinylpyrrolidone (CA-VP) were considered as macroligands containing functional groups capable of interacting with metal ions. Preliminary studies by spectroscopy in the visible region showed that, upon mixing and incubation of a solution of a metal salt and a copolymer solution, a shift of the absorption band maximum to the long-wavelength region of the spectrum and a change in the shape of the spectrum are observed (Fig. 1). This indicates a possible complexation in the CA-VP-Me system.

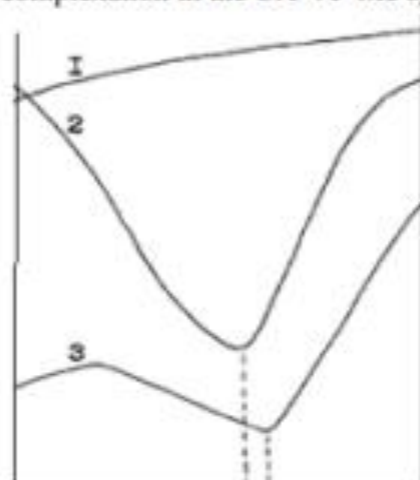


Fig. 1: Absorption spectra of CA-VP copolymers (1) CoCl_2 (2) and PMC CA-VP-Co (3)

The course of the complexation process was also judged by the change in the optical density of the solutions. The results obtained are shown in Fig. 2, from which it can be seen that with an increase in the polymer concentration, the optical density of solutions increases, and at the ratio [copolymer]: [metal] = 2: 1, a break appears, and at a higher concentration of the ligand, the optical density does not change, this indicates that under these conditions metal complexes of the composition 2:1 [copolymer]: [metal] are formed. Elemental analysis of the studied complex compounds also allows us to assign them the gross formula: $[\text{MeCl}_2 (\text{L})_2]_n$ (L- monomer units of vinyl lactams). Those. each metal ion is coordinately linked to two monomer units of vinyl lactam copolymers. When low-molecular-weight lactams are complexed with transition metal ions, complex compounds are formed, where each metal ion is coordinated with four or six molecules of the low-molecular-weight ligand.

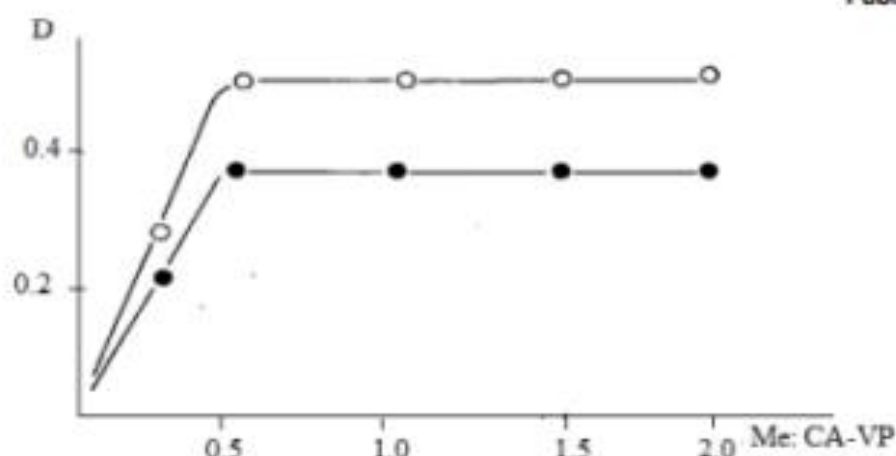


Fig. 2. Optical density versus ratio Me: CA-VP, (- o -) CoCl₂ (- ● -) and CuCl₂

The decrease in the number of coordinated lactam molecules during the transition from low-molecular to high-molecular digand can be explained by the polymer nature of the latter, which is characterized by steric hindrances, the chain effect, which affects the complexing ability of polyligands.

It is known that the properties of polymer compounds depend on the depth of polymer-analogous transformations; therefore, the properties of metal complexes should depend on the degree of completion of the complexation reaction, i.e. on the metal content in the PMC.

In order to identify the conditions for the synthesis of metal complexes, a study of complexation in organic solvents (acetone-ethanol, acetone-dichloroethane) was carried out.

The dependence of the metal content in the KA-VP metal complex and the yield of the complex on the initial metal: copolymer ratio is shown in Figs. 3 and 4. It can be seen that the proposed technique allows one to obtain PLA with a metal content of 0.3 to 11%. However, with a decrease in metal concentration, the yield of the target product sharply decreases. Therefore, the most optimal [metal]: [copolymer] ratio is 1: 2, which makes it possible to obtain PC with a fairly high yield from 70 to 100%.

