

New Iron Containing Water-soluble Acrylic Copolymers

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ABSTRACT

Water-soluble polymers have gained a great importance in oil and gas producing industry because they are widely used in many technological processes and operations including drilling of wells. Among them, iron containing ones are not so numerous but they also attract much attention due to such interesting properties as tendency to swelling, complexation capacity, magnetic susceptibility, etc.. In this work, studies are made on the possibilities of obtaining new water-soluble iron-containing polymers based on acrylic acid (AA) and propylene oxide (PO) which are significant industrial products. Thus, the new water-soluble iron-containing copolymers have been synthesized by using the neutralization and radical copolymerization reactions. Iron content in these copolymers has been determined by using atomic absorption spectroscopy. Magnetic measurements by Faraday method have confirmed showed that the obtained copolymers are ordinary paramagnetics and the existing iron in them has an oxidation state of +3. Potentially they find application as insulating agents upon drilling of oil and gas wells and as magnetic indicators.

Key Words:

acrylic copolymers;
propylene oxide;
water-soluble copolymers;
neutralization and radical copolymerization;
iron containing copolymers.

INTRODUCTION

Water-soluble polymers have found a great importance in oil and gas producing industry because they are widely used in many technological processes and operations including drilling of wells [1-4]. Among them iron-containing polymers are not so

numerous but they have also attracted the attention of specialists due to such interesting properties as tendency to swelling, complexation capacity, magnetic susceptibility and other properties [5-7]. Although no study could be seen on iron-containing

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water-soluble acrylic copolymers in the literature, a growing interest is observed by some recent publications. For instance, a comprehensive review is published on organoiron polymers [8]. Another interesting study found in the literature is about synthesis and investigation of novel cross-linked acrylic polymers [9]. Additionally, a study on new water-soluble iron-containing organic coating materials [10] is found in the more recent literature and a few studies on water-soluble and surface-active polymers are completed by our research groups [11-13].

In the present work, the possibilities of obtaining new water-soluble iron-containing polymers based on acrylic acid (AA) and propylene oxide (PO), which are industrial products of a large scale, were studied. Trivalent iron was incorporated into the oxypropyl derivatives of polyacrylic acid (PAA) in order to afford more hydrophobicity as well as magnetic properties to the polymer.

EXPERIMENTAL

Materials and Methods

Acrylic acid (AA) was used as a product of Shostka Factory of Chemical Products (Ukraine). It had a purity of 99.5% and was vacuum distilled before the experiments. The fraction with boiling point 309-311 K/20-21 mm Hg was selected.

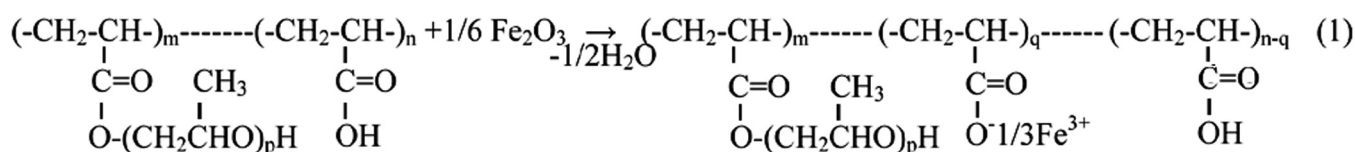
Propylene oxide (PO) was used as an industrial product of the factory □Organic Synthesis□ (Sumgait, Azerbaijan). It had a purity of 99.97%. Ferric oxide and ferric hydroxide were products of Shostka (Ukraine) of purity not less than 99.0%. Oxypropylated PAA was synthesized according to the method described in literature [14]. Interaction between oxypropylated PAA and ferric oxide as well as between AA and ferric hydroxide was carried out in the glass reactor equipped by

heating and mixing systems. Radical homopolymerization of ferric acrylate and radical copolymerization of this salt with AA in the presence of PO were carried out in the sealed glass reactors at the inert atmosphere of nitrogen. The degree of incorporation of Fe^{3+} into the polymer was determined by the gravimetric method and by using atomic absorption spectroscopy (Spectrometer AAS-30 of Carl Zeiss Jena Co.). Reference solutions were used for determination of Fe^{3+} cations contents in the samples of water-soluble copolymers. Measurements were carried out with a use of the lamp, having a hollow cathode, in acetylene-air flame at two values of the wavelength, 248.3 and 372.0 nm. Magnetic susceptibility (X) of the copolymers was measured by Faraday method on the apparatus with photoelectric compensation in the range of 80-300 K and the intensity of magnetic field $H=500-700$ gauss.

