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EFFECT OF THE MATRIX OF A NATURAL POLYMER CELLULOSE ON THE INTERFACIAL REDUCTION OF SILVER(I) COMPLEXES WITH 1,10-PHENANTHROLINE TO STABILIZED SILVER CLUSTERS

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Summary:Mechanism of diffusion-reduction interaction of silver(I) complexes containing biologically active heterocyclic ligand 1,10-phenanthroline with microcrystalline cellulose at cellulose/solvent interface in thermally activated reaction conditions was developed. The resulting compounds are of considerable interest for medical application.

INTRODUCTION

Coordination compounds of silver(I) (Ag(I)) and silver clusters exhibit strong antibacterial, antiviral, and antitumor activity (Ref. 1). One of the paths to prepare new Ag-containing drugs is their combination with microcrystalline cellulose (MCC).

Specific features of surface reactivity of microcrystalline cellulose (MCC) are its distinct nucleophilicity and reducing properties. We have recently studied the reducing reactivity of MCC with respect to redox active metal ions Ag^+ (Ref. 2), Pt^{2+}, and Pd^{2+} (Ref. 3).

It has been shown that as a result of silver ions reduction silver clusters are obtained (Refs. 2, 4, 5). The direct evidence of the formation of silver clusters stabilized by 1,10-phenanthroline (phen) intercalated into the MCC matrix was obtained by WAXS, TEM, Raman and XPS spectroscopy. The aim of this paper is to clarify the mechanism of diffusion-reduction interaction of bulky hydrophobic Ag(I) complexes containing π-electron-deficient, biologically active heterocyclic ligand 1,10-phenanthroline (Ref. 6) with the cellulose/solvent interface in thermally activated reaction conditions.

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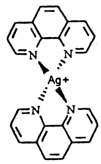
EXPERIMENTAL PART

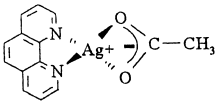
Initial materials: MCC, 1,10-phenanthroline, $[Ag(H_2O)_2]NO_3$, $[Ag(phen)_2]OAc$ and $[Ag(phen)OAc]$. The last two complexes were prepared for the first time (Ref. 7).

A complex cation $[Ag(phen)_2]^+$ (I) and a neutral complex $[Ag(phen)OAc]$ (II) have the following structure:

I



II



Interfacial chemisorption and subsequent reduction of Ag(I) complexes with 1,10-phenanthroline were carried out using different reducers and solvents as well as the MCC matrix itself as a reducer. The specific properties of reactive MCC surface in redox reactions were also studied.

The interaction of MCC with Ag(I) complexes proceeds via a multistage process. The first stage is the diffusion of the $[Ag(H_2O)_2]NO_3$ complex into the MCC matrix. It is accompanied by primary reduction with MCC functioning as a reducer. Subsequently, the addition of 1,10-phenanthroline to $[Ag(H_2O)_2]NO_3$/MCC and, hence, the replacement of H_2O molecules by 1,10-phenanthroline ligands occur (Ref. 8). Further reduction of silver ions in $[Ag(phen)_2]NO_3$/MCC to silver clusters stabilized by 1,10-phenanthroline is carried out in the presence of additional chemical reducers (glycerol or EtOH).

In the case of previously prepared $[Ag(phen)_2]OAc$ and $[Ag(phen)OAc]$ complexes, the first step is their diffusion into the MCC matrix. The diffusion is accompanied by the reduction of complexes to silver clusters by MCC itself. Reduction process is also developed by the addition of $Na[BH_4]$ as a reducer.

