

A NOVEL EOR POLYMER(I)—STUDY ON GELATION OF RESORCINOL-FORMALDEHYDE SYSTEMS

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ABSTRACT

Factors affecting the gelation of resorcinol-formaldehyde systems have been examined over variable ranges applicable to oilfield use. Gelation of resorcinol-formaldehyde (RF) system was sensitive to pH, salinity and hardness. Generally, this gel system could be used in fresh water or low salinity brine at pH higher than about 9. The application would require careful monitoring of injection fluids to avoid premature gelation or prolonged shut-in times, especially under conditions of low salinity and high pH. Salinity and hardness compatibilities of the system were improved by sulfomethylation of resorcinol. Aqueous sulfomethylated resorcinol formaldehyde (SMRF) system could be used in brine with higher salinity and hardness and at a wider pH range of 5–10.

INTRODUCTION

Profile modification (in-situ gelation) is a means of enhancing oil recovery (EOR) by diverting flood water into previously underswept zones of the reservoir. In this technique, a gel system is injected into the high permeability, watered-out zones to block or plug-off that portion of the reservoir. This results in diversion of water subsequently injected into the oil-rich zones, improving sweep efficiency of the water and increasing oil recovery.

Comparing with the common gelled polymer system of partially hydrolyzed polyacrylamide or a polysaccharide such as xanthan biopolymer with a metal ion, usually chromium, the phenolic system has attractive features for use as an injected gel-forming solution. This system gels through covalent and not ionic bonds. Prior to gelation, the aqueous solution of the reactive monomers is a low viscosity fluid which can be pumped as

easily as water, and may be injected at relatively high rates and preferentially enters the high permeability zones. Polymerization occurs within the rock matrix forming a gel that greatly reduces rock permeability. These gels have been proposed for application in diversion of flow from high permeability regions in porous media^[1-9].

This paper reports results from an experimental investigation of the gelation of the resorcinol-formaldehyde systems. The objectives were to characterize the gelation of the resorcinol-formaldehyde (RF) gel system in bulk solution and to chemically modify the system to improve performance in terms of long gel times on the order of days and tolerance to chemical compositions.

EXPERIMENTAL

Two series of gel solutions were prepared. The RF gel solutions consisted of resorcinol, formaldehyde, water or brine [e. g. Brine B 1% NaCl, 0.1% Ca^{+2} (0.36% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$)]. The SMRF gel solutions consisted of resorcinol, formaldehyde, sodium sulfite and brine. SMRF gel solutions were made in two steps: sulfomethylation of resorcinol and preparation of SMRF gel solution.

pH of the gel solution was adjusted with aqueous sodium hydroxide (or acetic acid). A Fisher Accument Model pH Meter equipped with a combination type electrode was used to measure pH (accuracy: $\pm 0.01\text{pH}$). Gelation was carried out in a beaker at the experimental temperature. Gelation and gel quality (e. g., formation of gel, gelatinous-precipitate or precipitate) were observed visually. The time during which period of rapidly increasing viscosity was defined as the gel time.

RESULTS AND DISCUSSION

Many variables influence the rate of gelation and the gel strength. Factors that were investigated are: mol ratio of reactants, pH of reaction medium, monomer concentration, salinity and hardness.

Mol ratio F/R

Gel times as function of the formaldehyde to resorcinol ratio (F/R) are shown in Fig. 1 for a system at a selected composition. The polymerization can lead to a completely gelled system of equivalent quantities are used. When the mol ratio was more than 1.5, the extent of polymerization depended on the deficient reactant (formaldehyde). It was possible to obtain

a gel and the gel time did not vary greatly. Gel times increased significantly as the mol ratio F/R decreased below the value 1.5. But the mol ratio F/R could not be too low. In this case a network polymer might not be formed (no gel or precipitate).

