Potentiometric Studies of Oxidation–Reduction Reactions with Redox Copolymers

Romuald Bogoczek, Elżbieta Kociołek-Balawejder, Ewa Stanisławska

Department of Industrial Chemistry, Wroclaw University of Economics, Komandorska ul. 118/120, 53-345 Wroclaw, Poland

ABSTRACT: Polymeric oxidants in the bead form that were macroporous styrene/divinylbenzene copolymers containing N-chlorosulfonamide functional groups (in sodium or hydrogen form) or N-bromosulfonamide groups (in sodium form) were synthesized and investigated to determine their oxidizing powers. The redox potentials of the N-chlorosulfonamide/sulfonamide and N-bromosulfonamide/sulfonamide systems were determined by potentiometric studies at different pH values with aqueous solutions of Na_2SO_3, KCN, and KSCN as reducers. The formal redox potentials of the N-chlorosulfonamide copolymers were 0.79, 0.44, and -0.12 V at pH's of 1.8, 8.45, and 13.6, respectively. The formal redox potential of the N-bromosulfonamide copolymer was about 100 mV higher in comparable conditions and in solutions over pH = 5 (e.g., 0.56 V at pH = 8.56). The comparatively higher oxidizing power of the N-bromosulfonamide copolymer was particularly evident in a strong alkaline medium (in which the N-chlorosulfonamide copolymer was not reactive). In contrast, the N-chlorosulfonamide copolymer showed strong oxidative properties in acidic media (in which the N-bromosulfonamide copolymer decomposed itself). © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2190–2195, 2008

Key words: functionalization of polymers; heteroatom-containing polymers; macroporous polymers; supports; redox copolymers

INTRODUCTION

Redox polymers have been synthesized and studied on the laboratory scale for a long time.[1–3] They display special properties that can be very useful for solving chemical, biochemical, industrial, and environmental problems. Redox materials that show a very high or very low redox potential that are very stable chemically and mechanically have very long-lasting reversible redox properties, and particularly, redox materials that can react persistently for a long time are few and are difficult to produce. Ion-exchange redox products dominate the commercial offerings of major world-known companies, whereas clear redox copolymers are few, are produced in small quantities and have special destinations. For example, Novabiochem offers redox polymers in reagent quantities for solution-phase organic synthesis.[4] Polymer-supported oxidants comprise anion-exchange resins in the form of the perruthenate, metaperiodate, and oxoammonium moieties, whereas the polymer-supported reductants are anionites in the form of cyanoborohydride or borohydride. These products have a fundamental flaw: the redox group undergoes elution because it is combined by ion-exchange ionic bonds. One can observe a lack in the market of real redox copolymers with wide uses, for example, for the treatment of natural and industrial waters.

One important group of intensively studied macromolecular oxidants are the copolymers that incorporate active halogen atoms covalently bound to a nitrogen atom. The halogen atoms are at $+1°$ of oxidation. Solid supports of the halogens are styrene/divinylbenzene (S/DVB) copolymers, which include (1) sulfonamide groups (in this case, they are macromolecular analogues of p-toluenosulfonamide) or (2) heterocyclic amines, which have five or six atom rings and include one, two, or three nitrogen atoms (these are macromolecular analogues of oxazolidine, hydantoine, melamine, or cyanuric acid). Attention should be given to the numerous articles on this subject by Emerson and coworkers[5,6] and Worley and coworkers,[7,8] who studied the possibility of using bead-form biocide products in water disinfection.

In our earlier investigations, we dealt with the synthesis of copolymers that included active halogens in functional groups comprising N-chlorosulfonamide, N-bromosulfonamide, or iodosulfonamide as well as dichlorosulfonamides and dibromosulfonamides of the S/DVB copolymer, and we look forward to their application in the amelioration of diluted solutions of harmful residual matter. We have shown so far that they are effective in the

removal of some toxic admixtures from waters, which as the result of oxidation, transform into environmentally safe substances (e.g., sulfides to sulfates, nitrites to nitrates).

The aim of this study was to provide answers to the following questions:

1. What is the oxidation power of the N-chlorosulfonamide copolymer in comparison with its low-molecular counterparts, that is, Chloramine T or elementary chlorine?
2. What is the oxidation power of the N-bromorosulfonamide copolymer in comparison with the N-chlorosulfonamide copolymer (when the different halogen atoms are combined to the same macromolecular rest)?
3. What is the impact on the oxidation reaction course of medium pH and the ionic form of copolymeric oxidants functional groups (Na^+ or H^+)?

