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## MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

# Silver Recovery with Complexing Sorbents Based on 1-Vinyl-1,2,4-triazole

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**Abstract**—The sorption activity of copolymers based on 1-vinyl-1,2,4-triazole toward silver ions was studied in relation to the copolymer structure and to the kind and concentration of acids. The copolymers were prepared by radical copolymerization of 1-vinyl-1,2,4-triazole with 1,1,3-trihydrotetrafluoropropyl methacrylate and divinylbenzene, with 1,1,3-trihydrotetrafluoropropyl methacrylate, methyl methacrylate, and *N,N*'-methylenebisacrylamide, with diethylene glycol divinyl ether, and with divinyl sulfide. The copolymers exhibit high sorption activity. They efficiently recover silver cations from acid solutions and behave as anion exchangers.

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Synthesis of complexing sorbents is aimed at formation in their structure of functional groups ensuring efficient and selective interaction with metal ions. The action of functional groups is determined by the basicity of their donor atoms and by the conformational mobility which strongly depends on the supramolecular structure of the compounds [1–3].

The recovery of silver from acid solutions with complexing polymeric sorbents containing in the macrochain heterocyclic groups of 3(5)-methylpyrazole, (vinyl)imidazole, (vinyl)benzimidazole, and 2-mercaptobenzothiazole has been reported [4–7]. Previously we examined the sorption activity of copolymers of 1-vinyl-1,2,4-triazole with diethylene glycol divinyl ether and divinyl sulfide toward mercury ions [8].

Here we report on purposeful synthesis of copolymers of 1-vinyl-1,2,4-triazole (VT) with diethylene glycol divinyl ether (DEGDVE) (C-1), with 1,1,3-trihydrotetrafluoropropyl methacrylate (FAMA) and divinylbenzene (DVB) (C-2), with 1,1,3-trihydrotetrafluoropropyl methacrylate, methyl methacrylate (MMA), and *N,N*'-methylenebisacrylamide (MBAA) (C-3), and with divinyl sulfide (DVS) (C-4), and also on their sorption activity toward silver ions.

## EXPERIMENTAL

The monomers were synthesized and purified by published procedures: 1-vinyl-1,2,4-triazole [9], bp 48°C/3 mm Hg, $n_D^{20}$ 1.5075, $d_4^{20}$ 1.0857; divinyl sulfide [10], bp 86°C/730 mm Hg, $n_D^{20}$ 1.5060; diethylene glycol divinyl ether [11], bp 85°C/14 mm Hg, $n_D^{20}$ 1.4430; 1,1,3-trihydrotetrafluoropropyl methacrylate [12], bp 46°C/1.73 kPa, $n_D^{20}$ 1.3740. 2,2'-Azobis(isobutyronitrile) (AIBN) was purified by the common procedure. Radical copolymerization was performed in sealed glass ampules in the bulk under the action of AIBN at 60°C for 0.25 (C-1), 8 (C-2), 12 (C-3), and 3 h (C-4). The products formed were filtered off, washed to remove unchanged monomers with ethanol in a Soxhlet apparatus, and vacuum-dried to constant weight at 40°C.

The copolymer composition was calculated from the results of elemental analysis (N, S, F). The degree of swelling of the copolymers was determined gravimetrically. The IR spectra were recorded on a Bruker IFS-25 spectrometer using KBr pellets. The sorption properties of the copolymers were studied using the batch technique at room temperature. The weighed portion of the sorbent was 10 mg, and the total solution volume was

**Table 1.** Composition and yield of copolymers studied

| Copolymer | Elemental analysis, % | | | Copolymer composition, mol % | | | | | | | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | N | F | S | VT | DEGDVE | DVB | FAMA | MMA | MBAA | DVS | |
| C-1 | 23.23 | – | – | 65 | 35 | – | – | – | – | – | 56 |
| C-2 | 25.43 | 14.93 | – | 74 | – | 3 | 23 | – | – | – | 97 |
| C-3 | 23.96 | 9.21 | – | 66 | – | – | 11 | 22 | 0.06 | – | 99 |
| C-4 | 35.83 | – | 2.81 | 80 | – | – | – | – | – | 20 | 71 |

20 ml. The content of silver and other metals in solutions was monitored by atomic absorption spectroscopy.

The obtained network copolymers C-1 and C-4 are pale yellow powders. Copolymers C-2 and C-3 are transparent glassy blocks, which were pulverized in a mill. The copolymers are insoluble in organic solvents, acids, and alkalis and are well wetted with water. The results of elemental analysis and the compositions of the copolymers are given in Table 1.