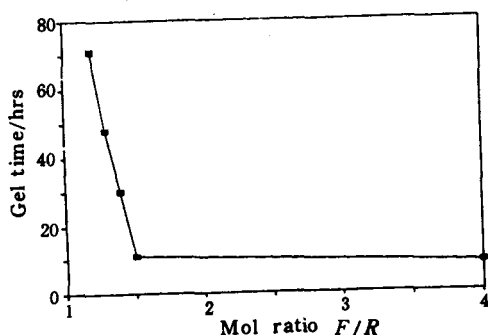


Fig. 1 Effect of mol ratio on gel time at 41°C, 0.5% resorcinol, brine B, initial pH 9.5

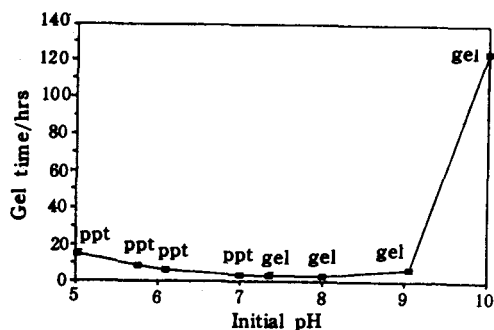


Fig. 2 Effect of initial pH on gelation at 41°C, 3% resorcinol, 3% formaldehyde, 0.5% KCl

pH of the reaction medium

Gelation behavior of the RF system was sensitive to the initial pH of the system. The methylation reaction takes place quickly on mixing the reactants to yield a series of hydroxymethyl resorcinols that have higher acid strength; the rate of this reaction is increased as the hydroxyl ion concentration is increased. While the polymerization rate is decreased as the hydroxyl ion concentration is increased. There exists a pH range (about 7–8 here) (Fig. 2) within which, the reaction between resorcinol and formaldehyde takes place faster. When pH was lower, the reaction time was longer and the salinity compatibility was worse. Sometimes the reaction system could not form a gel or gelatinous-precipitate, but only formed a precipitate. When pH was higher ($\text{pH} > 9$), the gel time was longer and the salinity compatibility was better. Higher pH was beneficial to forming a stronger gel. However, if the pH of the reaction medium is too high, it will inhibit the polycondensation. When pH is higher than 10, formaldehyde undergoes a disproportionation reaction obviously, known as the Cannizzaro reaction.

pH of the reaction medium may be changed by changing the initial pH or the pH in the reaction process or using a buffer.

Monomer concentration

Gel times as function of resorcinol concentration are shown in Fig. 3 for

a series of samples prepared at constant F/R ratio, F, R molal quantity of formaldehyde or resorcinol added in the preparation of RF system, salt concentration and initial pH. Gel times ranged from 30 minutes to 7 days for the resorcinol concentration of 0.5 and 10 wt. %, respectively. As resorcinol concentration was decreased, gelatinous-precipitate or precipitate formed and the amount of free water in the product increased. The gel strength by visible inspection decreased with decreasing concentration.

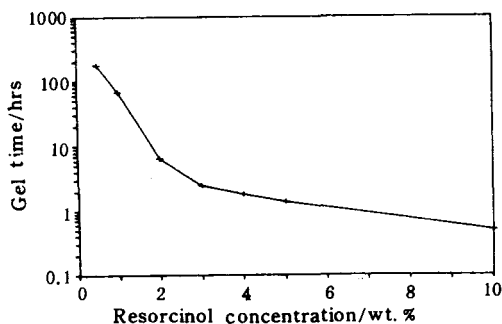


Fig. 3 Effect of monomer concentration on gel time at 41 °C, F/R = 1.3, 0.5% KCl, initial pH 8.0