Chlorine and its low-molecular derivatives are strong oxidants, and this is not always favorable. The redox potential of chlorine varied from 1.50 V in acidic media to 0.90 V in alkaline media. The redox potential of Chloramine T varied from 1.14 V at pH 0.65 to 0.61 V at pH 9.2.[9,10]

The oxidizing powers of S/DVB copolymers with functional groups of N-chlorosulfonamide or N-bromosulfonamide were determined by means of a special potentiometric reductometric titration method followed by the analysis of the resulting titration curves, obtained in different conditions. The potential of the copolymer dispersion in the central point of the titration curve is the formal redox potential of the copolymer.

Redox reactions run considerably slower than the ionic reactions, and this is particularly true when the reaction partners form different phases. The reaction of medium insoluble macromolecular oxidants sometimes requires long-lasting substance contact, which can even amount to hours (it depends on the resin-grain dimensions and on the resin porosity); in our case, this was 10 h. In this research, the traditional potentiometric titration was replaced by a procedure whose purpose was to limit the long-lasting gradual dosage of the titrant, to prevent the reaction mixture's contact with air, and to prevent the mechanical destruction of the copolymer bead structure during mixing.

The following chemical compounds were used as reducers in various pH values of their solutions: Na_2SO_3, KCN, and KSCN. The properties of the chemicals used in this study gave rise to some limitations in the range of investigations:

1. The N-bromosulfonamide copolymer could not be studied in an acid medium, nor could its functional groups be transformed into hydrogen form because the copolymer decomposed itself, losing its active bromine atoms below pH = 5, whereas the N-chlorosulfonamide copolymer was stable in the whole range of pH values, and so its functional group could well appear in the form of hydrogen.
2. Reducers such as Na_2SO_3 and KCN decomposed in acid media, and therefore, their reductive properties toward macromolecular oxidants were studied in a limited pH range.

Knowledge of the reagent redox potentials measured in this study may be significant from a practical point of view. The values obtained in this research may be helpful in the estimation and design of new oxidation methods by means of the these investigated redox copolymers.

EXPERIMENTAL

Materials

Three reactive crosslinked S/DVB copolymers were used as heterogeneous oxidants:

1. RCl/Na stands for the sodium form of the N-chlorosulfonamide copolymer; it contained 2.15 mmol/g —SO_2NClNa groups (i.e., 4.30 mequiv of active chlorine/g of resin).
2. RCl/H stands for the hydrogen form of the N-chlorosulfonamide copolymer; it contained 2.40 mmol/g —SO_2NClH groups (i.e., 4.80 mequiv of active chlorine/g of resin).
3. RBr/Na stands for the sodium form of the N-bromosulfonamide copolymer; it contained 1.65 mmol/g —SO_2NBrNa groups (i.e., 3.30 mequiv of active bromine/g of resin).
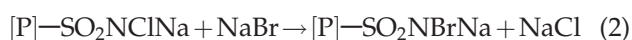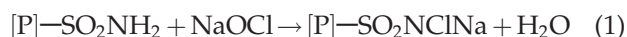
The quoted contents of active halogen in the copolymers always refer to the constant-mass air-dried products. All of the copolymers contained a small quantity of sulfonic groups in the sodium form (ca. 0.50 mmol/g).

The copolymers were prepared by chemical modification of sulfonic cation exchangers by methods published elsewhere.[11,12] As a starting material, Amberlyst 15 (Rohm and Haas Co., Philadelphia, PA), a commercially available sulfonic cation exchanger, was used. This was a macroporous poly(S/20%DVB) resin, which in the air-dried state, contained 4.7 mmol of —SO_3H/g and had a surface area of 45 m^2/g, an average pore diameter of 25 nm, a uniformity coefficient of less than 1.70, and a harmonic mean size of 600–850 μm. We transformed its initial functional groups to the chlorosulfonyl and then to sulfonamide groups, which joined the active chlorine atoms as a
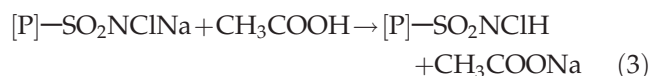
TABLE I
Solutions Used as Titrants

