Investigation of Gelation Behavior of Polyvinyl Alcohol–Glutaraldehyde System

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SYNOPSIS

The polyvinyl alcohol–glutaraldehyde gel system was investigated in this work. The gelation kinetics under oil field environments and effects on the structures and properties of the gels formed were discussed. The basic characteristics of this gel system were determined. The fundamental data during gelation were obtained and application of the gel system for the tertiary oil recovery was evaluated. Under the experimental condition, among the gelation time t, initial pH of the system, and glutaraldehyde concentration x, there exists the relation

$$\ln t(\mathrm{pH}, x) = 2.35\mathrm{pH} - 0.85 \ln x - 10.91$$

It is conspicuous that the gelation of this gel system is less sensitive to hardness and salt contents; the gels formed under the relevant condition were quite stable. Thus, the application of this gel system for tertiary oil recovery under hostile environments is very promising. © 1997 John Wiley & Sons, Inc.

INTRODUCTION

Primary and secondary oil recovery together recover only 25–50% of the oil originally in place in a reservoir. A major reason for low oil recovery efficiency in waterflooding and other displacement processes is poor performance due to reservoir heterogenetics. Volumetric sweep efficiency of displacement processes can be improved significantly by using gelled polymers to modify *in situ* permeability. This process, which is typically referred to as polymerflooding, is among several methods known as enhanced oil recovery (EOR) techniques applied to extract additional oil beyond primary and secondary productions. Gel treatment technology is a technique used to block high permeability zones. When high permeability zones are blocked, injected solutions will flow through the previously unswept low permeability zones resulting in an increase in oil recovery. *in Situ* gelation refers to development of a region of high resistance due to the gelation process taking place inside of a porous medium when gel solution is injected. The use of gelled polymers to alter the volumetric sweep of waterflooding has developed within the last twenty years.

There are two main types of polymer gels developed in *in situ* gelation in tertiary oil recovery: crosslinked polymers and reactive monomers. Polymers react with crosslinkers to form gels, and reactive monomers polymerize to produce gels.[1] Partially hydrolyzed polyacrylamides or polysaccharides are most commonly used in polyflooding. But the application of metallic or organic crosslinkers for gelation of polyacrylamide or polysaccharides is limited to relatively low temperatures and hardness levels. This is due to production of additional carboxylated sites through hydrolysis of the amide groups. The carboxylate groups unfortunately crosslink with calcium and magne-
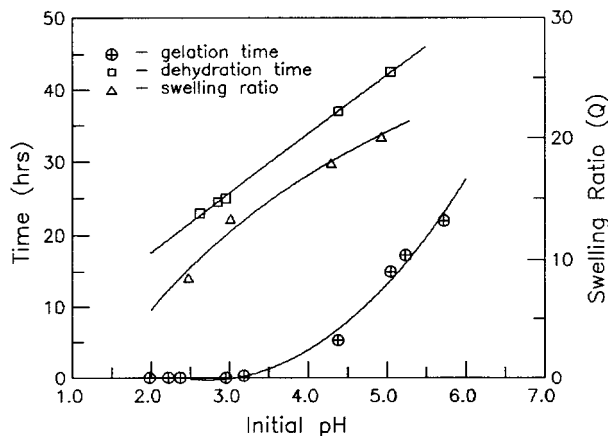

Figure 1 Effect of initial pH. 5% PVA, 8.5% glutaraldehyde, 50°C.

sium ions, commonly present in most oilfield brines, and cause polyacrylamides to precipitate. Polysaccharide gels break down due to thermal degradation of the polymer. Biopolymers such as xanthan and scleroglucan are not stable to microbial degradation. Environmental concerns have stimulated the research for other polymer systems that do not rely upon chromium or other highly toxic chemicals for crosslinking. No optimal EOR polymer currently exists. It is difficult for one single polymer to meet all of the requirements. This situation is caused by the various physical conditions (e.g., pH, salinity, temperature, porosity, clay, rock formation, etc.) which the polymer is subjected to in the underground formations. In recent years, considerable attention has been given to the EOR products used under hostile environments (higher temperature, salinity, and hardness levels) encountered in reservoirs.[2] Fortunately, the macromolecule design provides an efficient way to choose a synthetic polymer which exhibits the desired behavior for the specific oil bearing formation.