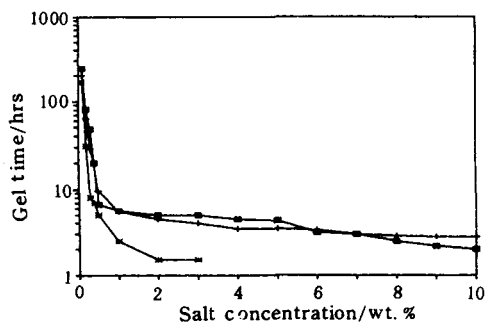


Fig. 4 Effect of salt concentration on gel time 41 °C, 3% resorcinol, F/R = 1.5, initial pH 9.0

■ KCl; + NaCl; * CaCl₂

Salinity and hardness

Gelation behavior was too sensitive to salinity and hardness. Small change of salinity would result in great change of gel time. Bivalent cations (e. g., Ca^{+2}) have an especially strong influence^[10] (Fig. 4). For example, the reaction system of 3% resorcinol and 3% formaldehyde, without salt, and at an initial pH of 9.0, the gel time was several days. But when only 0.5% KCl was added to that reaction mixture, the gel time was less than 3 hours. These compositions could tolerate mono- and divalent ions up to certain concentrations. Above these concentrations, a gel could not be formed.

To obtain better salinity compatibility, higher pH or higher monomer concentration should be adopted. Generally, these gels could be prepared in fresh water or low salinity brine. There exist more or less brines in the reservoir. It is expected that the injected gel solution would replace the brine and premature gelation or precipitation would occur only in the interface between the gellable solution and the reservoir brine. The rest of the gellable solution would not be affected by the presence of brine in the

interface. It is advisable to conduct a preflush field brine with a higher pH. Then there is a longer gelation time and better salinity compatibility at the interface.

Reaction time

In order to obtain the gel (not precipitate) and longer gel time, lower monomer concentration, lower mol ratio F/R, lower salinity or higher pH could be adopted. Unfortunately, mol ratio and monomer concentration should not be too low. pH of RF gel solution should be above about 9. But when pH was between 9 and 10, small change of pH would result in great change of gel time. The same situation would happen under lower salinity. So that the operation of RF system was difficult to control.

Sulfomethylation

The effect of salt concentration on the gelation time of the RF system showed undesirable characteristics: gelation occurred in the matter of hours, not days, at salt concentration above approximately 1%; and gelation times were very sensitive to small changes in salt concentration below 1% salt. Often in an oil field, sources of large amounts of fresh water (i. e. <1% TDS, TDS total dissolved salts) are not available or are available at great expense. So it is highly desirable

to have gel-forming system that are soluble in the reservoir brine. SMRF gel system could tolerate the brines with higher salinity and hardness. In order to guarantee the polymerization between formaldehyde and sulfomethylated resorcinol to form the network, the average functionality of sulfomethylated resorcinol generally should be higher than about 2. Under experimental conditions, the higher the mol ratio of Na_2SO_3 to R, the higher the degree of sulfomethylation, and the better the salinity and hardness compatibilities of this gel system, the longer the gel time. When the mol ratio of Na_2SO_3 to R is constant, the higher the mol ratio of F_2 (F_2 molal quantity of formaldehyde added in polycondensation of sulfomethylated resorcinol) + F_1 (F_1 molal quantity of formaldehyde added in sulfomethylation of resorcinol)

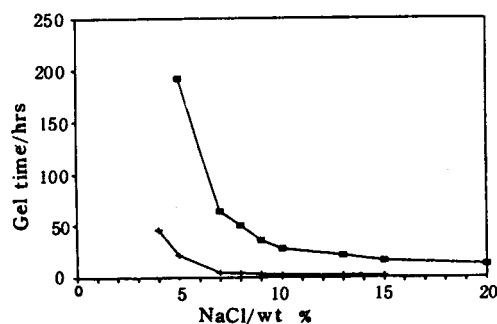


Fig. 5 Effect of salt concentration on gel time
41°C, 3% resorcinol, $\text{F}_2 : \text{F}_1 : \text{S} : \text{R}$
= 1.3 : 0.75 : 0.5 : 1
■ initial pH=9.5 + initial pH=7.0

to R, the worse the salinity and hardness compatibilities of this gel system.