Symbol of solution	Reducing agent	Concentration (M)	Medium	Potential (mV)	pH
A	Na_2SO_3	0.01	H_2O	+56	9.69
B	KCN	0.01	0.001M NaOH	−168	11.8
C	KCN	0.01	0.01M NaOH	−180	12.7
D	KCN	0.01	0.1M NaOH	−192	13.5
E	KSCN	0.005	H_2O	+124	5.93
F	KSCN	0.005	0.01M NaOH	−35	13.10
G	KSCN	0.005	0.01M H_2SO_4	+406	2.06

result of the sodium hypochlorite reaction. [P] stands for the copolymer S/DVB macroporous structure:

$$[P]-SO_3H \rightarrow [P]-SO_2Cl \rightarrow [P]-SO_2NH_2$$

$$[P]-SO_2NH_2 + NaOCl \rightarrow [P]-SO_2NClNa + H_2O \quad (1)$$

$$[P]-SO_2NClNa + NaBr \rightarrow [P]-SO_2NBrNa + NaCl \quad (2)$$

The transformation of the N-chlorosulfonamide groups from sodium form to hydrogen form was carried out by means of treatment with 0.1M CH_3COOH of the RCl/Na:[12,13]

$$[P]-SO_2NClNa + CH_3COOH \rightarrow [P]-SO_2NClH$$
$$+ CH_3COONa \quad (3)$$

The chemical compositions of the solutions used in the redox titrations are shown in Table I. Analytical grades of Na_2SO_3, KCN, and KSCN were used as the reducing agents. With the differentiated stoichiometric relations of the studied reactions taken into account, the quantities and concentrations of the reacting substances were chosen so that comparable volumes of the solutions were consumed during the titration.

Measurements

The following increasing solution volumes of the reducing agents were loaded into seven equal separate samples of RCl/Na, RCl/H, or RBr/Na: (1) 0.0, (2) 12.5, (3) 25, (4) 37.5, (5) 50, (6) 62.5, and (7) 75 cm^3 (Table II). To the first (1) samples of the copolymers, the sole reaction medium was added (12.5 cm^3, see Table I, column 4). The said increasing volumes of the reducing agent solutions were needed to bring about the reduction of (1) 0, (2) 25, (3) 50, (4) 75, and (5) 100% of the active chlorine or active bromine functional group. However, the last two samples of each copolymer contained (6) 125 and (7) 150% of the reducer. The samples of the macromolecular oxidant loaded with the solution of the reducer were placed in separate, tightly closed,

light-proof glass cells and shaken out on a shaking machine. The pH and redox potentials values (with a platinum and a calomel electrode couple) were measured after 1, 2, 4, and 24 h, with a Milivolt-meter CPI-551 (Elmetron, Zabrze, Poland). To measure the potentials, the solution sample was placed in a closed glass vessel protected from air contact during the measurements. The reading was made after 1–5 min, when the value was fixed.

RESULTS AND DISCUSSION

Reductometry is an analytical method used in the analysis of low-molecular or high-molecular but soluble oxidants. In reference to high-molecular, crosslinked, insoluble substances, this technique has not been given much attention in the literature. We used this method for the first time in a previous investigation to oxidize nitrites to nitrates by RCl/Na and RCl/H.[13] In this study, we extended the investigation to three heterogenic oxidants (with different reactive groups but with similar macromolecular structures) and various reaction media.

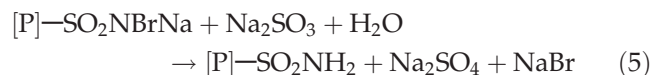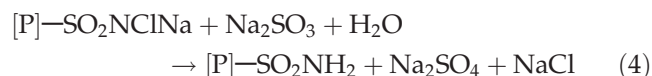First, we examined the reaction of RCl/Na and RBr/Na with sodium sulfite:

$$[P]-SO_2NClNa + Na_2SO_3 + H_2O$$
$$\rightarrow [P]-SO_2NH_2 + Na_2SO_4 + NaCl \quad (4)$$

$$[P]-SO_2NBrNa + Na_2SO_3 + H_2O$$
$$\rightarrow [P]-SO_2NH_2 + Na_2SO_4 + NaBr \quad (5)$$

