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Poly(styrene-divinylbenzene) copolymers with *N*-chlorosulfonamide functional groups as oxidants for arsenite ions in aqueous media — redox studies

Summary — Two macromolecular oxidants that were macroporous styrene/divinylbenzene copolymers containing *N*-chlorosulfonamide functional groups in the sodium form — RCl/Na (a macromolecular analog of chloramine-*T*) or in the hydrogen form — RCl/H (there is no analog among low-molecular compounds) were synthesized and used as oxidants of arsenites in dilute aqueous solutions. The reaction course was examined depending on stoichiometric ratios of reagents by special reductometric, potentiometric measurements at different pH values. In weak alkaline medium (pH ~11.5) the RCl/Na copolymer was ineffective as an As(III) oxidant, the reaction proceeded with difficulty, and the redox potential reached a negative value. In weak acidic medium (pH~3.0) the reaction proceeded efficiently enough, but the flat titration curve indicated the unfavorable kinetics of As(III) oxidation by means of RCl/H (despite the high redox potential in the reaction medium). In neutral medium (pH ~6.5) the reaction proceeded with the highest effectiveness. In this case the titration curve had a characteristic, classic shape, indicating the advantageous kinetics of As(III) oxidation by means of RCl/Na (despite the lower redox potential in the reaction medium).

Keywords: redox copolymer, heterogeneous oxidant, *N*-chlorosulfonamide S/DVB copolymer, active chlorine, arsenic oxidation.

KOPOLIMERY POLI(STYRENO-DIWINYLOBENZENOWE) ZAWIERAJĄCE *N*-CHLOROSUL-FONAMIDOWE GRUPY FUNKCYJNE JAKO UTLENIACZE ARSENINÓW W ROZTWORACH WODNYCH — REDOKSYMETRYCZNE BADANIE PRZEBIEGU REAKCJI

Streszczenie — Zsyntezowano dwa wielkocząsteczkowe utleniacze o strukturze makroporowatej będące kopolimerami styrenu i diwinylobenzenu zawierające grupy funkcyjne *N*-chlorosulfon-amidowe, w formie sodowej — RCl/Na (wielkocząsteczkowy odpowiednik chloraminy-*T*) lub w formie wodorowej — RCl/H (produkt taki nie ma małocząsteczkowego odpowiednika), po czym wykorzystano je do utleniania arseninów zawartych w rozcieńczonych roztworach wodnych. Badano zależność przebiegu reakcji od stosunku molowego reagentów w różnych warunkach pH, dokonując pomiaru potencjału redoksowego w środowisku reakcyjnym. W środowisku zasadowym (pH ~11,5) kopolimer RCl/Na był nieaktywny jako utleniacz As(III), reakcja przebiegała z trudem, a potencjał redoksowy środowiska reakcyjnego spadł poniżej zera (rys. 1a, krzywa D). W środowisku kwasowym (pH ~3,0) reakcja z udziałem RCl/H przebiegała dość sprawnie, ale płaski kształt krzywej miareczkowania wskazywał na niekorzystną kinetykę reakcji (mimo wysokiego potencjału redoksowego środowiska reakcyjnego) (rys. 1a, krzywe A, B). W środowisku obojętnym (pH ~6,5) reakcja przebiegała najkorzystniej. Krzywa potencjometrycznego miareczkowania miała charakterystyczny, klasyczny kształt, co świadczyło o korzystnej kinetyce reakcji utleniania As(III) za pomocą RCl/Na (mimo niezbyt wysokiego potencjału redoksowego środowiska reakcyjnego) (rys. 1, krzywa C). Interesująca zależność obserwowana w zakresie pH ~2—7 [wzrost szybkości reakcji utleniania As(III) towarzyszący spadkowi potencjału redoksowego] wynikała z bardzo niskiego stopnia dysocjacji cząsteczek kwasu arsenowego(III) w warunkach kwasowych. W efekcie, mimo wysokiego potencjału redoksowego w tych warunkach, proces przebiegał wolno ze względu na obecność w roztworze prawie wyłącznie cząsteczek niezdysocjowanych (rys. 2).