Thus, the MCC/solvent interface-mediated interaction with silver(I) complexes proceeds via the following:

Initial complex $[Ag(H_2O)_2]NO_3$	Initial complexes $[Ag(phen)_2]OAc$ and $[Ag(phen)OAc]$
1. diffusion-sorption	1. diffusion-sorption
2. the complexation of $[Ag(H_2O)_2]NO_3$ with 1,10-phenanthroline directly in the MCC matrix	2. the redox process initiated by the additional reducer $Na[BH_4]$
3. the redox process initiated by the additional reducers (EtOH, glycerol)	3. the clusters redox growth and aggregation
4. the clusters redox growth and aggregation	

RESULTS AND DISCUSSION

Initial silver complex $[Ag(H_2O)_2]NO_3$. Diffusion-sorption of silver complex into the MCC matrix and formation of primary reduction centres with MCC functioning as a reducer

Interaction of $[Ag(H_2O)_2]NO_3$ with 1,10-phenanthroline and subsequent reduction of Ag^+ ions in Ag(I) complexes with 1,10-phenanthroline on the MCC surface and in bulk can be described as follows:

1. Diffusion of $[Ag(H_2O)_2]NO_3$ into the MCC bulk;
2. Formation of Ag^o/MCC primary centres induced by electron-donor properties of MCC itself and by visible light (Ref. 8):

$[Ag(H_2O)_2]NO_3 + MCC \rightarrow [Ag(H_2O)_2]NO_3/MCC$

$[Ag(H_2O)_2]NO_3/MCC + h\nu \rightarrow Ag^o/MCC$

Specific model for describing of the diffusion-sorption of aqua Ag(I) complex $[Ag(H_2O)_2]NO_3$ and Ag(I) complexes with 1,10-phenanthroline into the MCC matrix is proposed (Fig. 1). Shaitan's concept of surface activation of a densely packed polymer globule at the interface of globule/solution phases (Ref. 9) was applied for development of our model. Activation of the MCC surface is considered as a result of diffusion of solvent microcavities (density fluctuations) (Ref. 10) from the volume of solution located in the MCC macropores via the MCC/solvent interface into the MCC bulk.

Fig. 1 shows that hydrophilic complex cations $[Ag(H_2O)_2]^+$ play the role of hydrophilic probes (Ref. 11) and are originally bound to hydrophilic reducing sites. In contrast, hydrophobic silver(I) complexes with 1,10-phenanthroline are hydrophobic probes and are originally bound to hydrophobic non-reducing sites.

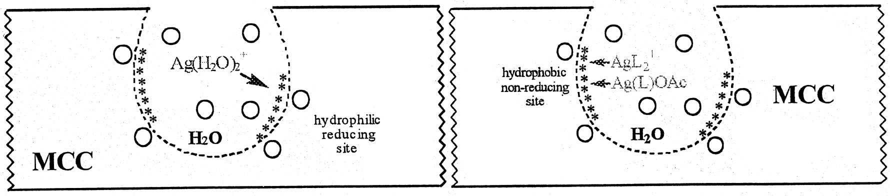


Fig.1. Diffusion-sorption of aqua Ag(I) complex $[Ag(H_2O)_2]NO_3$ and Ag(I) complexes with 1,10-phenanthroline (L) into the MCC matrix; o - microcavities, density fluctuations

Complexation of $[Ag(H_2O)_2]NO_3$ with 1,10-phenanthroline directly in the MCC matrix. Redox processes initiated by additional reducers (EtOH, glycerol)

1. Complexation of $[Ag(H_2O)_2]NO_3$ with 1,10-phenanthroline hydrate on the MCC surface and in bulk proceeds as follows:

$[Ag(H_2O)_2]NO_3/MCC + 2\ phen(H_2O) \rightarrow [Ag(phen)_2]NO_3/MCC$

2. Electron-donor reactivity of the MCC surface and bulk in redox reactions is provided by its aldehyde end groups and alcohol groups. The latter are less reactive but, nevertheless, are potential reducers. In thermally initiated electron-transfer reactions, both types of groups react as two electron donors.

Reduction of $[Ag(phen)_2]NO_3/MCC$ on primary centres Ag^o/MCC initiated by additional reducers (glycerol or EtOH) to silver clusters stabilized by 1,10-phenanthroline proceeds as follows:

$[Ag(phen)_2]NO_3/MCC \rightarrow Ag^o_nAg^+_m(phen)_l(NO_3)^-_m/MCC^*$

Ag^0_n - cluster nucleus, Ag^+_m - ionic shell of cluster nucleus, $(phen)_l$ - peripheral ligands,

$(NO_3^-)_m$ - cluster ionic shell, MCC*= -COOH-rich oxidized MCC forms.