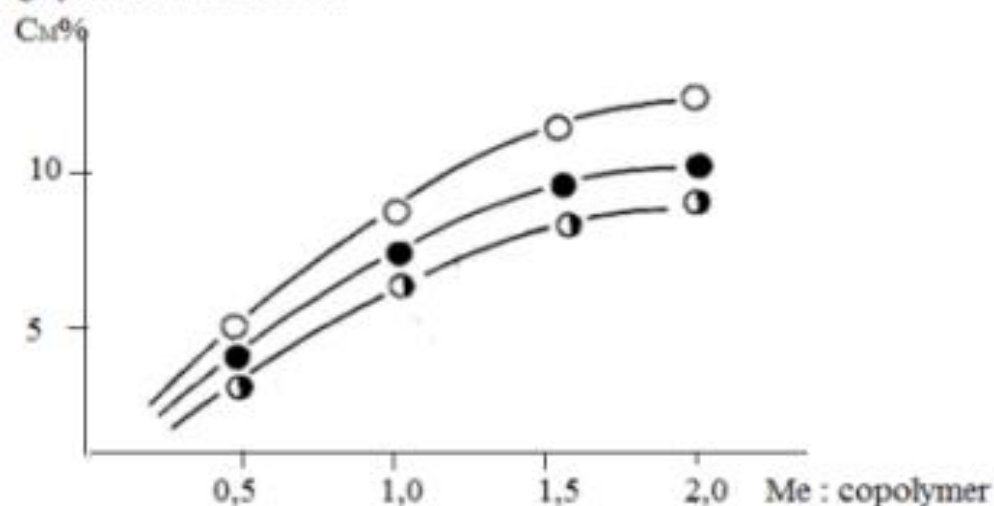


Fig. 3. Influence of the initial ratio Me: CA-VP (molar) on the content of copper (---), cobalt (- - -) in the medium acetone-dioxane (- ~ - -), acetoneethanol (- -)

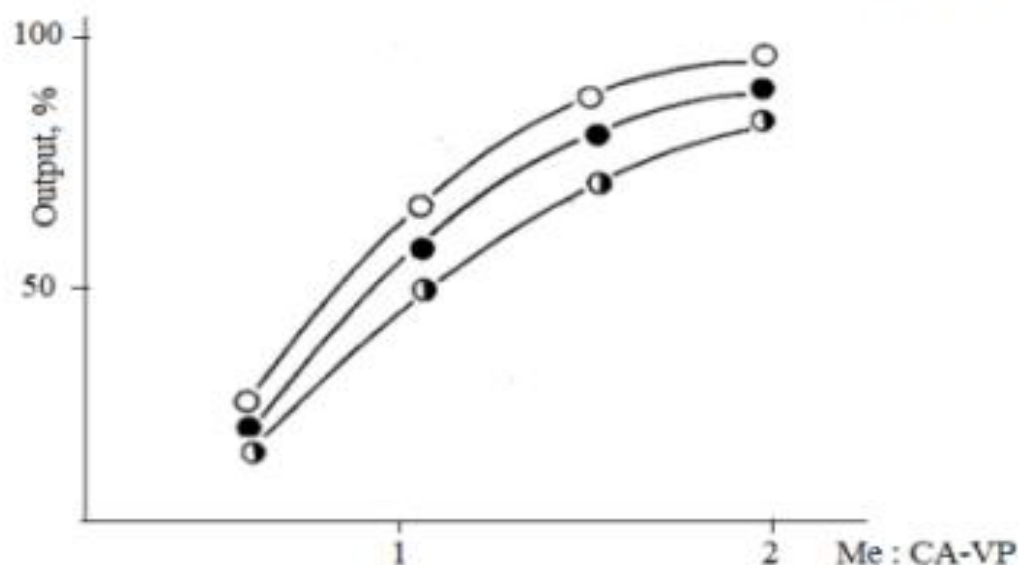


Fig. 4. Influence of the initial Co: CA-VP ratio on the yield polymer complex in a solvent medium acetone-dioxane (- o -) acetone-dichloroethane

(- ● -), acetone ethanol (- ◐ -)

The degree of metal incorporation into PLA and the yield of reaction products depend both on the nature of the metal (Fig. 3, curve 1.2) and on the nature of the solvent (Fig. 4, curve 2.3). Upon complexation in an acetone-dioxane medium, the copper content in the metal complex is higher than that of cobalt. This is apparently due to the high affinity of copper compounds for polymers containing carbonyl groups. Replacing the solvent with an acetone-ethanol medium leads to a decrease in the cobalt content in the metal complex. The use of a polar solvent enhances the polymer-solvent interaction, which leads to a decrease in the metal content in the metal complex.