The synthesized copolymers C-1–C-4 (yield 56–99%) are enriched in VT units. Copolymers C-1 and C-4 show 40 and 60% swellability in water, respectively. In acid solutions, the swellability is essentially the same. The swellability of copolymers C-2 and C-3 in water is 44 and 42%, respectively, and after treatment with 0.1 M HCl it increases to 45%. The copolymers are heat-resistant: The softening point is as high as 290–350°C.

As follows from the IR data and elemental analysis, the copolymer macromolecules consist of the following fragments:

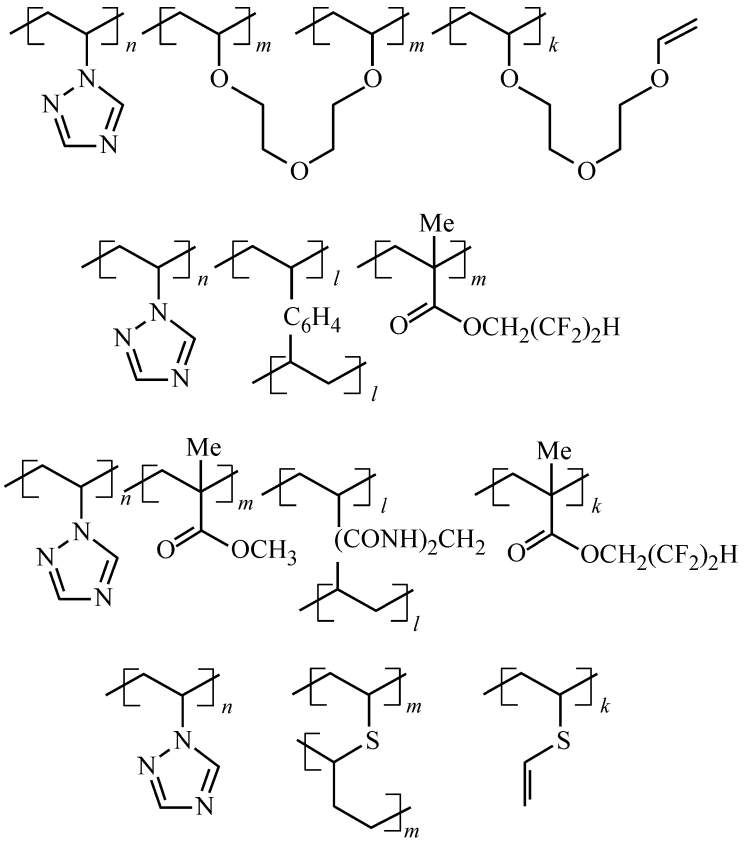

**Table 2.** Recovery of silver ions from acid solutions with copolymers. $Ag^+$ concentration: C-1 1.00 mg/10 ml, C-2–C-4 1.00 mg/20 ml

| Acid concentration, M | Recovery of silver ions, % | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | C-1 | | C-2 | | C-3 | | C-4 | |
| | $HNO_3$ | $H_2SO_4$ | $HNO_3$ | $H_2SO_4$ | $HNO_3$ | $H_2SO_4$ | $HNO_3$ | $H_2SO_4$ |
| 1 | 75 | 82 | 75 | 70 | 70 | 78 | 86 | 88 |
| 2 | 45 | 63 | – | – | – | – | – | – |
| 3 | 22 | 33 | 55 | 36 | 48 | 63 | 53 | 61 |
| 5 | 12 | 12 | 47 | 24 | 40 | 38 | 51 | 61 |
| 7 | 7 | 6 | 40 | 10 | 33 | 7 | 50 | 60 |

In the IR spectra of copolymers C-1–C-4, the absorption bands at 960, 1650, and 3130 $cm^{-1}$, corresponding to vibrations of the vinyl group in the comonomers, are absent, whereas the vibration bands of the triazole ring are preserved (1120, 1429, 1490 $cm^{-1}$).

The presence of the ether group C–O–C of the DEGDCE fragment in copolymer C-1 is confirmed by stretching vibration bands at 1100–1120 $cm^{-1}$. A weak band at 1620 $cm^{-1}$, corresponding to stretching vibrations of residual C=C bonds in DEGDVE, is also observed.

In the IR spectra of copolymers C-2 and C-3, there are stretching vibration bands at 1130, 1205, 1240, and 1270 $cm^{-1}$ and bending vibration bands at 400–1000 $cm^{-1}$, belonging to $CF_2$ groups of the FAMA fragment, and also stretching vibration bands of the C=O bond in the MMA ester group at 1725 $cm^{-1}$.