TABLE II
Reagents (Oxidants and Reducers) in the Potentiometric Titration

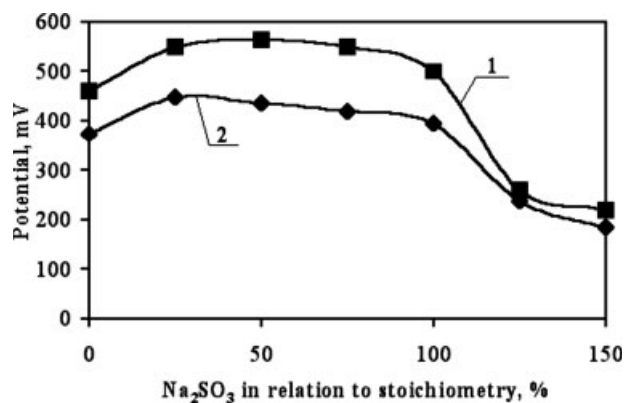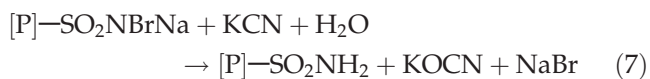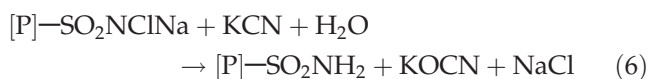| Resin	Weighed portion (g)	Active halogen in sample (mequiv)	Solution[a]
RCl/Na	0.2325	1.0	A, B, C, D
RCl/Na	0.4650	2.0	E, F
RCl/H	0.4167	2.0	E, G
RBr/Na	0.3030	1.0	A, B, C, D

[a] See Table I.

Figure 1 Redox titration curves of (1) RBr/Na and (2) RCl/Na with 0.01M Na$_2$SO$_3$ (reaction time = 24 h).

This reducer was chosen because of its smooth one-stage oxidation course without any intermediate products and with a favorable molar quotient. Na$_2$SO$_3$ is a reducer of medium strength,; its aqueous solution is, in due measure, stable; and the oxidation product, Na$_2$SO$_4$, is stable in the reaction medium. Both curves in Figure 1 have a shape characteristic of the titration of an oxidant by a reducer. From their location in the coordinates system, it is clear that the N-bromosulfonamide copolymer was a stronger oxidant than the N-chlorosulfonamide copolymer: the determined redox potential of RBr/Na was 0.56 V (see point 3 on curve 1, pH = 8.56), and that of RCl/Na was 0.44 V (point 3 on curve 2, pH = 8.45). The pH measurements for successive samples (in line with our expectations) showed a gradual drop in value from about. 9.5 to about 7.80 (the sodium sulfite hydrolyzed to an alkaline reaction, whereas the product of its oxidation, the sodium sulfate, was a neutral salt).

It is known that the value of a redox potential is pH dependent. Samples of RCl/Na and RBr/Na were subjected to potentiometric titration in alkaline media with different strengths during successive stages of this investigation. KCN was applied as the reducer, and its 0.01M solution was prepared in 0.001, 0.01, and 0.1M NaOH aqueous media:

$$[P]\text{—}SO_2NClNa + KCN + H_2O$$
$$\rightarrow [P]\text{—}SO_2NH_2 + KOCN + NaCl \quad (6)$$

$$[P]\text{—}SO_2NBrNa + KCN + H_2O$$
$$\rightarrow [P]\text{—}SO_2NH_2 + KOCN + NaBr \quad (7)$$

In this cyanide oxidation process, the oxidation product were cyanates, which were unstable in aqueous solution. They underwent hydrolysis to carbonates and ammonia:

$$OCN^- + 2H_2O \rightarrow HCO_3^- + NH_3 \quad (8)$$

In both drawings shown in Figures 2(top) and 3(top), the curves of titration are situated on different levels in relation to the axis of abscissae in the following order: the more alkaline the medium was, the lower and flatter was the position of the titration curve. In the experiments discussed here, the determined redox potentials of RCl/Na were 0.33, 0.04, and −0.12 V (potentials in point 3 on curves 1, 2, in Figures 2(top) and 3(top); the pH values were 9.52, 12.56, and 13.58, respectively). For the RBr/Na copolymer, the respective results were the following: 0.33, 0.07, and −0.08 V (pH = 9.20, 12.31, and 13.61, respectively). A comparatively low pH of the postreaction solution deserves our attention. It was the case in the titration of 0.01M KCN in 0.001M NaOH (the pH value of the titrant was 11.8; see Table I). We attributed this drop in NaOH concentration to the neutralization of HCO$_3^-$ ions, which formed as a result of the reaction (8). We confirmed that the higher the pH was, the lower were the redox potentials of the RCl/Na and the RBr/Na. In the medium of 1M NaOH, they even had a negative value, whereas the potential of the RBr/Na in each medium under investigation was higher than the respective value for RCl/Na.

