Colloids and Surfaces A: Physicochem. Eng. Aspects 483 (2015) 96–103

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Experimental research of syneresis mechanism of HPAM/Cr^{3+} gel

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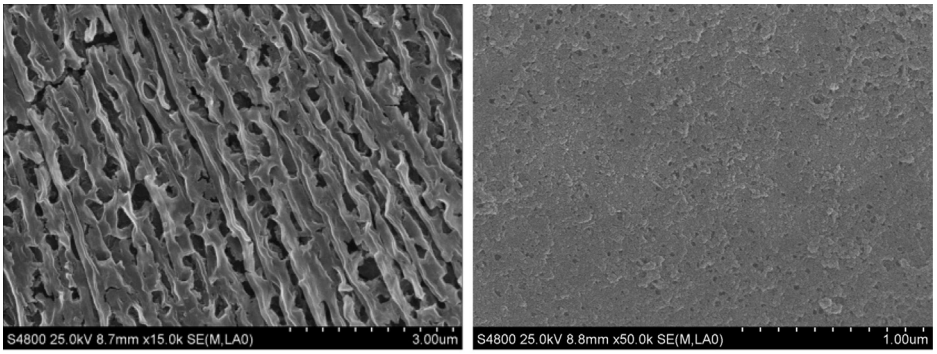
HIGHLIGHTS

- The over-crosslinking is occurred between C—O bond in —COO^- of HPAM and Cr^{3+}.
- The Ca^{2+} reacts with the C—O bond in —COO^- of HPAM.
- The syneresis water originates from the water bounded to carboxylate group of HPAM.
- Syneresis inhibitor restrains the generation of the Cr^{3+} polynuclear olation complex.

GRAPHICAL ABSTRACT

SEM images of different gels. (a) Gel with 0% syneresis; (b) gel immersed with $CaCl_2$ solution.



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ARTICLE INFO

Article history:
Received 1 April 2015
Received in revised form 1 June 2015
Accepted 25 July 2015
Available online 29 July 2015

Keywords:
Gel
HPAM
Syneresis
Crosslinking

ABSTRACT

Experimental investigations have been conducted to elucidate the syneresis mechanism of HPAM (partly hydrolyzed polyacrylamide)/Cr^{3+} gel. The gel prepared with HPAM of high hydrolysis degree is apt to result in the syneresis, since HPAM with more carboxylate group is easier to be over-crosslinked. The over-crosslinking, which contributes a lot to the syneresis, occurs between C—O bond in —COO^- of HPAM and Cr^{3+}. The decreasing hydrophilicity of HPAM molecule, the increase of crosslinking density, and the complexation of the carboxylate group with Ca^{2+} are the main syneresis mechanisms of the gel influenced by the inorganic salt. The Ca^{2+} reacts with the C—O bond in —COO^-, and the reaction produces a tabular structure when the concentration of Ca^{2+} is high, whereby the water in the initial gel is extruded. The produced water resulted from the syneresis mainly originates from the water bounded to the carboxylate group of HPAM, and this confirms that the decreasing hydrophilicity of the carboxylate group in HPAM molecule is one of the important reasons to the gel syneresis. Sodium D-isoascorbate inhibits the generation and growth of the polynuclear olation complex by coordinating with Cr^{3+}, whereby the crosslinking speed is decreased and the syneresis is suppressed.

1. Introduction

Gels formulated with partly hydrolyzed polyacrylamide (HPAM) and Cr^{3+} have been used extensively as water-shutoff agents to reduce water production [1–5]. HPAM/Cr^{3+} gel placed in situ in water dominated channels reduces water permeability and therefore water production. The gelation criteria, kinetics of gelation,

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http://dx.doi.org/10.1016/j.colsurfa.2015.07.048
0927-7757/

transport properties of the gel fluid and long-term stability of the gel in the formation are generally the major concerns in the design of such a profile modification treatment, and the last one is an important part since it is directly associated with the effect of the water-shutoff treatment. Gels typically used in profile modification applications share a common phenomenon, termed syneresis, in which the solvent phase separates from the gel phase as a result of gel shrinkage. The rate of this separation determines the lifetime of the gel under any given set of circumstances. For HPAM/Cr^{3+} gel in reservoir, this shrinkage in volume reduces the ability of the gel to reduce water flow [6]. As such, syneresis is the mechanism whereby the effectiveness of the gel decreases with time. Therefore, inhibiting the syneresis of HPAM/Cr^{3+} gel is a key to extend the duration of water-shutoff treatment.

When HPAM/Cr^{3+} gel is in contact with excess brine or high temperature over a long period of time, the amide group in HPAM hydrolyzes to form carboxylate groups. The interaction of the carboxylate group with the divalent cations results in a sharp reduction in polymer solubility, which is an important reason of the gel syneresis [7,8]. In order to decrease the syneresis, some novel polymers with comonomers meeting the criteria of resistance to hydrolysis and inactivity toward divalent cations have been investigated and used in the gel. Although a fairly wide number of new acrylamide polymers have been described in the literature [9–15]. only a relatively small number of them, including acrylamide copolymers of *N*-vinyl pyrrolidone (*N*-VP), 2-acrylamido-2-methyl-propanesulfonate (AMPS), and *N*-vinyl acetamide (*N*-VA), have been commercialized. Although the novel polymers were generally found to possess excellent thermal stability and resistance to brine, their suitability for petroleum applications is limited by their unreasonable cost. Besides, it is worth emphasizing that a more serious problem for most of the new polymers used in the gel treatments is their relatively high adsorption on reservoir rock. Hence, finding the syneresis mechanism and applying the common polyacrylamide in the gel for water-shutoff is a better way to improve the effectiveness of the profile modification treatment.