**Table 3.** Kinetic characteristics of sorption. [a] $Ag^+$ concentration: C-1 1.00 mg/10 ml, C-2–C-4 1.00 mg/20 ml

| Sorbent | $t/\tau_{1/2}$, min/min | |
|---|---|---|
| | $HNO_3$ | $H_2SO_4$ |
| C-1 | 15/5 | 15/5 |
| C-2 | 17/6 | 22/10 |
| C-3 | 14/8 | 14/8 |
| C-4 | 30/15 | 20/8 |

[a] ($t$) Time of equilibrium attainment and ($\tau_{1/2}$) half-sorption time.

The IR spectrum of copolymer C-4 contains an absorption band at 660 $cm^{-1}$, corresponding to stretching vibrations of the C–S–C bond in DVS. The absorption band of vinylthio groups $CH_2$=CHS in DVS does not fully disappear, and a weak peak remains at 1585 $cm^{-1}$.

We found that copolymers C-1–C-4 are capable of forming a donor–acceptor bond with the cationic form of silver, which is due to presence in their macromolecules of nitrogen-containing heterocyclic fragments. The copolymers also exhibit the properties of anion exchanges, recovering anionic silver complexes.

Data on the recovery of silver ions in relation to the concentration and kind of acids are given in Table 2.

With an increase in the acid concentration from 1 to 7 M, the sorption of silver ions decreases. For copolymer C-1, the decrease in the sorption activity with increasing acid concentration is more pronounced, whereas for C-4 copolymer it is insignificant. If we take into account that the recovery occurs via nitrogen donor atom, then the decrease in the sorption is determined by the competing effect of protons on the donor–acceptor interaction with silver cations and by the strength of the complexes formed. For the copolymer containing divinyl sulfide fragments (C-4), coordination interaction with sulfur atoms is possible. At the same time, silver ion forms weakly dissociating sulfate complexes $[AgSO_4]^-$, $[Ag(SO_4)_2]^{3-}$ [13], which are recovered by the ion-exchange mechanism, increasing the overall silver recovery in sulfuric acid solutions.

The donor–acceptor interaction is confirmed by

changes in the positions of the absorption bands in the IR spectra. The bands at 1120, 1429, and 1490 $cm^{-1}$, characteristic of the triazole ring, in the spectrum of copolymer C-1 are shifted to 1141, 1438, and 1514 $cm^{-1}$ in the spectrum of the concentrate. The C–S–C stretching vibration bands of the DVS fragment of sorbent C-4 are observed at 670–750 $cm^{-1}$ (in the initial copolymer, at 660 $cm^{-1}$). The positions of the stretching vibration bands of the ether group C–O–C (1100–1120 $cm^{-1}$) remain unchanged.

A study of the influence of time on the sorption process showed that the sorption equilibrium was attained fairly rapidly. According to the results obtained (Table 3), higher rate of equilibrium attainment is observed with copolymers C-1 and C-3, but the shortest half-sorption time is observed with the copolymer containing DEGDVE units in the macromolecule. The longest time is required for equilibrium attainment with copolymer C-4 containing the largest number of donor atoms (N, S), which is associated with the structure of the macromolecule.

To evaluate the sorption capacity, we studied the equilibrium distribution of silver ions between the phases at increased concentration of silver in 1 M acid solutions and sorption time of 1 h. The characteristics of the sorption process are given in Table 4.

As seen from Table 4, sorbent C-1 in which DEGDVE acts in copolymerization as both a comonomer and a cross-linking agent exhibits the highest sorption capacity. DEGDVE units ensure the linear structure of the macromolecules of copolymer C-1, which leads to less dense packing and facilitates the interaction of silver cations with coordination centers.

Units of macromolecules of copolymers C-2–C-4 are bonded to each other by cross-links, which ensures their denser packing and complicates the access of silver cations to coordination-active centers of the sorbents. The highest distribution coefficient is observed with sorbent C-1 ($1.5 \times 10^4$), which makes it promising for silver recovery from solutions with a low silver concentration.

We demonstrated the possibility of eluting silver ions from the concentrate of sorbent C-1 with a 3% solution of thiourea in 1 M sulfuric acid. At an Ag(I) content in the concentrate of 40 μg, 95–97% desorption is ensured by 10 ml of the thiourea solution in 15–20 min. The sorbent can be used repeatedly in sorption–desorption cycles. Data on sorption with the regenerated sorbent are given in Table 5.