Figure 3 shows the change in the redox potential value in relation to the time for the reaction of RBr/
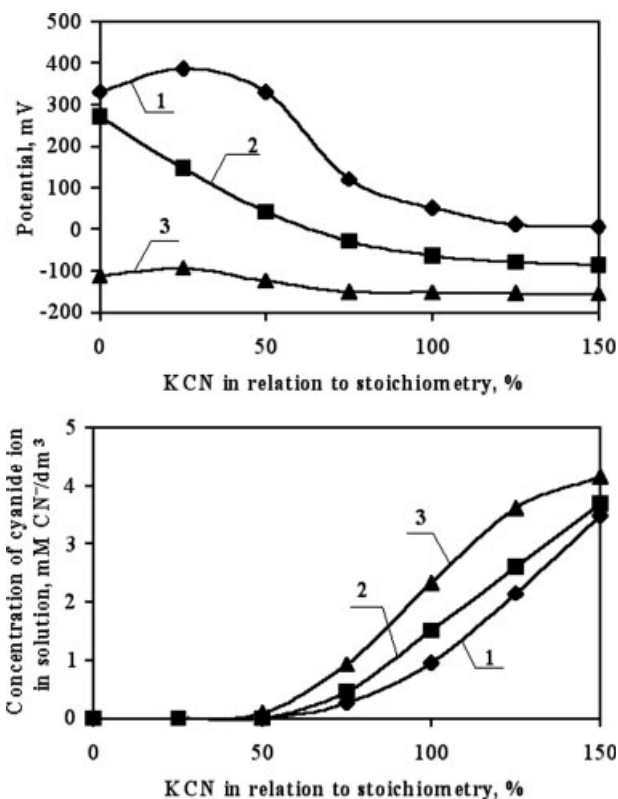

Figure 2 (Top) Redox titration curves of RCl/Na by 0.01M KCN in (1) 0.001, (2) 0.01, and (3) 0.1M NaOH (reaction time = 24 h) and (bottom) the concentration of cyanides in solution after the reaction.

Figure 3 (Top) Redox titration curves of RBr/Na by 0.01M KCN in (1) 0.001, (2) 0.01, and (3) 0.1M NaOH (reaction time = 24 h) and (bottom) concentration of cyanides in solution after the reaction.
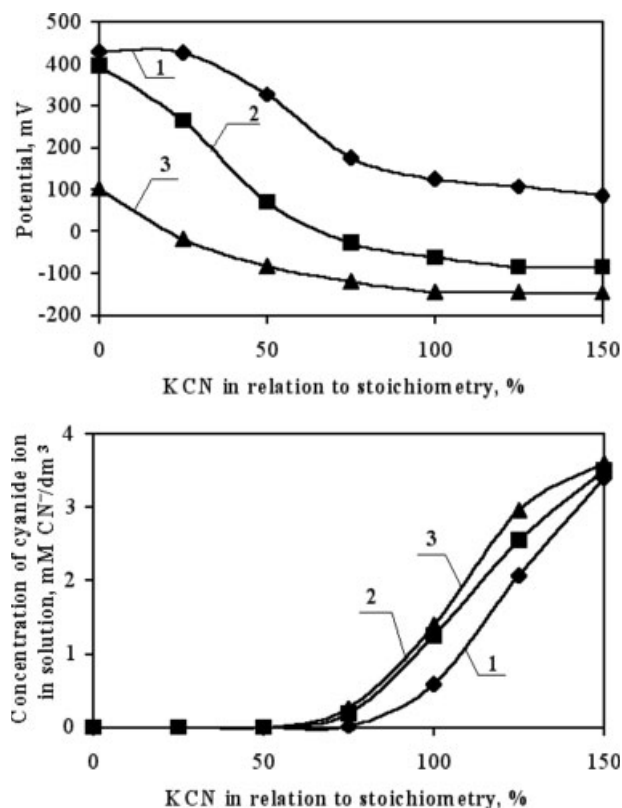
Na and the titrants 0.01M KCN in 0.001M NaOH. From the curves taken after 1, 2, 4, and 24 h, it follows that the final shape of the titration curve required long-lasting contact of the reagents (several hours).

