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Examination of the reaction of a macromolecular sulfonamide with sodium nitrite in acidic media

RAPID COMMUNICATION

Summary — In this study we have examined the reaction of macromolecular sulfonamide (styrene/divinylbenzene copolymer with the macroporous structure containing $-\text{SO}_2\text{NH}_2$ groups) with nitrites in acidic media. We found that the lowest admissible pH of the reaction medium providing the stability of the functional groups was 4.0. The lower the pH, the quicker the functional group lost its nitrogen atom and transformed to a sulfonic group. Knowledge of the chemical stability of sulfonamide groups in the presence of nitrites is not only of cognitive but also of practical value, because *N*-chloro derivatives of a sulfonamide copolymer (containing so-called active chlorine) are useful for the elimination of nitrites from waters through their oxidation to less toxic nitrates.

Key words: macromolecular sulfonamide, styrene/divinylbenzene copolymer containing sulfonamide functional groups, destruction of sulfonamide groups, reaction of sulfonamide with nitrite.

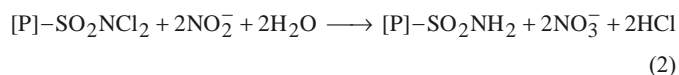
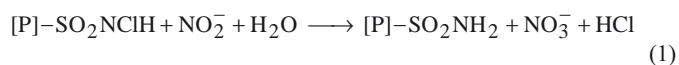
BADANIE REAKCJI WIELKOCZĄSTECZKOWEGO SULFONAMIDU Z AZOTYNEM SODU W ŚRODOWISKU KWAŚNYM

Streszczenie — Badano reakcję wielkocząsteczkowego sulfonamidu (kopolimer styren/diwinyllobenzen o strukturze makroporowatej zawierający grupy $-\text{SO}_2\text{NH}_2$) z azotynami w środowisku kwaśnym. Stwierdzono, że najniższe dopuszczalne pH środowiska reakcyjnego zapewniające trwałość grup funkcyjnych wynosi 4.0, a im niższe jest pH tym grupy funkcyjne szybciej tracą azot i przekształcają się w grupy sulfonowe. Zbadanie trwałości grup sulfonamidowych w obecności azotynów ma znaczenie praktyczne, ponieważ *N*-chloropochodne kopolimeru sulfonamidowego (zawierające tzw. chlor aktywny) są przydatne do eliminowania z wód toksycznych azotynów przez ich utlenianie do znacznie mniej szkodliwych azotanów.

Słowa kluczowe: wielkocząsteczkowy sulfonamid, kopolimer styren/diwinyllobenzen o sulfonamidowych grupach funkcyjnych, destrukcja grup sulfonamidowych, reakcja sulfonamidu z azotynem.

The macromolecular sulfonamide which has a styrene/divinylbenzene skeleton ($[\text{P}]-\text{SO}_2\text{NH}_2$) is a reactive polymer with especially valuable properties. It has the property of binding the so-called active chlorine in a reaction with ClO^- . The sulfonamide group binds either one or two chlorine atoms dependently on pH of the reaction's medium, and the reaction products are copolymers: *N*-monochlorosulfonamide ($[\text{P}]-\text{SO}_2\text{NClNa}$) or *N,N*-dichlorosulfonamide ($[\text{P}]-\text{SO}_2\text{NCl}_2$). They can be placed in a column as swollen with water, the column beds containing active chlorine in a high concentration 1.3 and 2.5 mol/dm³, respectively. These copolymers are heterogeneous oxidants that are macromolecular, insoluble in water, and capable for regeneration by certain

chlorinating agents. These mono- and dichloro derivatives of the sulfonamide copolymer have been used as disinfecting agents [1–3], as reagents in organic syntheses [4], as oxidants to remove toxic micro pollutants (cyanides, thiocyanates, sulfides) from waters [5–10]. Recently we studied their oxidative properties in relation to nitrites, which are undesirable (toxic pollutants) in natural as well as industrial waters [11, 12]:



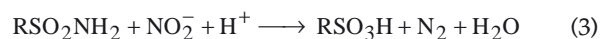
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As the result of contact with the copolymers containing active chlorine, these admixtures turned into consi-

derably less harmful nitrates whereas the functional groups of both copolymers (after losing the active chlorine) turned back into sulfonamide groups.