Polyvinyl alcohol hydrogel was widely used in cooling medium, contact lenses, and materials for drug delivery systems.[3–5] In this work, the gelation behavior of polyvinyl alcohol–glutaraldehyde (PVAG) system was investigated. The gelation kinetics under oil field environments and effects on the structures and properties of the gels formed were discussed. The basic characteristics of this gel system were determined. The fundamental data during the gelation were obtained, and the application of this gel system for the tertiary oil

recovery under hostile environments was evaluated.

EXPERIMENTAL

Materials

Polyvinyl alcohol used in this study was PVA-124, which had an average polymerization degree of 2400 with a saponification value of 98.5%. Glutaraldehyde, sodium chloride, calcium chloride, and sulfuric acid were commercial products of analytical reagent grade and were used without further purification. Water used in all experiments was double-distilled and deionized.

Gelation

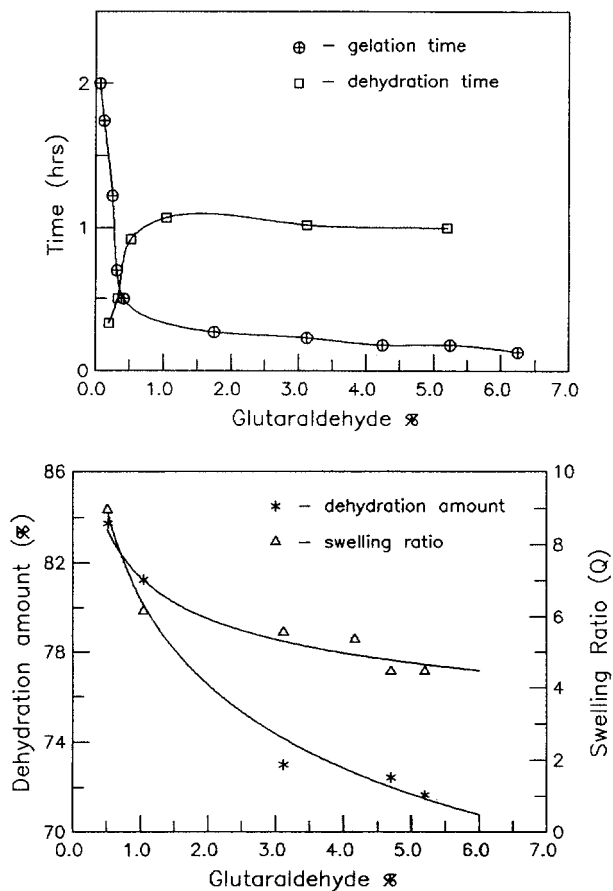A stock solution of polyvinyl alcohol, glutaraldehyde, and salt was prepared according to certain

Figure 2 Effect of glutaraldehyde. 5% PVA, initial pH 2.5–3.0, 50°C.
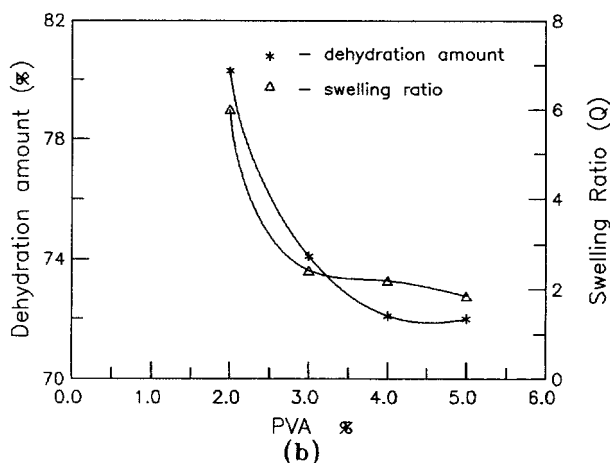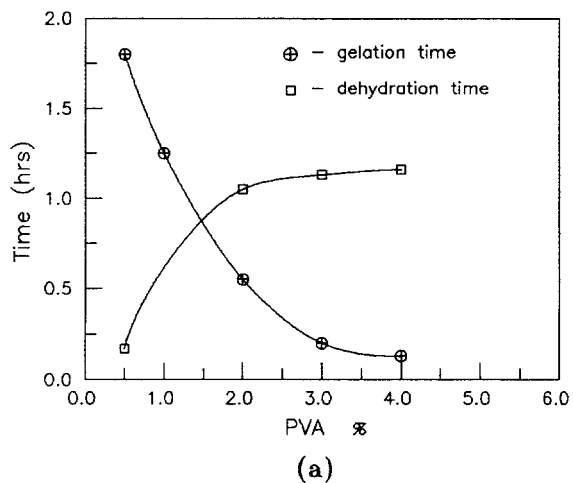
Figure 3 Effect of PVA. 2.5% glutaraldehyde, initial pH 2.5–3.0, 50°C.