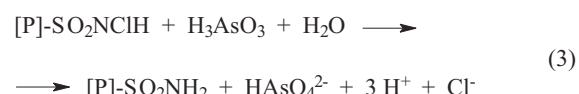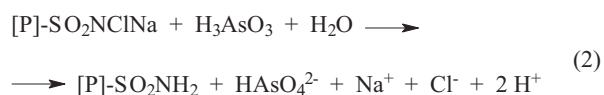[*)] Corresponding author; e-mail: elzbieta.kociolek-balawejder@ue.wroc.pl

INTRODUCTION

The reactive polymers are macromolecular species that contain functional groups providing specific chemical reactivity. These materials act most often as ion exchangers, chelating agents, selective sorbents, catalysts and the like. Typically they take the form of spherical beads characterized by excellent hydraulic properties. The main applications of reactive polymers relate to water or wastewater treatment in industrial plants as well as on the laboratory scale. Special kinds of these materials are redox polymers, with the ability to transfer electrons between functional groups and species present in the reaction medium. They are valuable and useful reagents, but they have the disadvantages of being difficult to produce and exhibiting gradual decrease of redox activity with time (especially in the case of cation-exchange or anion-exchange resins in the redox-active forms). An important group of redox polymers, intensively studied for a long time, is that of macromolecular oxidants containing active halogen atoms (at +1 degree of oxidation) covalently bound to a nitrogen atom of functional groups. These materials consist of styrene-divinylbenzene (S/DVB) matrix and attached *N*-chlorosulfonamide groups. They were tested as biocides in water disinfection [1, 2] and as oxidizing and chlorinating factors in organic syntheses [3—6]. Our investigations concern the synthesis of macromolecular sulfonamides and their application in the removal of some toxic admixtures from waters — as a result of oxidation they transform into environmentally safe substances (sulfides to sulfates [7], nitrites to nitrates [8]) or into less toxic substances (arsenites to arsenates [9]). Polymeric oxidants as heterogeneous reagents show excellent properties in water treatment processes. The most important advantage of solid phase oxidation is the possibility of using a large excess of oxidant without introducing into treated water some micromolecular compounds which lower its quality.

Exploring the reaction of oxidation of As(III) to As(V) by means of *N*-chlorosulfonamide redox polymers, it was assumed that the key factors influencing its efficiency were the ionic form of the functional groups (sodium or hydrogen form) and pH of the reaction medium. Comparing reactions of [P]-SO$_2$NClNa and [P]-SO$_2$NClH with arsenites in the batch as well as in the column experiments it was found that in the case of [P]-SO$_2$NClH a similar reaction requires a considerably longer contact time [9]. This is worth careful research and explanation because acidic conditions are usually favorable for redox reactions. To solve this issue, which concerns redox processes, it is necessary to determine the redox potential of the reaction system depending on stoichiometric ratios of reagents as well as on the solution pH.

The aim of the present study was to conduct potentiometric, reductometric investigation of the courses of reactions (2) and (3):

$$NaAsO_2 + 2\ H_2O \longrightarrow H_3AsO_3 + Na^+ + OH^- \qquad (1)$$

$$[P]\text{-}SO_2NClNa + H_3AsO_3 + H_2O \longrightarrow$$
$$\longrightarrow [P]\text{-}SO_2NH_2 + HAsO_4^{2-} + Na^+ + Cl^- + 2\ H^+ \qquad (2)$$

$$[P]\text{-}SO_2NClH + H_3AsO_3 + H_2O \longrightarrow$$
$$\longrightarrow [P]\text{-}SO_2NH_2 + HAsO_4^{2-} + 3\ H^+ + Cl^- \qquad (3)$$

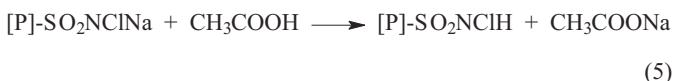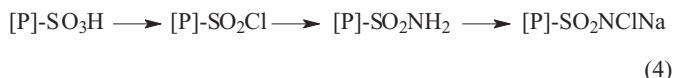[P] stands for the copolymer styrene/divinylbenzene macroporous structure

and determination of the standard redox potential of the heterogeneous system (copolymer with active chlorine/aqueous solution of NaAsO$_2$) at various pH values. The influence of different stoichiometric ratios of heterogeneous oxidant to arsenite for reaction efficiency was also examined. The results enabled determining the factors influencing the course of the studied redox reactions. Previously the same method was used to investigate the oxidation of NaNO$_2$, Na$_2$SO$_3$, KCN and KSCN in dilute solutions by means of heterogeneous polymeric oxidants [8, 10].