So far, we have investigated the reaction of oxidizing of the nitrites in the neutral and alkaline media. The next research task was to test the possibility of this reaction conducting in acidic media. A low pH influences the level of the redox potentials, and so the velocity of the oxidizing reaction is favorable. However, it is still not known whether the passing of an acidified solution of nitrite ions through the column will not cause the destruction of the chlorine-free sulfonamide groups. These groups appear in the upper part the column beds after the redox reaction has finished; see the right side of the reaction (1) as well as (2).

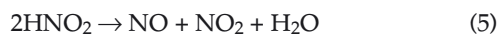
In the literature we find the descriptions of reactions of low-molecular sulfonamides with nitrites in acidic media, which proceed by eliminating of nitrogen atom and causing the destruction of the amide groups [13]:



A similar chemical reaction is known to occur with low-molecular carboxylic acids amides. It is not known whether a similar chemical reaction will take place in the case of macromolecular sulfonamide and what conditions are needed for that to happen.

The knowledge of the reaction course [eq. (3)] in the case of a macromolecular sulfonamide is not only of cognitive but also of practical value. The transformation of sulfonamide groups into sulfonic groups, according to reaction (3), will result in the copolymer losing its active chlorine binding ability, so it will not be capable for simple regeneration any longer.

It should be mentioned that nitrites are not stable in an acidic medium. The weak nitrous acid ($\text{pK}_a = 3.4$) gradually decomposes, eliminating the nitrogen oxides:



Please note that reactions (3), (4) and (5) are accompanied by an emission of gaseous products. This always creates serious difficulties for the conducting of column processes.

The aim of the present study is to answer the following questions:

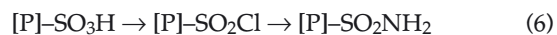
— Does the destruction of the copolymeric sulfonamide group, in the presence of nitrite in acidic media, take place if the functional group is not protected by active chlorine?

— What is the lowest possible pH of the reaction medium during the column process, if we want to avoid any decomposition reactions (of both sulfonamide groups in the copolymer and the nitrite anions in the solution)?

EXPERIMENTAL

Materials

The copolymer that had sulfonamide groups we prepared by the earlier published method [14]:



As a starting material Amberlyst 15 (produced by Rohm and Haas Co.), a commercially available sulfonate cation exchanger, was used. This is a macroporous poly(styrene/divinylbenzene) resin that contained 4.75 mmol/g of $-\text{SO}_3\text{H}$ groups in the dry state (surface area 45 m²/g and average pore diameter 25 nm). The product contained 4.25 mmol/g of $-\text{SO}_2\text{NH}_2$ groups and 0.50 mmol/g of $-\text{SO}_3\text{H}$ groups. A small amount of sulfonic groups in the product is a result of hydrolysis which occurs as a side reaction during the sulfonamide preparation.

Analytical grade sodium nitrite was used for the preparation of the aqueous solutions containing NaNO_2 in a mixture with acetic or hydrochloric acid in different proportions. Solutions used in the batch regime were: 0.08 M NaNO_2 (i.e. 3.60 g of $\text{NO}_2^-/\text{dm}^3$) in: 0.005, 0.01, 0.05 and 0.1 M CH_3COOH or HCl . Solution used in the experiments carried out in a dynamic regime were: 0.005 M NaNO_2 (i.e. 230 mg of $\text{NO}_2^-/\text{dm}^3$) in 0.005 or 0.1 M CH_3COOH .

Treatment of the sulfonamide copolymer by acidified nitrite solutions

In the studies carried out in the batch regime at room temperature, a measured amount of the resin (0.50 g in the dry state) placed in a flask was shaken mechanically with acidified nitrite solutions (50 mL of 0.08 M NaNO_2). Time dependent measurements of the residual NO_2^- in solution were made. After the reaction, the polymeric reagent was separated from the reaction medium by filtration and was analyzed for nitrogen and sulfonic groups content.