the constant temperature bath. The weight (W_e) of the gel and the amount of free water coming out from the gel at equilibrium state were determined. Then the gel was dried to constant weight (W_o) at 120°C. The swelling ratio of the gel was calculated.

$$Q = \frac{V_e}{V_o} = \frac{V_e}{W_o \cdot C_d}$$

Here C_d was the specific volume of the dried gel.

RESULTS AND DISCUSSION

Polyvinyl alcohol may react with aldehydes, with acid as a catalyst. Intermolecular acetylation reaction results in crosslinking of PVA; ultimately,
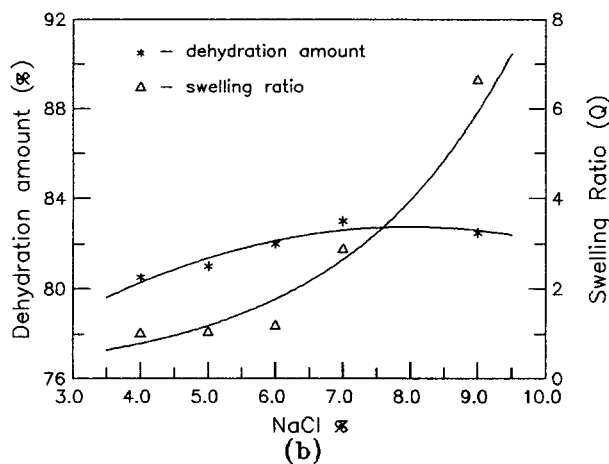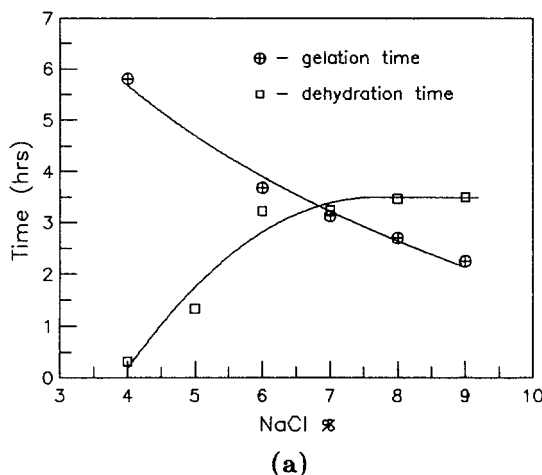
compositions. pH of the solution was adjusted with acid and measured by pH S-3C model pH meter (accuracy: ±0.01 pH). Sealed samples were placed in a constant temperature bath. The gelation time (the time during which period of rapidly increasing viscosity was defined as the gelation time) was recorded. After the gel was formed by the reaction of polyvinyl alcohol and glutaraldehyde, with the time past, free water began to come out from the gel. This period of time was defined as the dehydration time. Afterward, the dehydration was gradually decreased, and at last reached zero; the PVAG gel system was at equilibrium state.