Effective oxidation of arsenites present in natural waters in low concentrations is a crucial environmental problem. In many parts of the world, including some European countries, elevated arsenic concentrations have been detected in aquifer waters [11, 12]. Arsenic is a hazardous element for humans and causes some serious health problems, including cancer [13]. The efficiency of arsenic removal from water depends mainly on its oxidation state. Most methods used to remove this element from aqueous solutions [including best available technologies (BATs), such as adsorption or ion exchange] are less effective, or ineffective towards As(III) compounds. Furthermore, those ones are more toxic than As(V) compounds. Thus, intensive studies to find effective reagents which could solve this problem are currently underway. For the removal or transformation of toxic admixtures present in low concentration in solutions, heterogeneous reagents applied in column processes can be especially useful.

EXPERIMENTAL

Materials

Copolymers having *N*-chlorosulfonamide groups in the sodium form (RCl/Na) or in the hydrogen form (RCl/H) were prepared in accordance with the methods described previously [8, 9, 14]:

$$[P]\text{-}SO_3H \longrightarrow [P]\text{-}SO_2Cl \longrightarrow [P]\text{-}SO_2NH_2 \longrightarrow [P]\text{-}SO_2NClNa$$

$$(4)$$

$$[P]\text{-}SO_2NClNa + CH_3COOH \longrightarrow [P]\text{-}SO_2NClH + CH_3COONa$$

$$(5)$$

— Amberlyst 15 (Rohm and Haas) — a commercially available sulfonate cation exchanger — was used as the starting material. It is macroporous poly(S/20 % DVB) resin containing 4.70 mmol -SO_3H/g in the dry state (surface area 45 m^2/g, average pore diameter 25 nm). The end product contained 2.1 mmol/g -SO_2NClNa groups (*i.e.* 4.20 mequiv of active chlorine/g) and 0.70 mmol/g -SO_3Na groups. The *N*-chlorosulfonamide groups were transformed from the sodium form into the hydrogen form by treating the R/ClNa product with an excess of 0.05 M CH_3COOH. The R/ClNa resin was placed in a glass column and was washed first with 0.05 M CH_3COOH and then with distilled water. For a sample containing 10 mequiv of active chlorine (~2.5 g of resin), 200 cm^3 of the acid was used. The product was analyzed after drying to a constant weight in normal conditions. The active chlorine content of the hydrogen form resin was 4.80 mequiv/g.

All the reagents were of analytical grade. The arsenite stock solution (1 mg As(III)/cm^3) was prepared from sodium (meta)arsenite $NaAsO_2$ (Fluka, purity >99 %). The solutions used in the investigations contained arsenic alone or in a mixture with sulfuric acid or with sodium hydroxide.

Reaction of oxidation of arsenites

Into 7 separate samples of RCl/Na (0.24 g ~1.0 mequiv of active chlorine) or RCl/H (0.21 g ~1.0 mequiv of active chlorine) the following increasing solution volumes of 0.005 M $NaAsO_2$ (in water, 0.01 M NaOH or 0.01 M H_2SO_4) were loaded: (1) 0.0 cm^3, (2) 25 cm^3, (3) 50 cm^3, (4) 75 cm^3, (5) 100 cm^3, (6) 125 cm^3 and (7) 150 cm^3. Exclusively the reaction medium (25 cm^3 of water, 0.01 M NaOH or 0.01 M H_2SO_4) was added to the first samples (1) of the copolymers. Increasing solution volumes of $NaAsO_2$ were required to bring about a (1) 0 %, (2) 25 %, (3) 50 %, (4) 75 %, and (5) 100 % reduction in the active chlorine functional group. However, the last two samples of each copolymer contained 125 % (6) and 150 % (7) of the arsenic relative to the stoichiometry. Each sample was placed in a separate, tightly closed, light-proof glass cell and shaken at room temperature. After 24 h the pH and redox potential values were measured using a platinum/calomel electrode pair (Millivoltmeter CPI-501, Zabrze, Poland). The vessels were protected from contact with air during the measurements. Additionally, the As(III) and As(V) concentration in each sample was determined by the described methods.