In the experiments carried out in the dynamic regime, a sample of sulfonamide copolymer (~3.0 g in the dry state) was swollen in distilled water and was packed into a glass column (inner diameter ~0.3 cm; height of the package ~21.0 cm). NaNO_2 solutions acidified by acetic acid were passed through the column bed. The observed flow rate were 20–30 bed volumes per hour. Fractions (100 mL) were collected to estimate their composition in terms of pH and nitrites. After the reaction the copolymer was removed from the column and then water-washed and dried at 105 °C. It was subjected to the analysis of nitrogen and sulfonic groups content.

Analytical methods

The nitrogen in a resin was examined by elemental analysis and the sulfonic groups content was deter-

mined by alkalimetric potentiometric titration in 1 M NaCl medium.

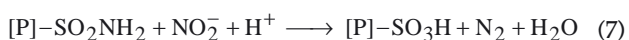
The nitrite ion concentration in solution was determined by colorimetric method (545 nm, Specol 1200, Analytic Jena, Jena, Germany). The reaction of a violet diazo dye formation of sulfanilic acid and dihydrogen chloride of *N*-(1-naphthyl)ethylenediamine (*i.e.* a modified Griess-Ilsovoy method) was used [15].

RESULTS AND DISCUSSION

The sulfonamide copolymers displaying the valuable and unique property of covalent binding of active chlorine atoms (as well as of bromine and iodine atoms) are important semi-finished products for the synthesis of reactive polymers with oxidative properties. Very few investigations have been devoted to the study of their other properties.

Since the aim of this study was to investigate the reactivity of sulfonamide copolymers in the presence of nitrites in acidic media, we started from the copolymer life-testing in the presence of a strong mineral acid. We found that copolymer treated at room temperature for a period of several days with solutions of hydrochloric acid in a concentration ranging from 0.001–1.0 M, did not show any decrease in the contents of the sulfonamide groups. The same result was obtained when the copolymer was treated with a solution of sodium nitrite alone, observing the same concentration.

We first treated the copolymer samples in the batch regime with NaNO₂ in the concentration of 0.08 M, containing a different admixtures of a moderate strength acid (acetic acid) and a strong mineral acid (the hydrochloric acid) (Table 1). In relation to the sulfonamide groups (2.10 mmol of -SO₂NH₂), the content of the sodium nitrite in each sample (4.0 mmol NO₂⁻) was in excess; it was *ca.* 200 % of the resulting quantity from the stoichiometry of reaction:



In all the samples containing HCl (E-H), bubbles of gas appeared in minutes after the beginning of the reaction. The most intense evolution of gaseous products was in case of the samples G and H. For sample H (presence of 0.1 M HCl), we observed the emission of a yellow gas with a characteristic odor. So, in the strongly acidic medium the reaction of sodium nitrite decomposition took place with the emission of nitrogen oxides. In the solutions containing the acetic acid only, samples C and D displayed a small number of gas bubbles.

As follows from Table 1, the copolymer lost part of its nitrogen — and so its sulfonamide groups — proportionally to the strength of the acid used and its concentration. Sulfonic groups appeared in their place. The largest decrease in nitrogen content in the copolymer took place in the solution of the lowest pH (sample H). In that copolymer only *ca.* 15 % of the sulfonamide groups were left after the reaction. In this case the total contents of both functional groups in the copolymer are lower than expected, possibly due to a partial splitting off of the functional groups, which could be the result of the oxidative aggressiveness of that medium. In the samples where the copolymer was in contact with sodium nitrite in the presence of the least concentrated acetic acid (samples A and B) there was only a small decrease in nitrogen content (< 5 %).