RESULTS AND DISCUSSION

Oxypropylated PAA was obtained and used in the form of aqueous solution with concentration of 7.4% by mass. The concentration of oxypropylated PAA in the system for interaction with 1.09 mol/L Fe_2O_3 (calculated according to the molecular masses of monomeric units, which is commonly accepted for reactions of macromolecules) and that of ferric oxide were equal to 0.11 mol/L. The reaction was conducted at 25°C and upon intense mixing during 5 days. The part of ferric oxide remains in the form of precipitate. After the reaction, the initial clear solution of oxypropylated PAA becomes turbid-orange and this is an evidence of iron insertion into the polymer.

The reaction scheme of neutralization of carboxylic groups of the above-mentioned polymer matrix may be described as in Scheme I in where $m:n = (35-40) : (65-60)$ and $p = 1-3$



Scheme I

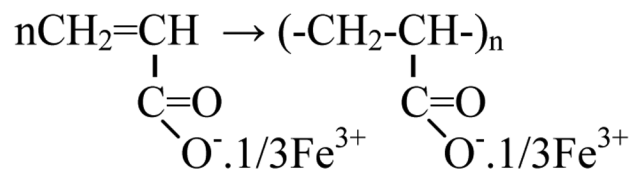
It has been found by gravimetric method that ferric oxide conversion reaches 42.7% of the taken amount of ferric oxide reacted with the polymer. The interaction between oxypropylated PAA and Fe₂O₃ in aqueous medium was also carried out at lower concentrations of the reagents, respectively 0.38 (calculated, as it is shown above, according to the molecular masses of monomeric units) and 0.01 mol/L. The extent of involvement of Fe₂O₃ into the reaction turned out to be equal to 33.9%. The final solution contained 4.14% of copolymer by mass. According to the atomic-absorption spectroscopic measurements, the content of Fe³⁺ in the final solution amounts to 43.0 ppm, i.e. 4.3 × 10⁻³ % by mass. Therefore, the Fe³⁺ content in the polymer itself equals 0.104% by mass. It corresponds to approximately 1 atom of Fe per 600 acrylic units.

It has been established experimentally that increasing the temperature would have negative effect on the reaction course. Thus, at 50°C the extent of Fe₂O₃ involvement into the reaction decreases down to 14%. Further increase in temperature up to 65°C and 80°C prevents the reaction completely.

Iron-containing oxypropyl derivatives of PAA have also been obtained by another way. First, AA was partially neutralized by ferric oxide (Scheme II):

The conditions of the experiment were taken as the following: molar ratio of the reagents 60:1 (i.e., equivalent ratio 10:1), reaction medium-water temperature 25°C. The reaction lasted 2 days with mixing. The extent of Fe₂O₃ involvement was 13.13% which corresponded to 1.31% neutralization extent of AA. The content of iron acrylate in the final mixture was equal to 0.13% mass. Then radical copolymerization in the presence of PO was conducted with an aid of 2% (of the total mass of AA and iron acrylate) ammonium persulphate (APS) according to the method given in literature [15] in where r = qxp (Scheme III).

The amount of PO was taken equal to 90% mol of AA. The final conversion of PO was 44.1%, i.e. about



Scheme II

a half of acrylic units underwent oxypropylation. The concentration of the final solution was 10.73% by mass. According to the atomic-absorption spectroscopy data, iron content in this solution is equal to 139.7 ppm (i.e., 4 × 10⁻²% mass) and in the polymer itself 0.13% mass. This corresponds to approximately one iron atom per 480 acrylic units.

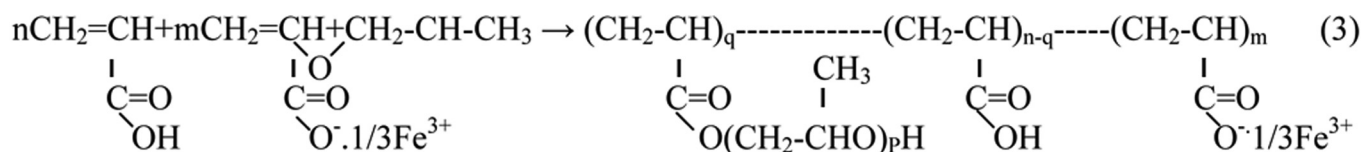
It is observed that iron can be introduced into oxypropylated PAA no more than 0.1% by mass because of the low reactivity of Fe₂O₃. On interaction of ferric oxide with AA and further copolymerization of iron acrylate with AA in the presence of PO, this value does not exceed 0.13% by mass.