Swelling Equilibrium

The volume (V_e) of the gel at equilibrium state was measured by calibrated swelling meters in

Figure 4 Effect of NaCl. 5% PVA, 2.5% glutaraldehyde, initial pH 4.4–4.5, 50°C.
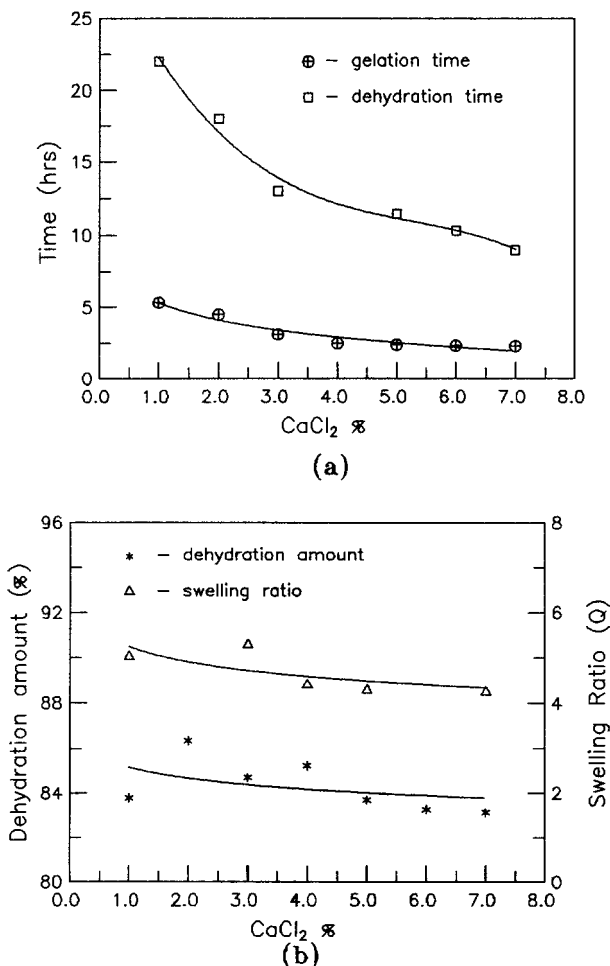
Figure 5   Effect of CaCl$_2$. 5% PVA, 2.5% glutaraldehyde, initial pH 4.0–4.5, 50°C.

the gels may be formed. Many variables influence the rate of the gelation and the structure of the gel. Factors that were investigated were: initial pH of the system, concentrations of the polymer and crosslinker, salinity, hardness, and temperature.

Initial pH of the System

The gelation behavior of the PVAG system was relative to initial pH of the system. The gelation appeared very fast at lower pH. When initial pH was increased, the gelation time, the dehydration time, and the swelling ratio of the gel increased (Fig. 1). The viscosity of aqueous PVA solution was in accordance with the rule of usual neutral polymer solution,[6] and was irrelevent to pH of the solution. Under the experimental conditions,

when initial pH was <2.0, the rates of gelation and dehydration were too fast, and dehydration amount was too much; when initial pH was >8.8, there was precipitate from the system, and the gel was less formed. In the application for the tertiary oil recovery, initial pH of this system was accepted between 2.0 and 4.0; within this range, smaller change of gelation time happened with the variation of pH; the operation was easier to control.

Glutaraldehyde Concentration

There was no gelation at very low glutaraldehyde concentration. The higher the glutaraldehyde concentration, the shorter the gelation time, the longer the dehydration time, and the less the dehydration amount (Fig. 2). When glutaraldehyde concentration was above 1%, effect of concentration variation on gelation time was much less. In order to get longer gelation time or reduce the cost, quite low glutaraldehyde concentration (e.g., 0.66%) may be accepted, and quite good gels may be still obtained.

Polyvinyl Alcohol Concentration

When PVA concentration was reduced, a longer gelation time was obtained. But when PVA concentration was too low, the products were flocculent, dehydration appeared early, and dehydration was high (Fig. 3). When PVA concentration was very low (e.g., 0.25%), the gels were not
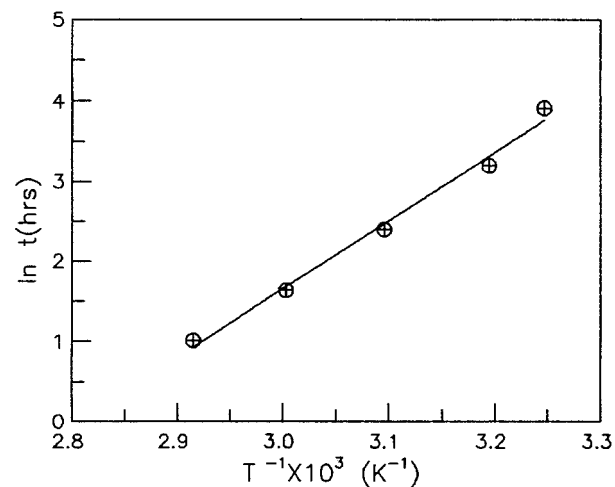

Figure 6   Effect of temperature on gelation time. 5% PVA, 2.5% glutaraldehyde, initial pH 4.37.

formed. While PVA concentration was too high (>6%), the viscosity of the system was higher; it was not beneficial to the operation, and the cost was enhanced. The favorable PVA concentration was 2–5%.