The titration curves of both copolymers with KCN had less favorable runs than the titration curves with Na$_2$SO$_3$. They deviated considerably from the shapes of classic titration curves, which are well known
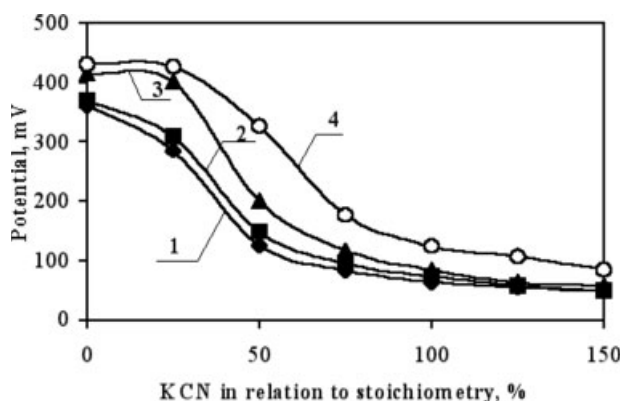
from the titration of an oxidant with a reducer in reductometry. We explained this by analyzing the contents of cyanides in the postreaction solutions [Figs. 2(bottom) and 3(bottom)]. As we found in samples 3–5, the concentration of cyanides was considerably higher, and the more alkaline the medium was, the higher it was. As we said earlier, the reactivity of the RBr/Na copolymer was larger than that of the RCl/Na copolymer, and this property was particularly distinctive in the high-pH medium. Comparing the two parts in Figures 2 and 3, we deduced the oxidation reaction progress from the shape of the titration curve.

The aim of the next investigation step was to establish the reductometric titration curves of the RCl/Na and RCl/H copolymers in a wide range of pH values. The acetic acid transformed the weak acidic N-chlorosulfonamide groups from sodium form to hydrogen form (p$K_a \approx 7.2$), but it could not transform the residual sulfonic groups (which were also present in the copolymer) from their sodium to hydrogen form. In this part of the investigation, 0.005M KSCN was used as the reducer:

$$4[P]-SO_2NClNa + KSCN + 5H_2O$$
$$\rightarrow 4[P]-SO_2NH_2 + KOCN + H_2SO_4 + 4NaCl \quad (9)$$

$$4[P]-SO_2NClH + KSCN + 5H_2O$$
$$\rightarrow 4[P]-SO_2NH_2 + KOCN + H_2SO_4 + 4HCl \quad (10)$$

The solution applied here had a lower concentration than the previously applied solutions because of a less favorable stoichiometric ratio of the thiocyanate oxidation reaction. The reaction of the N-chlorosulfonamide copolymer with KSCN had a considerably more complicated course than the previously studied reactions. There were more reaction products; one of the products underwent a consecutive hydrolysis reaction [see eq. (8)].
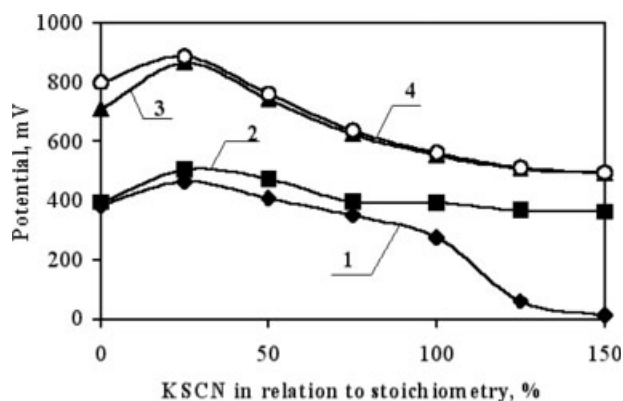

Figure 4 Redox titration curves of RBr/Na by 0.01M KCN in 0.001M NaOH with reaction times of (1) 1, (2) 2, (3) 4, and (4) 24 h.

Figure 5 Redox titration curves of RCl/Na by 0.005M KSCN in (1) 0.01M NaOH and (2) water and RCl/H by 0.005M KSCN in (3) water and (4) 0.01M H$_2$SO$_4$.

The titration curve of RCl/Na with 0.005M KSCN alone is shown in Figure 5, curve 2; the redox potential at point 3 was 0.47 V (pH = 7.30). Our attention was drawn to the relatively flat course of this curve. This was caused by the pH of the reaction environment, which fell proportionally to the reaction progress. In the case when 0.005M KSCN in 0.01M NaOH was applied as the titrant (the NaOH in solution was taken in the amount suitable to neutralize the acidic reaction products), the titration curve had a more favorable shape (see Fig. 5, curve 1). In points 1–5, a pH downfall from alkaline to neutral reaction is shown. An increase in pH took place at points 6 and 7 (the contents of NaOH in solution surpassed the acidic products). The redox potential in point 3 was 0.41 V (pH = 8.52).