The progress of reaction described by eq. (7) can also be deduced from the concentration of sodium nitrite in the post reaction solution. In samples A and B the sodium nitrite concentration dropped only slightly. In the other samples solutions, the decrease in the sodium nitrite was quite high and greater than could be expected from the progression of reaction only. In the samples under consideration both components underwent decomposition: the sulfonamide groups in the copolymer and the sodium nitrite in the solution itself. The quoted data show that if the medium contains three reacting substances (*i.e.* sulfonamide copolymer, sodium nitrite, and an acid of suitable strength) then several reactions can take place concurrently, producing among others:

Table 1. The results of the reaction of sulfonamide copolymer and nitrites in acidic media (0.50 g of the resin, 50 mL of 0.08 M NaNO₂, time of reaction 24 h)

Symbol of the sample	Reaction medium	pH before reaction	pH after reaction	Nitrogen in a resin mmol N/g	-SO ₃ H groups in a resin mmol/g	Concentration of nitrites in a solution g of NO ₂ ⁻ /dm ³
A	0.005 M CH ₃ COOH	4.88	4.46	4.05	0,74	3.59
B	0.01 M CH ₃ COOH	4.66	4.34	3.87	0,90	3.58
C	0.05 M CH ₃ COOH	4.22	4.07	3.73	0,97	3.05
D	0.1 M CH ₃ COOH	4.01	3.87	3.66	1.04	2.70
E	0.005 M HCl	4.49	4.23	3.95	0.75	2.93
F	0.01 M HCl	3.77	3.63	3.65	1.05	1.87
G	0.05 M HCl	3.18	2.07	1.88	2.86	0.33
H	0.1 M HCl	1.91	1.48	0.68	3.40	0.24

N_2 , NO and NO_2 . All these products are disadvantageous and undesirable in a column process.

As follows from Table 1, a comparison of pH before and after the reaction of each sample informs us about the increase in acidity of the reaction medium. The pH drop is due to the binding of the cations of sodium (introduced with $NaNO_2$) by the strongly acidic sulfonic groups of the copolymer. Whilst the amount of $-SO_3H$ groups in the copolymer is small before the reaction, in several cases it can be considerably greater after the reaction.

To test whether the sulfonamide groups are stable in the presence of sodium nitrite and dilute acetic acid, we conducted further investigations in dynamic conditions. We first passed 0.005 M $NaNO_2$ solution in the presence of 0.005 M CH_3COOH (pH of the effluent was 4.20) through the column bed of the sulfonamide copolymer. Admittedly, the solution has a lower concentration of $NaNO_2$ compared with the solution used in stationary research; however it is a very high concentration for this type of investigation. It should be noted that reactive

polymers are especially useful and predisposed to eliminate micro-pollutants from waters, best to the "undetectable" level. In Poland, under the First-Class Cleanness Regulations, admissible concentration of nitrogen content in nitrites in waters is 0.02 mg/dm^3 , while that of nitrates is 5.0 mg/dm^3 . Reactive polymers are used to deal with the concentrations at this level. In many respects they exceed the low-molecular oxidizing agents.

Unfortunately, during the collection of the first fraction, gaseous bubbles already appeared in the copolymer column bed, slowing down the flow. In the course of the process, during which we let 1000 mL of $NaNO_2$ solution pass through the column, it was essential to "degass" the column bed several times. As illustrated by Fig. 1a, curve 1, the outflow pH dropped considerably at the beginning of the process, and at the same time we found a considerable decrease in sodium nitrite concentration in the outflow (Fig. 1b, curve 1). The pH decrease was due to the ion exchange reaction of the sulfonic groups and $NaNO_2$. When the sulfonic groups converted to the sodium-form (this happened when ca. 500 mL of the solution was passed through the column), the pH of the outflow increased to the initial value; similarly, the content of the sodium nitrite in the solution also increased to the initial value. After completing the process the copolymer was subjected to analysis. We found a decrease in nitrogen content (to 3.75 mmol N/g) and a proportional increase in the sulfonic groups content (the copolymer lost ca. 10 % of the sulfonamide groups).

To avoid the acidification of the processing solution in the next stage of our investigation, a sulfonamide copolymer sample was first rinsed with an excess of 0.1 M NaCl solution (with the aim to turn the sulfonate groups into their sodium form). Having thus prepared the column bed, the solution — which had the same composition as previously — was passed through it. This time neither pH of the leakage changed (Fig. 1a, curve 2), nor the sodium nitrite concentration was diminished (Fig. 1b, curve 2). During the passing of 1000 mL of the solution through the column we did not observe any emission of gaseous reaction products. Examining the copolymer after the reaction, we did not observe any changes in its chemical composition.