The selected synthesis conditions for metal complexes of CA-VP copolymers in an acetone-dioxane, acetone-ethanol medium make it possible to obtain compounds with a controlled metal content and quantitative yield.

The distribution of electron density in the pyrrolidone ring shows that the oxygen atom (-0.415) has the highest donor ability. It is he who, first of all, will take part in coordination with the metal, as is the case in the interaction of metals with low-molecular-weight analogs. However, during the complexation of metals with copolymers, due to the long-chain nature of the ligand, steric effects appear, which impede the formation of complexes of 1: 4 and 1: 6 (metal: monomer unit).

Viscometric studies of dilute solutions of PLA showed that with an increase in the metal content in the complex, $[\eta]$ of solutions decreases (Fig. 5).

Complexation of the metal with polymers leads to the contraction of the macromolecule coil due to the intramolecular coordination of functional groups, which causes a decrease in the viscosity of solutions. It can be argued that the decrease in $[\eta]$ in the case of copolymers in solutions is due to the same factor.

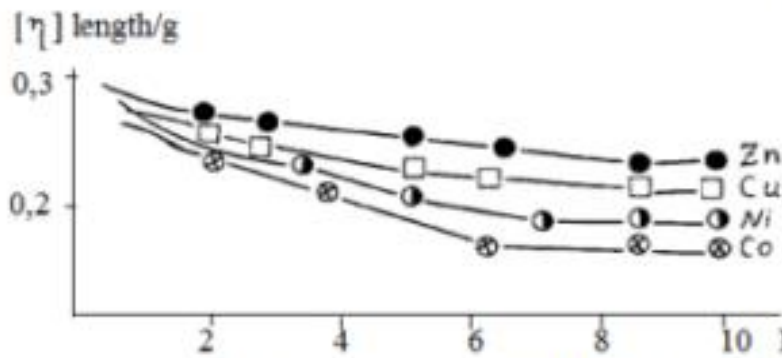


Fig. 5. Influence of the metal content in the CA-VP-Me²⁺ metal complex on the viscosity of solutions

This is evidenced by the results of measuring the diffusion coefficients of solutions and complexes, which showed that with an increase in the content of metal ions, the value of the diffusion coefficients correspondingly increases (Fig. 6, Table 1). The values of thermodynamic slenderness of metal complexes containing 10% metal ions are estimated. An increase in the amount of metal in the complex leads to a slight increase in the rotation retardation in the chain.

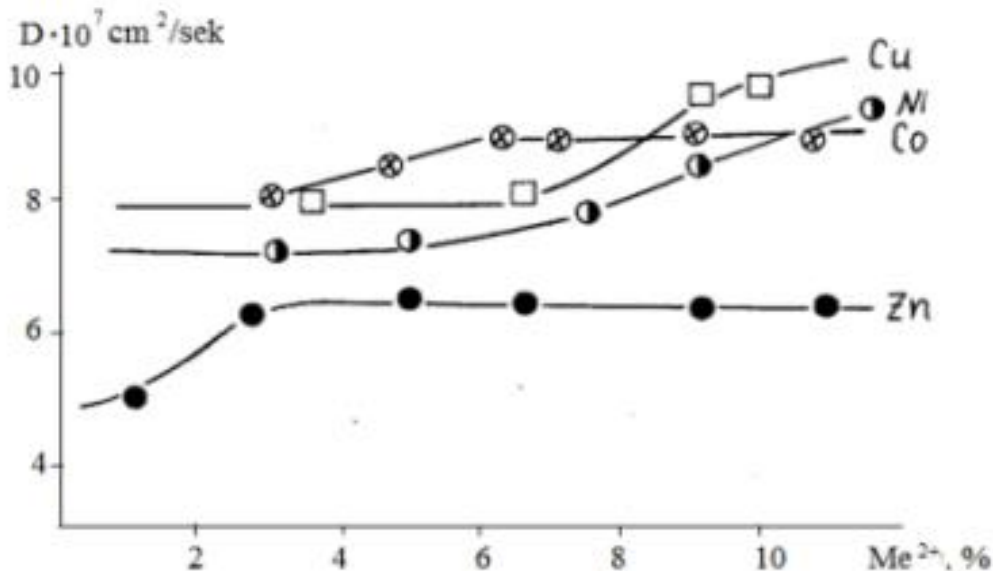


Fig. 6. Influence of the metal content in the CA-VP-Me²⁺ metal complex on the diffusion constants

In this case, the thermodynamic segment increases to 23.3 Å (compared to the 21 Å segment), which is apparently explained by an increase in the effective volume of the side group during complexation

Table 1.