Because of the improved salt resistance, the gel time was prolonged obviously and the gel could be formed at a pH from 5 to 10 (Figs. 5,6). When pH was about 7, the gel time was shorter, and easier to control, especially at pH about 6-8. Sulfomethylation could also be taken as an effective means to prolong the gel time. For example, under the condition of 41°C, 0.5% NaCl, and an initial pH of 9.5, the gel time of RF gel-forming solution (3%R, F : R=1.5) was about 3 days; while the gel time of SMRF gel-forming solution [3%R, mol ratio of SMRF : F₂ : F₁ : S (S molal quantity of sodium sulfite added) : R=1.3 : 0.75 : 0.5 : 1] was more than two months (Fig. 7). Use of SMRF gel system in modifying the permeability of reservoirs has not been reported.

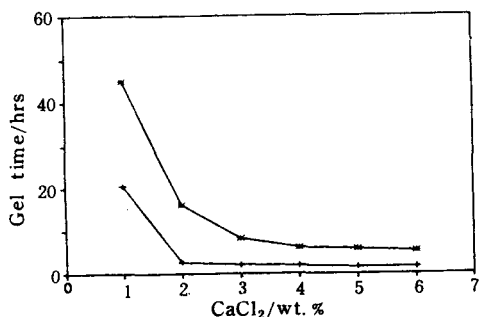


Fig. 6 Effect of salt concentration on gel time
41°C, 3% resorcinol, F₂ : F₁ : S : R
= 1.3 : 0.75 : 0.5 : 1
+ initial pH=7.0; * initial pH=5.0

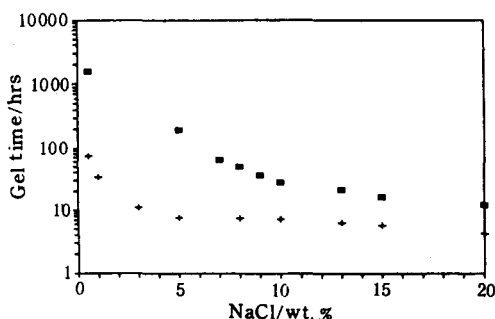


Fig. 7 Relation between gel time and salinity
41°C, 3% resorcinol, initial pH 9.5
■ SMRF; + RF

CONCLUSIONS

1. Gelation of resorcinol-formaldehyde(RF)system was sensitive to pH. When pH was higher (pH>9), as the pH increased, the gel time become longer, and the salinity compatibility was improved. Higher pH was beneficial to forming a stronger gel.
2. Gelation of RF system was too sensitive to salinity and hardness. The presence of a brine caused acceleration of gelation, and sometimes precipitation. This gel system only could tolerate mono- and divalent ions up to certain concentrations (usually about 1% TDS) and thus should be used in fresh water or low salinity brine.
3. Various gelation times might be obtained to permit emplacement at

varying distances from the wellbore. Application of RF system as a diverting agent for profile modification in tertiary oil recovery required careful monitoring of injection fluids to avoid premature gelation or prolonged shut-in times, especially under lower salinity or higher pH. It is advisable to conduct a preflush field brine with a higher pH.

4. Aqueous sulfomethylated resorcinol formaldehyde (SMRF) gel system could tolerate the brines with higher salinity and hardness, and could be used above at a pH of 5–10. The gel time was easier to be controlled at pH about 6–8. Sulfomethylation could also be taken as an effective means to prolong the gel time. Gel times might be adjusted by mol ratio, pH, salinity and monomer concentration.
5. Thus, by careful selection of the gel-forming composition, resorcinol-formaldehyde systems (RF and SMRF) could be gelled ranging from fresh water to brines with higher salinity and hardness, at a pH of above 5–10, and at lower temperature.

Keywords:

Gelation; Resorcinol formaldehyde; Oil recovery; EOR polymer

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