In the final column process we applied a sulfonamide bed of the copolymer similar to the previous one (rinsed with NaCl solution), while as the inflow we used 0.005 M $NaNO_2$ solution, this time in 0.1 M CH_3COOH (pH of the inflow was 3.41). We observed a small, but continuous decrease in pH of the effluent solution leaking out of the column (Fig. 1a, curve 3), and also a small but continuous decrease in sodium nitrite content (Fig. 1b, curve 3). In the foot of the column bed we observed the emission of gaseous reaction products. The process was concluded after passing 2000 mL of the solution, at which time the gaseous bubbles reached up to 2/3 of the height of the column bed. The analysis of the copolymer after the column process showed the content of

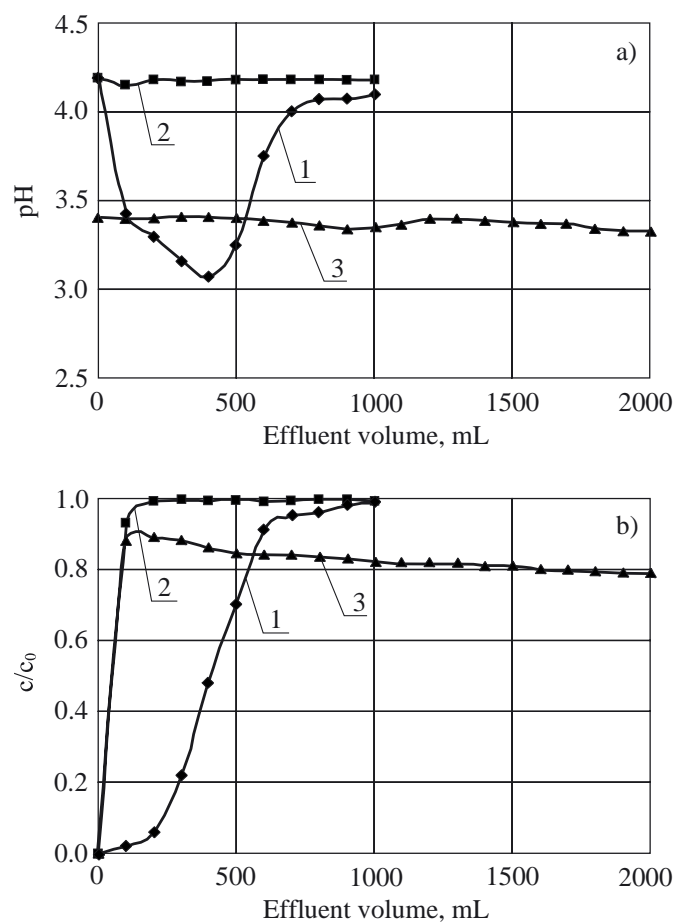


Fig. 1. The effect of effluent volume on outflow pH (a) and on the reduction of sodium nitrite concentration (c/c_0) in the outflow (b) for inflow 0.005 M $NaNO_2$ in: 1 — 0.005 M CH_3COOH , 2 — 0.005 M CH_3COOH but after previous rinse of the sample with an excess of 0.1 M NaCl solution, 3 — 0.1 M CH_3COOH ; flow rate 25 bed volumes/h

0.94 mmol/g of sulfonic groups as well as 3.80 mmol/g of nitrogen content.

CONCLUSIONS

The sulfonamide copolymer is stable in the presence of a dilute solution of sodium nitrite in the acid medium, if the pH in the reaction space is not less than 4.0. The significance of this paper is in the discovering of an acidity window for the stability of sulfonamide group in the reaction with nitrites *i.e.* in pH range from 6.0 to 4.0. If the pH reaches *ca.* 3.5 (that is, it is close to pK_a of the nitrous acid), a decomposition of sulfonamide groups takes place, with the emission of nitrogen and the formation of sulfonic groups. When pH is even lower, decomposition of both the sulfonamide groups and the nitrites, which decompose with the emission of nitrogen oxides, occur. In this extreme case the strongly oxidative reaction medium can cause a splitting off of the functional groups of the copolymer.

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