**Table 4.** Sorption capacities (SC) for silver and distribution coefficients (D) of silver in sorption on vinyltriazole-based copolymers

| Sorbent | SC, mg $g^{-1}$ | | $D$, $cm^3$ $g^{-1}$ | |
|---|---|---|---|---|
| | $HNO_3$ | $H_2SO_4$ | $HNO_3$ | $H_2SO_4$ |
| C-1 | 390 | 370 | $1.5 \times 10^4$ | $1.5 \times 10^4$ |
| C-2 | 190 | 250 | $4.3 \times 10^3$ | $4.7 \times 10^3$ |
| C-3 | 250 | 250 | $4.7 \times 10^3$ | $4.7 \times 10^3$ |
| C-4 | 180 | 325 | $2.4 \times 10^3$ | $2.3 \times 10^3$ |

**Table 5.** Results of Ag(I) determination in sorption–desorption cycles using sorbent C-1 ($c_{Ag^+} = 0.5$ μg $ml^{-1}$, $V_{solution} = 100$ ml, $V_{TU} = 10$ ml)

| Ag amount | Cycle 1 | Cycle 2 | Cycle 3 | Cycle 4 |
|---|---|---|---|---|
| Sorbed, μg | 50 | 45 | 32 | 30 |
| Eluted, μg | 48 | 40 | 26 | 17 |
| % | 98 | 80 | 52 | 33 |

With the aim to evaluate the selectivity of the copolymer, we examined the sorption power of C-1 toward Cu(II), Fe(III), Co(II), Zn(II), and Pb(II) ions (metal content 1 mg in 20 ml of a 1 M $HNO_3$ or $H_2SO_4$ solution). We found that, in sorption of silver from multicomponent salt solutions, only Cu(II) ions were recovered (~30%).

The results of silver determination in solutions containing base metal cations using the sorption–desorption operation are given in Table 6.

As already noted, the sorbents behave as anion exchangers. The possibility of recovering anionic silver species was checked with sorption of silver thiosulfate complexes $[Ag(S_2O_3)_2]^{3-}$ as example. We found that the highest degree of recovery of the complex is observed at the ratio $[Ag^+] : [S_2O_3^{2-}] = 1 : 10$ (pH 4), and at a large excess of thiosulfate ions the sorption of the complex decreases.

The recovery of the thiosulfate complex is characterized by fast kinetics. The sorption equilibrium is attained within 15 min at $\tau_{1/2} = 6$ min, i.e., at approximately

**Table 6.** Determination of silver in solutions containing ferrous and nonferrous metal cations with sorbent C-1 ($m_{sorbent}$ =30 mg, $n$ = 4)

| $Ag^+$ in initial solution, μg/100 ml | Total metal concentration in initial solution, μg/100 ml | Found $Ag^+$ after sorption, $X_i \pm \Delta X$, μg | $V$, % |
|---|---|---|---|
| 2.50 | 40 | 2.44 ± 0.13 | 3.4 |
| 2.50 | 100 | 2.41 ± 0.11 | 2.9 |

**Table 7.** Recovery of silver thiosulfate complexes with sorbent C-1 ($m_{sorbent}$ =20 mg, pH 4.0)

| Solution containing $[Ag(S_2O_3)_2]^{3-}$, ml | $m_{Ag}$+ in solution, μg | | Recovered, % |
|---|---|---|---|
| | before sorption | after sorption | |
| Fixing, 100 | 2760 | 900 | 61 |
| Developing, 50 | 88 | 12 | 86 |

the same rate as in recovery of the cationic form. The sorption capacity (250 mg $g^{-1}$) was calculated from the equilibrium distribution of silver thiosulfate complexes between the solution and solid phase with an increase in their concentration. The isotherm obtained, compared to the isotherms for the cationic form of the metal, shows that the equilibrium is attained at a lower concentration of ions in the solution.

Using sorbent C-1, we performed recovery of Ag(I) in the form of its thiosulfate complex from fixing and developing solutions (Table 7).

## CONCLUSIONS

(1) New copolymers of 1-vinyl-1,2,4-triazole with 1,1,3-trihydrotetrafluoropropyl methacrylate, divinylbenzene, methyl methacrylate, *N,N*'-methylenebisacrylamide, diethylene glycol divinyl ether, and divinyl sulfide were prepared by radical copolymerization.

(2) The dependence of the recovery of silver ions with the synthesized copolymers on the kind and concentration of acids was found. The possibility of sorption of thiosulfate complexes was demonstrated.

(3) The structure of macromolecules affects the sorption characteristics of the synthesized copolymer: The highest sorption capacities and distribution coefficients are observed with the sorbent of a linear structure with a lower content of donor atoms.

(4) The sorbents can be recommended for sorption–atomic absorption determination of silver in solutions containing ferrous and nonferrous metals using thiourea as an eluent, and also for recovery of anionic silver complexes.

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