Methods of testing

— Arsenic determinations (for concentrations >0.05 mg/dm^3) were carried out using the spectrophotometric molybdenum blue method (Specord 210, Analytical Jena, Germany). Arsenate ions formed a colorless antimonyl-arsenomolybdate complex, which was reduced with ascorbic acid, producing a blue species. The absorbance measurement was taken at 730 nm [15]. Since arsenite does not form a molybdenum complex, the obtained absorbance value was for arsenate only. In order to determine the total arsenic concentration, prior to the analysis an oxidizing agent (potassium iodate) was used to convert As(III) into As(V). The arsenite concentration was calculated as the difference between the total arsenic concentration and the arsenate concentration.

— The content of chloride ions in solutions were estimated by argentometric titration, using 0.01 M $AgNO_3$ with a system of Ag/AgCl/calomel electrodes.

— The active chlorine content in the heterogeneous oxidants (RCl/Na, RCl/H) was determined by the iodometric method modified by the longer interaction of the reagents.

RESULTS AND DISCUSSION

N-chlorosulfonamide groups, attached to the macromolecular S/DVB copolymer, contain active chlorine atoms, which provide them some oxidizing properties. These groups have weak acid properties (pK_a = 7.2) and, depending on the pH of the reaction medium, can exist either in the sodium or in the hydrogen form. Regardless of the ionic form, the *N*-chlorosulfonamide groups are stable in aqueous solutions in a wide pH range. It is worth mentioning that the *N*-chlorosulfonamide copolymer in the sodium form has a micromolecular analog in the form of chloramine-T, whereas the copolymer in the hydrogen form does not. The *N*-chloro-*p*-toluenesulfonic acid — which is formed after acidification of chloramine-T — is unstable and undergoes immediate decomposition.

The oxidizing powers of S/DVB copolymers with *N*-chlorosulfonamide functional groups in relation to arsenites were determined using a special potentiometric, reductometric method. This procedure is a modified reductometric titration, useful when the reaction partners form different phases and when the reaction requires long-lasting substance contact. Among the four titration curves shown in Fig. 1a, three have similar, decreasing, unfavorable shapes (curves A, B, D), whereas curve C clearly differs from the others. Its shape is characteristic of reductometric titration of an oxidant by a reductant.

Fig. 1a (curve C) shows the course of reaction between RCl/Na copolymer and $NaAsO_2$ in an aqueous environment. In water alone the system's redox potential for the first points increases to above 400 mV and then remains

at an almost unchanged level and as the amount of the reductant is further increased, gradually and systematically decreases. This is evidence of the considerable efficiency of the oxidation of As(III) to As(V), confirmed by the initial absence of As(III) in the solution and by the marked decrease in pH (consistently with reaction 2). The
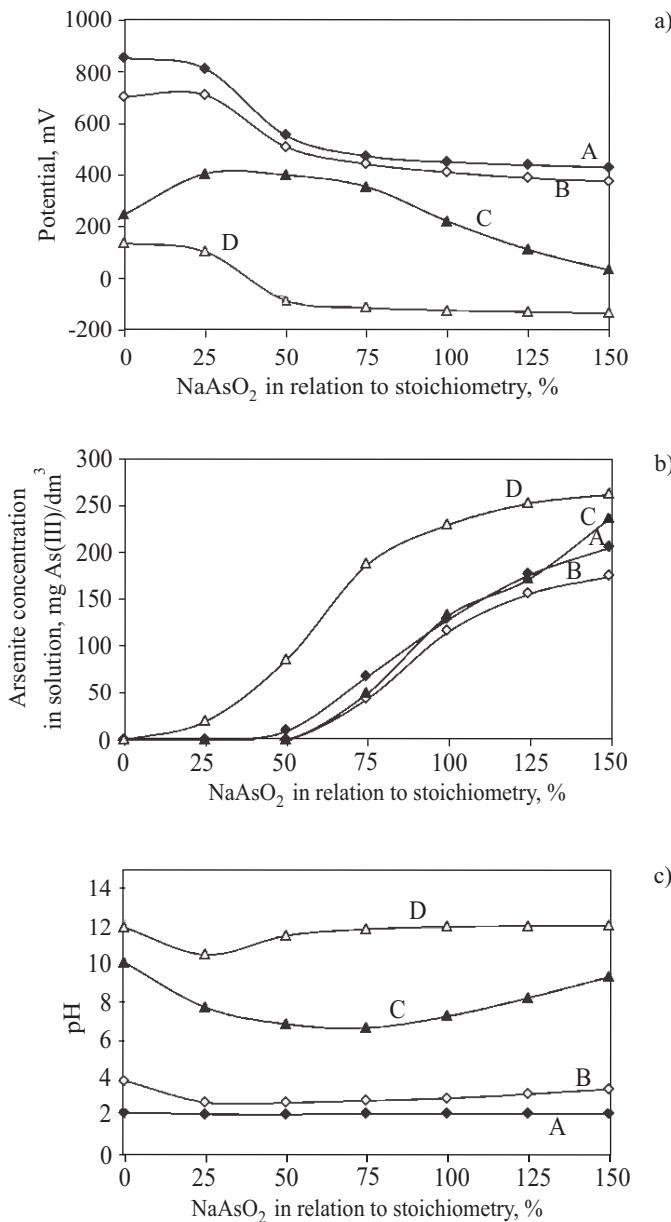