The syneresis mechanisms of the water-shutoff gel have been studied by some researchers, and the over-crosslinking mechanism is generally accepted as the primary reason of the gel shrinkage. Gales et al. [16] investigated the stability of xanthan gum/Cr^{3+} gel, and they showed that the increase of Cr^{3+} used in the gel led to the high degree of syneresis. They therefore concluded that reducing the crosslinking density is facilitated to decrease the syneresis, and pointed out the appropriate amount of crosslinking agent was the precondition to ensure the gel possessing the excellent stability. Eriksen et al. [17] confirmed Gales's point of view. They studied the stability of the polyacrylamide-formaldehyde gel at 120 °C, and they found that reducing the crosslinking ratio of formaldehyde and polyacrylamide increases the crosslinking time, which results in the low crosslinking density and the decreasing syneresis. Albonico and Lockhart [18] researched the syneresis of the HPAM/Cr^{3+} gel under the effect of the Ca^{2+} and Mg^{2+}. They stated that Ca^{2+} and Mg^{2+} may react with the carboxylate in HPAM, which increased the crosslinking density and decreased the water solubility of HPAM. As a result, the water seperated out from the gel phase whereby the gel stability reduced.

In summary, over-crosslinking is considered to be the main reason for the gel syneresis in the previous reports. However, the above conclusion was obtained by the inference based on the experiment result, and it still needs intuitive and sufficient evidence to be proved. Although the syneresis mechanism of the gel influenced by the Ca^{2+} has been speculated in the previous literature [18], it is necessary to be clearly clarified. In addition, to our best knowledge, the effect of the hydrophilicity of HPAM on the gel syneresis has not been investigated, so the research on the hydrophilicity will contribute a lot to elucidate the principle of gel syneresis. Therefore, a series of experiments were conducted in this work to further study the syneresis mechanism. This investigation will provide an improved understanding of the gel syneresis, which is conducive to select the formula of water-shutoff gels with high stability.

Table 1
Hydrolysis degree and molecular mass of HPAM.

HPAM	Molecular mass, 10^6	Hydrolysis degree (%)
H1	12	20
H2	12	30
H3	12	39

2. Experimental

2.1. Materials

Sodium bichromate ($Na_2Cr_2O_7$), sodium sulfite (Na_2SO_3), sodium chloride (NaCl), calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$) and ethylene diamine tetraacetic acid (EDTA) are all analytically pure, and purchased from Sinopharm. Besides, the additives, sodium D-isoascorbate, sodium oxalate, sodium lactate and sodium salicylate, are also obtained from Sinopharm. HPAMs were purchased from Beijing Hengju Chemical Group Corporation, and their hydrolysis degree and molecular mass are listed in Table 1. All concentrations in the paper are on a weight basis.

2.2. Measurements of gelation time and syneresis rate

First, a 0.4% HPAM stock solution was prepared by dissolving solid HPAM in fresh water. A container with a known amount of water was vigorously stirred to create a deep vortex. HPAM was slowly added to the shoulder of the vortex to effectively wet the HPAM beads. The container was sealed to minimize evaporation and was stirred continuously for 24 h to ensure complete dissolution of HPAM. The crosslinker, whose amount was carefully tuned, was dissolved in fresh water to prepare a crosslinker solution. Finally, the gelling solution was prepared by mixing the HPAM stock solution and crosslinker solution. Aqueous gellable compositions were obtained through many screening procedures, that is, 0.2% HPAM + 0.3% $Na_2Cr_2O_7$ + 0.6% Na_2SO_3. After the gelling solution was prepared, it (20 g) was sealed in a bottle and put into an oven at 60 °C, and then the gelation time and syneresis rate were measured. The gel strength code method [19], which is showed in Table 2, was used to determine the gelation time, and the gelation time is considered as the period of time when gelling solutions in code A state turn to code G in this paper. Syneresis rate is defined as the decrease in the gel weight at a given time relative to the initial gel weight, and the onset of the syneresis is referred to the time from which the gel actually formed, not from the moment that the solutions were placed in the oven.

2.3. Effect of inorganic salts on the syneresis

When the gel was formed in the bottle with stopper, the inorganic salt solution (NaCl: 0.05–0.5 mol/L; $CaCl_2$ and $MgCl_2$: 0.001–0.1 mol/L) of equal quality (20 g) was put in the bottle. As a result, the effect of inorganic salts on the syneresis can be investigated by measuring the weight of the salt solution at the given time.

2.4. Measurements of differential scanning calorimetry (DSC)

Two gel samples were prepared as the method in Section 2.2. When the syneresis of them reached to 0% and 25%, respectively,