Hydrodynamic parameters of copolymer metal complexes

$\bar{M}_{SD} \cdot 10^3$	r	$[\eta]$ length/g	$D \cdot 10^7$ cm ² /sec	S_0	Content of metal, %
	1	2	3	4	5
CA-VP-Co					
24,5		0,23	8,0	1,68	0
21,8		0,23	8,8	2,24	2,87

20,3	0,23	8,5	2,02	3,00
19,0	0,16	9,0	2,00	6,35
21,3	0,16	9,0	2,24	7,10
21,6	0,16	9,0	2,28	10,7
CA-VP-Cu				
24,5	0,23	8,0	1,68	0
21,3	0,22	8,1	1,99	3,50
22,0	0,22	8,2	2,05	5,37
21,4	0,21	8,6	2,00	6,60
19,2	0,20	9,5	2,14	9,97
18,0	0,20	10,0	1,97	9,07
CA-VP-Zn				
40,0	0,33	5,0	2,38	0
35,0	0,26	5,0	2,50	0,80
34,0	0,25	6,8	2,21	2,50
33,0	0,23	6,5	2,24	8,80
33,0	0,22	6,5	2,22	10,00
36,6	0,21	6,0	2,22	11,0
CA-VP-Ni				
28,0	0,28	7,75	1,87	0
24,0	0,22	8,0	2,40	6,44
30,0	0,16	6,2	2,30	3,11
28,0	0,16	7,3	2,21	7,47
23,0	0,16	7,1	1,77	7,50
15,0	0,13	9,5	1,46	11,66

In order to obtain additional data on the conformational changes of CA-VP macromolecules during complex formation, the pycnometric method was used to determine the partial specific volumes (volume change upon adding 1 g of a solute to an infinitely large volume of solvent) for CA-VP and its complexes at different metal contents (Fig. 7).

From the data in Fig. 7 it can be seen that with an increase in the metal content in the complex, the partial specific volume decreases. The dependence on the metal content in the complex can be explained by the change in the conformation of the macromolecules of the CA-VP complexes by the compression of the macromolecular coil of the complexes, since the partial specific volume in the first approximation is equal to the reciprocal of the effective density of the substance.

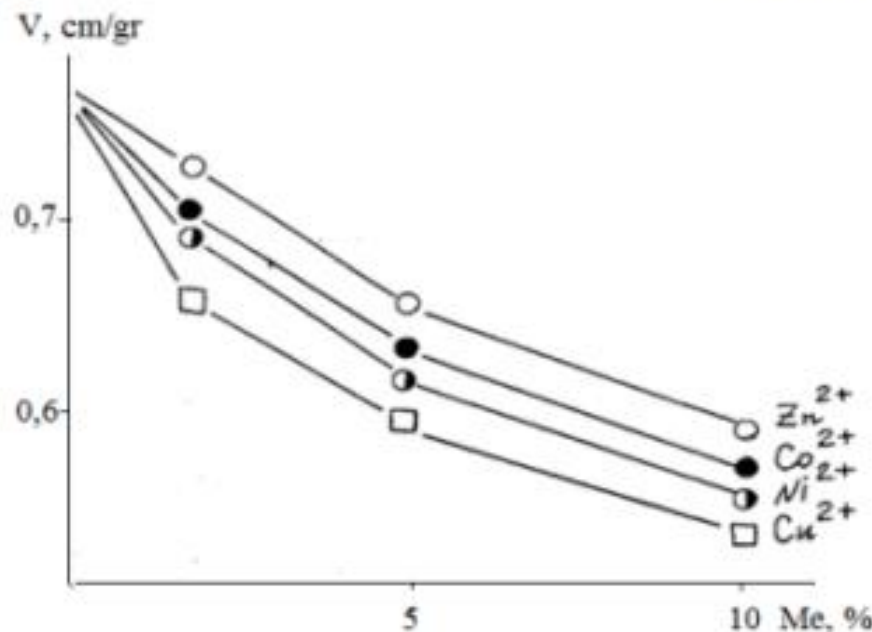


Fig. 7 - Dependence of the partial specific volume of CA-VP in water on the content of metal ions in the complex

Conclusion.

The study of the peculiarities of the processes of complexation of copolymers with transition metals indicates that the complexing ability of a polymer depends both on the properties of the macromolecule and metal, and on the nature and properties of the reaction medium. PLA with a quantitative yield can be obtained at the ratio [Me]: [copolymer] = 1: 2. It was revealed that PLA of the composition 2:1 [copolymer]: [Me] are formed and the metal interacts at the oxygen atom of the lactam cycle and the aldehyde group. Viscometric studies, diffusion and sedimentation measurements of dilute solutions of PLA showed that complexation of a metal with polymers leads to compression of the macromolecule coil due to intramolecular coordination of functional groups.

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