Fig. 1. (a) Redox titration curves of RCl/Na and RCl/H by 0.005 M NaAsO₂ in water, 0.01 M NaOH and 0.01 M H₂SO₄ (reaction time = 24 h), (b) the concentration of arsenites in solution, (c) pH value, denotation of curves in the text

high initial and final pH in the solution is the result of two factors: the hydrolysis of the *N*-chlorosulfonamide groups in the sodium form and the hydrolysis of sodium arsenite. In this case, the formal redox potential of the *N*-chlorosulfonamide copolymer was equal to 0.403 V

(Fig. 1a, point 3 on curve C, pH 6.88). The formal redox potential of the copolymer is the potential of the copolymer dispersion in the central point of the titration curve.

The oxidation of As(III) by RCl/Na in the 0.01 M NaOH environment proceeded efficiently enough only with a large excess of the oxidizing agent (Fig. 1a, point 2 on curve D). The system's redox potential is then positive (>100 mV), which is reflected in the marked decrease in the As(III) concentration in the solution (Fig. 1b, point 2 on curve D). The noticeable decrease in the solution's pH at this point is the result of oxidation reaction advancement accompanied by the acidification of the environment and the neutralization of some of the NaOH. As the amount of the reductant is further increased, the redox potential sharply decreases to negative values while the As(III) concentration in the solution decreases only slightly. The formal redox potential of the *N*-chlorosulfonamide copolymer, determined from the titration curve, amounted to -0.08 V (Fig. 1a, point 3 on curve D, pH 11.57).

The *N*-chlorosulfonamide copolymer in the hydrogen form, when used in a large excess, showed a very high capacity to oxidize As(III) in both environments. In the initial stage of the reaction at a small reductant addition the potential was very high [exceeding 0.85 V and 0.70 V for respectively 0.01 M H₂SO₄ (curve A) and water alone (curve B)], which was due to the total oxidation of the arsenites (Fig. 1b, point 2 on curve A and B). As the amount of the reductant was increased (points 3—5), the redox potential decreased in both environments (water alone and 0.01 M H₂SO₄) and a flattening of the titration curve occurred, indicating a decrease of the reaction rate. Interestingly enough, the reaction conducted at lower pH (0.01 M H₂SO₄), and therefore at higher redox potential, proceeded with lower efficiency than in water alone, which was reflected by the noticeably higher final concentration of As(III) in the reaction medium. It was found that the addition of the acid into the reaction medium had a negative effect on the reaction course. The formal redox potential of the investigated systems was 0.51 V and 0.56 V for water alone (Fig. 1a, point 3 on curve B, pH = 2.73) and 0.01 M H₂SO₄ (Fig. 1a, point 3 on curve A, pH = 2.1), respectively.