Curve 3 in Figure 5, showing the titration curve of RCl/H with 0.005M KSCN, alone was situated considerably higher in the coordinate system than the two former curves. The pH value for all measuring points fell to 2.0–2.1. The potential in point 3 was very high, almost 0.75 V. Curve 4 in Figure 5 concerns the titration of RCl/H with KSCN in acidic medium. As we expected, the redox potential in point 3 showed a higher value as it did previously, that is, 0.79 V. The pH value fell to about 1.8.

CONCLUSIONS

S/DVB copolymers, with a macroporous structure containing N-chlorosulfonamide or N-bromosulfonamide functional groups and being heterogeneous oxidizing reagents, were useful for the removal of various reducers from aqueous solutions. The reactivity of these high-molecular-weight reagents can be measured by platinum/calomel potentiometric studies with a reducing substance solution. The necessary time of the reagent contact should be at least several hours. The reaction progress can be deduced from the shape of the titration curve.

The high-molecular-weight oxidant containing active chlorine is a weaker oxidant than its low-molecular-weight analogues (Chloramine T and elementary chlorine). RCl/H ([P]—SO$_2$NClH) displayed considerably stronger oxidizing properties than RCl/Na ([P]—SO$_2$NClNa). In the acidic medium, the formal redox potential of the N-chlorosulfonamide co-

polymer was considerably higher (almost 0.80 V) than in the neutral medium (0.40 V) or in the alkaline medium (< 0 V).

The high-molecular-weight oxidant containing active bromine showed a higher oxidizing potential (by ca. 100 mV) than the N-chlorosulfonamide copolymer in analogous conditions. However, its oxidizing working conditions were limited to media with a pH value not lower than 5, when it was chemically stable. The advantage of the N-bromosulfonamide copolymer was its comparatively strong oxidizing activity in the alkaline media, where the N-chlorosulfonamide copolymer was not very active.

The experimentally determined formal redox potentials of all three copolymers permitted us to draw conclusions about their usefulness in oxidation reactions of different inorganic and organic substances. The established redox potential values are helpful for the projection of the conditions of a new batch or column oxidation processes when unfavorable side reactions should be avoided. Those side reactions occur often when one uses low-molecular homogeneous oxidants with a very high oxidizing power, for example, elementary chlorine and bromine.

References

1. Cassidy, H. G.; Kun, K. A. Oxidation–Reduction Polymers (Redox Polymers); Wiley: New York, 1965.
2. Kozhevnikov, A. V. Electron Ion Exchangers (in Russian); Khimiya: Leningrad, 1972.
3. Ergozhin, E. E.; Mukhitdinova, B. A. Redox Resins (in Russian); Nauka: Alma-Ata, Kazakhstan, 1983.
4. Novabiochem 2006/7 Catalog.
5. Emerson, D. W. Ind Eng Chem Res 1991, 42, 5959.
6. Emerson, D. W.; Grigorian, C.; Hess, J. W.; Zhang, Y. React Funct Polym 1997, 33, 91.
7. Chen, Y.; Worley, S. D.; Kim, J.; Wei, C.-I.; Chen, T.-Y.; Santiago, J. I.; Williams, J. F.; Sun, G. Ind Eng Chem Res 2003, 42, 280.
8. Chen, Y.; Worley, S. D.; Kim, J.; Wei, C.-I.; Chen, T.-Y.; Suess, J.; Kawai, H.; Williams, J. F. Ind Eng Chem Res 2003, 42, 5715.
9. Murthy, A. R. V.; Rao, B. S. Chem Abstr 1952, 47, 2077h.
10. Campbell, M. M.; Johnson, G. Chem Rev 1978, 78, 65.
11. Bogoczek, R.; Kociołek-Balawejder, E. Polym Commun 1986, 27, 286.
12. Bogoczek, R.; Kociołek-Balawejder, E. Polym Sci USSR 1987, 29, 2580.
13. Bogoczek, R.; Kociołek-Balawejder, E.; Stanisławska, E. Ind Eng Chem Res 2005, 44, 8530.