Initial silver complexes $[Ag(phen)_2]OAc$ and $[Ag(phen)OAc]$. Redox processes initiated by the additional reducer $Na[BH_4]$

Complexes of silver(II) with 2,2′-bipyridine $[Ag(bpy)_2]^{2+}$ are known to oxidize secondary alcohols (Ref. 12). The fact that similar complexes of silver(I) with 1,10-phenanthroline can be reduced by the OH groups in MCC and alcohols (EtOH and glycerol) is a novel one.

It has earlier been determined in the study of Pt(II), Ni(II), and Co(II) complexes with 1,10-phenanthroline that, in principle, at least two different thermally activated processes are possible (Refs. 13-15). This is the thermally activated electron transfer to a metal ion or a coordinated ligand which leads to the formation of an electron-rich complex with monomeric 1,10-phenanthroline ligands. The second variant of the above processes is the proton transfer, which leads to the C-C coupling of coordinated 1,10-phenanthroline and to the formation of an electron-rich complex with a dimeric dianion form of 1,10-phenanthroline. Developing the concept of higher stability of d^6-shells of octahedral complexes of transition metals in redox reactions (Ref. 16), we assumed that this concept would also be valid for the $4d^{10}5s^0$ configuration of the Ag^+ ion. This suggests that the initial species of one- and two-electron transfer are the electron-rich compounds: $[\text{Ag}^{+}(4\text{d}^{10}5\text{s}^{0})(\text{phen}^{-\cdot})\text{phen}]$, $[\text{Ag}^{+}(4\text{d}^{10}5\text{s}^{0})(\text{phen}^{-\cdot})_2]^{-}$, $[\text{Ag}^{+}(4\text{d}^{10}5\text{s}^{0})(\text{phen}^{-\cdot})\text{OAc}^{-}]^{-}$ which are formed according to the scheme:

$[\text{Ag}^{+}(4\text{d}^{10}5\text{s}^{0})(\text{phen})_2]^{+} + \text{e}^{-} \rightarrow [\text{Ag}^{+}(4\text{d}^{10}5\text{s}^{0})\ (\text{phen}^{-\cdot})(\text{phen})]$

$[\text{Ag}^{+}(4\text{d}^{10}5\text{s}^{0})\ (\text{phen}^{-\cdot})(\text{phen})] + \text{e}^{-} \rightarrow [\text{Ag}^{+}(4\text{d}^{10}5\text{s}^{0})(\text{phen}^{-\cdot})_2]^{-}$

$[\text{Ag}^{+}(4\text{d}^{10}5\text{s}^{0})(\text{phen})\text{OAc}^{-}] + \text{e}^{-} \rightarrow [\text{Ag}^{+}(4\text{d}^{10}5\text{s}^{0})(\text{phen}^{-\cdot})\text{OAc}^{-}]^{-}$

In general, the redox process between MCC and Ag(I) complexes with 1,10-phenanthroline can be shown as follows:

$[\text{Ag}^{+}(\text{phen})_2]^{+}\text{OAc}^{-}/\text{MCC} \rightarrow [\text{Ag}^{+}(\text{phen}^{-\cdot})_2]^{-}/\text{MCC}^{*}$

$2[\text{Ag}^{+}(\text{phen})\text{OAc}^{-}]/\text{MCC} \rightarrow 2\,[\text{Ag}^{+}(\text{phen}^{-\cdot})\text{OAc}^{-}]^{-}/\text{MCC}^{*}$

Electron transfer from the anion-radical phenanthroline ligands to metal cations (the spin-isomerisation) leads to the formation the Ag° species stabilized by peripheral phenanthroline ligands:

$[\text{Ag}^{+}(\text{phen}^{-\cdot})\text{OAc}^{-}]^{-}/\text{MCC}^{*} \rightarrow \text{Ag}^{\circ}(\text{phen})/\text{MCC}^{*} + \text{OAc}^{-}$