It has been experimentally revealed that in order to incorporate more iron into oxypropylated PAA it is expedient to use ferric hydroxide. The reaction scheme of neutralization of AA by Fe(OH)₃ (molar ratio 3:1) is given below Scheme IV:

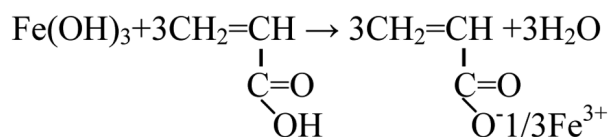
It does appear that this reaction did not occur at room temperature. After increasing temperature up to 95-100°C, a dense black mass well soluble in water is formed. The reaction lasted 6 h. It was found that 23.5% of the initial amount of Fe(OH)₃ enters into the reaction. It has been shown that iron acrylate may be homopolymerized by using the initiator APS at 50°C (Scheme V):

The formed homopolymer precipitated due to insolubility in water. The synthesized iron acrylate was copolymerized with AA in the presence of PO in water at 50°C according to the Scheme III.

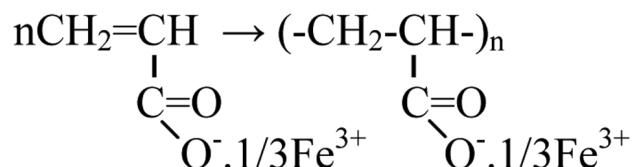
The initial molar ratio AA:PO was 1:1. The initial concentration of AA was 1.95 mol/L. APS was used as



Scheme III



Scheme IV



Scheme V

an initiator with the amount of 1% of the total mass of comonomers. Iron acrylate was taken at the amounts of 0.06, 0.64, 1.34 and 5.30% mol of AA. The conversion of PO after 11 h was equal to 24.5% in the first case, 52.2% in the second case and 50.5% in the third case. Iron contents in the synthesized water-soluble copolymers were 0.04, 0.29 and 0.71% by mass, respectively (according to the data of atomic-absorption spectroscopy). In the fourth case copolymer precipitates as a result of larger iron content.

It has been found that the obtained iron-containing oxypropylated derivatives of PAA possess magnetic properties. Calculations were made according to the formula [16]:

$$X = X_{\text{ref}} \times (m_{\text{ref}}/m) \times (f_z)/(f_z)_{\text{ref}}$$

where X and X_{ref} are specific susceptibilities of the studied substance and the reference substance [Mohr salt $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, the complex salt $\text{HgCo}(\text{SCN})_4$], m and m_{ref} are masses of the studied and reference substances, f_z and $(f_z)_{\text{ref}}$ are forces influencing the studied sample and the reference substance in non-uniform magnetic field in the direction of Z axis.

All samples showed X independence upon H which shows an absence of ferromagnetic admixtures (metallic iron)

Magnetic moment (μ) was calculated by the formula [16]:

$$\mu = 2.84 (x_a(T-\theta))^{1/2}$$

where X_a is atomic susceptibility, T is absolute temperature and θ is Weiss constant.

$X(T)$ obeys Curie-Weiss Law, Weiss constant having values in the range of -10 and +10 K. For computing X and μ , corrections to diamagnetism of the copolymer as well as to Fe^{3+} ions ($X_{\text{diamagnetic}}^{\text{specific}} = -0.31 \times 10^{-6}$ and $X_{\text{Fe}^{3+}} = 270 \times 10^{-6}$, respectively) were introduced. The calculated values of μ per one iron ion amounted to 5.9-6.0 μB which correspond well to a net spin value of μ for Fe^{3+} ion (5.2-6.0 μB). Therefore, it may be concluded that the obtained copolymers are ordinary paramagnetics and iron in them is in the oxidation state of +3.

Laboratory tests verify that the obtained copolymers may be used as insulating agents for isolation of separate zones of layers to prevent filtration of drilling fluids into porous media and thus to diminish their losses. They can also be used as magnetic indicators upon studies of hydrodynamics of insulating liquid flows.

CONCLUSION

New iron-containing water-soluble acrylic copolymer materials useful in oil and gas industrial production applications are synthesized and characterized.

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