The obtained results show that the pH of the reaction medium is the crucial factor for the oxidation of arsenites by means of *N*-chlorosulfonamide copolymer. Along with the decrease of pH the formal redox potential of the system increases, but simultaneously the reaction efficiency drops. Increasing the pH of the reaction medium leads, in turn, to a gradual decrease of the formal redox potential and to improvement of the course of the reaction. This seeming discrepancy can be explained by the fact that arsenites exist in aqueous solutions, at low pH, predominantly in the form of undissociated molecules (pK_{a1} = 9.2, pK_{a2} = 12.1, pK_{a3} = 13.4). Thus, despite the high formal redox potential of the heterogeneous oxidant in

these conditions, only some of the arsenite molecules (dissociated) undergo oxidation. The new equilibrium between dissociated and undissociated molecules has to be reached to continue the oxidation reaction. The precise influence of pH on the degree of dissociation of arsenites in aqueous medium can be obtained from Ostwald's dilution law. Using the dependence of the solution pH on weak acid concentration:

$$x^2 + K_a x - K_a F = 0 \qquad (6)$$
$$pH = -\log x \qquad (7)$$

and the percent dissociation (α) equation:

$$\alpha = x / F \qquad (8)$$

where: x — *the concentration of* H_3O^+, K_a — *the dissociation constant of acid*, F — *the concentration of acid*
the direct relationship is obtained between pH and the acid dissociation degree (for pK_{a1}):

$$\alpha = K_a/(K_a + 10^{-pH}) \qquad (9)$$

This equation can be used to show the exact dependence of the arsenite dissociation degree on pH. As can be seen from Fig. 2, even though the pK_{a1} of arsenites is
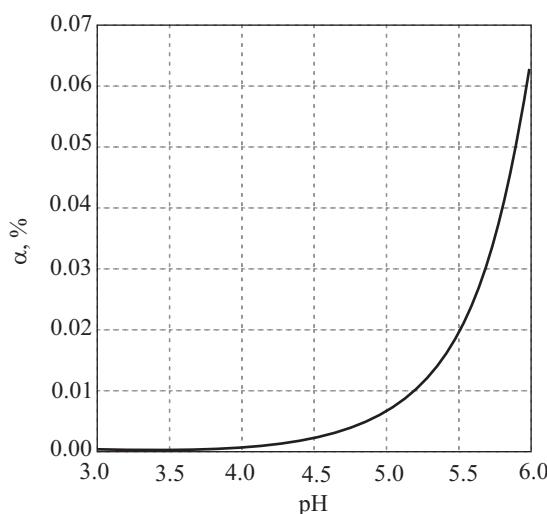

Fig. 2. Dependence of the dissociation degree of arsenites (α) on solution acidity in the pH range of 3 to 6

9.2, some $H_2AsO_3^-$ ions appear in the solution below pH 4. In these conditions the dissociation degree is low but noticeable, increasing considerably above pH 5. In slightly alkaline medium, above pH 9.2, the majority of arsenite molecules exist already in the form of deprotonated oxyanions, but these conditions are unfavorable for oxidation reaction by means of the studied copolymer (low formal redox potential). Electrolytic dissociation of arsenites is thus the crucial factor determining the efficiency and the rate of oxidation reaction.

CONCLUSIONS

Reactions with participation of high-molecular, heterogeneous oxidants are more difficult than those with the use of low-molecular, soluble oxidants. The shapes of the four reductometric titration curves indicate that the pH of the reaction medium is critical for the efficiency of As(III) oxidation by means of the *N*-chlorosulfonamide copolymer. The alkaline environment is definitely unfavorable for As(III) oxidation — the formal redox potential has a negative value, and the efficiency of the reaction is very low. An interesting dependence of pH of the reaction medium on the course of the As(III) oxidation reaction is observed in neutral to acidic conditions. With the decrease of pH, the reaction rate drops despite the increasing formal redox potential. This can be explained by a decreased degree of dissociation of arsenites in acidic conditions, which involve a longer reaction time to reach a new equilibrium between dissociated and undissociated arsenite molecules. The optimal pH conditions should ensure a proper balance between redox potential (favorable low pH) and the degree of arsenite dissociation (favorable high pH).

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