The spin-spin compensation of phenanthroline anion-radical ligands in electron-rich intermediates leads to the formation of Ag(I) complexes with one of the 1,10-phenanthroline fragment of the C-C-dimers (C-C-coupling reaction of coordinated 1,10-phenanthroline):

$[\text{Ag}^{+}(\text{phen}^{-\cdot})_2]^{-}/\text{MCC}^{*} \rightarrow \text{Ag}^{+}\ \text{phen}^{-}\text{—phen}^{-}/\text{MCC}^{*}$

$2[\text{Ag}^{+}(\text{phen}^{-\cdot})\text{OAc}^{-}]^{-}/\text{MCC}^{*} \rightarrow \text{Ag}^{+}(\text{AcO}^{-})\text{phen}^{-}\text{—phen}^{-}\text{Ag}^{+}(\text{AcO}^{-})/\text{MCC}^{*}$

$2[\text{Ag}^{+}(\text{phen}^{-\cdot})(\text{H}_2\text{O})]/\text{MCC}^{*} \rightarrow \text{Ag}^{+}(\text{H}_2\text{O})\text{phen}^{-}\text{—phen}^{-}\text{Ag}^{+}(\text{H}_2\text{O})/\text{MCC}^{*}$

Electron transfer with spin-spin compensation leads to the formation of Ag clusters stabilized by 1,10-phenanthroline/MCC*:

$[\text{Ag}^{+}(\text{phen}^{-\cdot})\text{OAc}^{-}]^{-}/\text{MCC}^{*} \rightarrow \text{Ag}^{\circ}_{n}\text{Ag}^{+}_{m}(\text{phen})_{l}(\text{OAc}^{-})_{m}/\text{MCC}^{*} + [\text{Ag}^{+}(\text{phen}^{-}\text{—phen}^{-})]^{-}/\text{MCC}^{*}$

In contrast, the reduction of $[\text{Ag}^{+}(\text{phen})_2]^{+}/\text{MCC}$ by $[\text{BH}_4]^{-}$ can proceed with the addition of $\text{Na}[\text{BH}_4]$ and leads to the formation of Ag clusters stabilized by 1,10-phenanthroline/ MCC:

$[\text{Ag}^{+}(\text{phen})_2]^{+}/\text{MCC} \rightarrow \text{Ag}^{\circ}_{n}\text{Ag}^{+}_{m}(\text{phen})_{l}(\text{OAc}^{-})_{m}/\text{MCC} + [\text{Ag}^{+}(\text{phen}^{-}\text{—phen}^{-})]^{-}/\text{MCC}$

In the case of reduction of silver complexes $[\text{Ag}(\text{phen})_2]\text{OAc}$ and $[\text{Ag}(\text{phen})\text{OAc}]$, the size of the resulting silver clusters is very small and their structure may be not totally crystalline. Therefore, they can be hardly detected by WAXS. They, probably, can be determined by SAXS. Subsequent redox aggregation proceeds in the MCC macrocavities and will be described in subsequent publication. The resulting compounds are of considerable interest for further medical application.

CONCLUSIONS

1. Both the MCC surface and its bulk exhibit relatively high electron-donor properties and reduce the initial silver(I) complexes. Diffusion and redox processes are mediated by the MCC/solvent interface.
2. Depending on the composition and structure of initial complex forms, either electron-rich silver(I) compounds or silver clusters stabilized by peripheral 1,10-phenanthroline ligands bound to MCC surface and/or intercalated into the MCC cavities are formed.
3. $[Ag(phen)_2]NO_3$ intercalated into the MCC matrix can be reduced to silver clusters stabilized by 1,10-phenanthroline peripheral ligands.
4. Cationic complexes $[Ag(phen)_2]OAc$ can be reduced by MCC to electron-rich complexes of silver(I) stabilized by bis-phenanthroline anionic ligands.
5. Neutral complexes [Ag(phen)OAc] can be reduced by MCC to small silver clusters stabilized by 1,10-phenanthroline peripheral ligands.

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