Salinity and Hardness

Gelation behavior was relative to salinity and hardness (Figs. 4 and 5). With added salt increased, the gelation happened faster, and the dehydration amount was varied a little bit. As the concentration of added NaCl was increased, the swelling ratio of the gel was increased; the variation of $CaCl_2$ concentration had less effect on the swelling ratio of the gel because there were different permeabilities in the network structures of polyvinyl alcohol hydrogel for these two kinds of salts.[7] Comparing with the known polymer gel systems used in the tertiary oil recovery, polyvinyl alcohol–glutaraldehyde gels were quite stable to salinity and hardness. For example, the gel system consisted of 3% resorcinol and 3% formaldehyde (RF system), initial pH 9.0 at 41°C. When no salt was added, gelation time was 7 days; when 0.5% NaCl was added, gelation time was less than 3 h.[8] The RF system only can be used when the total dissolved salt (TDS) is less than 1%.[9] The most commonly used polyacrylamide gel was very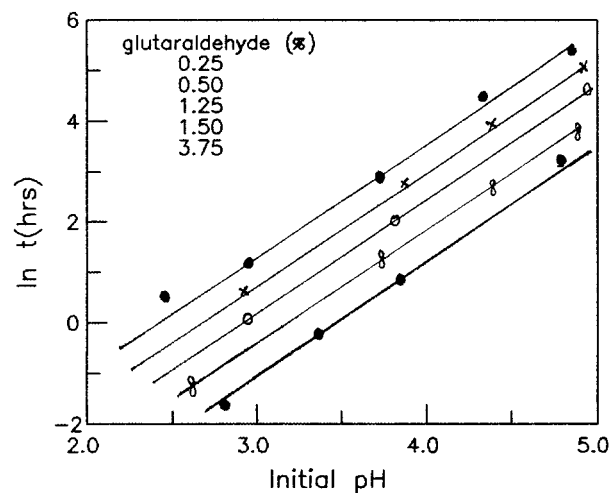 sensitive to hardness as the reason mentioned before; lower hardness results in the uselessness of the gelation of that system. This weakness may be overcome by polyvinyl alcohol hydrogel. It is very promising that PVA hydrogel can tolerate to the hardness of 3000–6000 ppm, and may be used under the environments of brackish water or sea water.

Figure 8 Relation between intercept and reciprocal of glutaraldehyde concentration. 5% PVA, 50°C.

Temperature

Influence of the temperature on gelation time was shown in Figure 6. From the graph of natural logarithm of gelation time ($\ln t$) versus the reciprocal of temperature ($1/T$), the activation energy of PVAG gel system at initial pH 4.37 was 62.4 KJ/mol. The less the initial pH, the less the activation energy.

In all these factors mentioned above, the effect of pH on the gelation behavior was quite important, especially at lower initial pH. In order to get the relation between the main factors and gelation time, and to guide the operation, the gels were prepared with 5% PVA solution and glutaraldehyde of different concentrations, and at different initial pH. The figures were plotted by natural logarithm of gelation times ($\ln t$) versus pH. A series of lines were obtained (Fig. 7). Their relations may be expressed as the following equation:

$$\ln t(\mathrm{pH}, x) = \ln t_0(x) + k(x) \cdot \mathrm{pH}$$

Figure 7 Relation between gelation time and initial pH at different glutaraldehyde concentration. 5% PVA, 50°C.

Here x was glutaraldehyde concentration, $\ln t_0(x)$ was the intercept, and $k(x)$ were slopes of the lines.

From Figure 7, $k = 2.35$. The relation between $\ln t_0(x)$ and glutaraldehyde concentration x was shown in Figure 8.

$$\ln t_0(x) = 0.857 \frac{1}{x} - 10.91$$

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