Research Article

Modeling of Partially Hydrolyzed Polyacrylamide-Hexamine-Hydroquinone Gel System Used for Profile Modification Jobs in the Oil Field

Upendra Singh Yadav and Vikas Mahto

Department of Petroleum Engineering, Indian School of Mines, Dhanbad 826004, India

Correspondence should be addressed to Upendra Singh Yadav, yadavupend@gmail.com
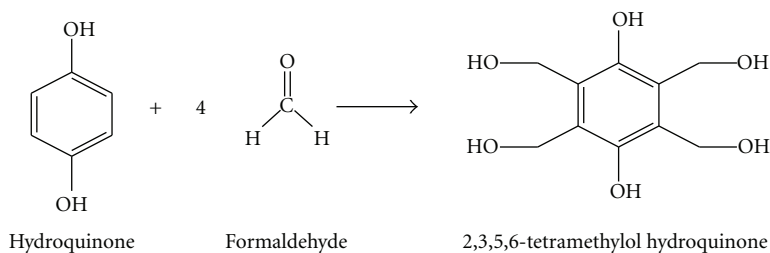
The cross-linked polymer gel systems are being used increasingly to redirect or modify reservoir fluid movement in the vicinity of injection wells for the purpose of permeability/profile modification job in the oil field due to their high temperature stability and capability to provide rigid gel having high mechanical strength. In this study, a partially hydrolyzed polyacrylamide-hexamine-hydroquinonegel is used for the development of polymer gel system. The experimental investigation demonstrates that the gelation time varies with polymer and crosslinker concentration and the temperature. The mathematical model is developed with the help of gelation kinetics of polymer gel and using Arrhenius equation, which relates the gelation time with polymer, crosslinker concentrations, and temperature. The developed model is solved with the help of multivariate regression method. It is observed in this study that the theoretical values of gelation time have good agreement with the experimental values.
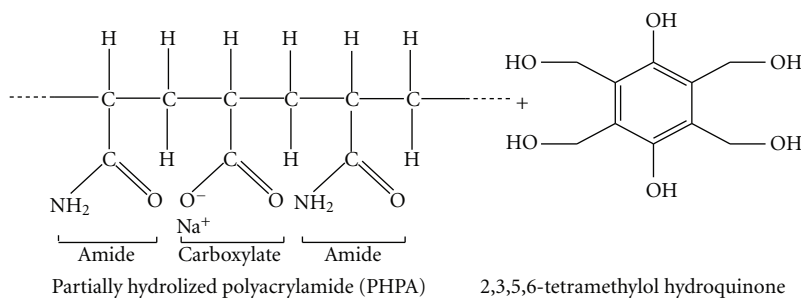
1. Introduction

The reservoir heterogeneity, permeability variations, and presence of fractures and fracture network in the reservoir are the main hurdles of the water flooding operations used to enhance the oil recovery from matured oil fields. Normally during water flooding, water sweeps through more permeable sections of the reservoir leaving back oil in low permeability channels leading to low oil recovery and early water breakthrough. This excessive water production from the producers leads to rise in handling and disposal costs and reduces the economic life of the well. The polymer gels block or reduce the permeability in high permeability channels and divert the injected water through the low permeability sections, which were not flooded or swept earlier, leading to improvement in oil recovery. This technique is known as profile modification or permeability modification technique and the proper application of this technique is essential for the success of water flooding projects in the oil fields [1–3].

Basically two types of polymers have been used for profile modification jobs. These are polyacrylamides with different degrees of hydrolysis and polysaccharide such as xanthan biopolymer. These are cross linked with inorganic and organic crosslinkers to produce a three-dimensional polymer structure of the gel [4–7]. The inorganic gel system based on the crosslinking of the carboxylate groups on the partially hydrolyzed polyacrylamide chain (PHPA) with a trivalent cation like Cr (III). This crosslinking is believed to rely on coordination covalent bonding. It should be mentioned that Cr (III) based polymer gel system were reported to be stable at temperatures up to 300°F [8–10]. The organically crosslinked gels developed using phenol and formaldehyde crosslinkers are thermally stable under harsh environmental conditions. But, these crosslinkers are not environment friendly. To overcome the toxicity issues associated with formaldehyde and phenol, the formaldehyde can be replaced with less toxic derivatives like hexamethylenetetramine, glyoxal, paraformaldehyde, acetaldehyde, propionaldehyde, butyraldehyde and so forth and phenol can be replaced with hydroquinone, resorcinol, pyrogallol, phenyl salicylate and so forth [11–13]. Other system is based on PEI crosslinker and a copolymer of acrylamide and t-butyl acrylate (PA-t-BA). PA-t-BA is a relatively low molecular-weight polymer is expected

Hydroquinone   Formaldehyde   2,3,5,6-tetramethylol hydroquinone

SCHEME 1

Partially hydrolized polyacrylamide (PHPA)   2,3,5,6-tetramethylol hydroquinone

Crosslinking 3-D gel structure

SCHEME 2

to provide rigid ringing gels. Polyethyleneimine (PEI) cross-linking a copolymer of acrylamide and tert-butylacrylate (PAtBA) as water shutoff gels has been widely used in recent years [14].

The gelation mechanism of organic crosslinkers is done by covalent bonding, which is much more stable than the ionic bonds. Organic crosslinkers were introduced to obtained gels that can remain stable over a wide temperature range. For high temperature (>90°C) reservoirs, acrylamide-based copolymers with organic crosslinking agents, such as phenol-formaldehyde and its derivatives, can be used to form a gel with thermal stability, and the gelation time is adjustable [15, 16].

The different methods are presented in the literature for the determination of the physical and chemical properties of polymer gel system such as bottle testing method, sealed tube method, dynamic shear method (rheometer), and static shear method (viscometer). Out of these methods, the bottle testing method is most suitable, faster, and inexpensive method to study the gelation kinetics [17].

Several models have been reported in the literature to relate the gelation time with temperature. Jordan found that the gelation time of a specified system decreases as the temperature is increased. Plots of the logarithm of gelation time versus the reciprocal of the absolute reaction temperature were found to be linear for the systems studied. This correlation showed that the system apparently followed the Hurd and Letteron model which assumed rate dependence on only one species. Hurd and Letteron studied the effect of temperature on the formation of silicic acid gels and found empirically that plot of the logarithm of the gelation time versus the reciprocal of the absolute temperature linear. They developed an equation, similar to the Arrhenius equation, which relates gelation time and the temperature and support the linear relationship [15]. But very few or rare models relate the gelation time with polymer and crosslinker concentration
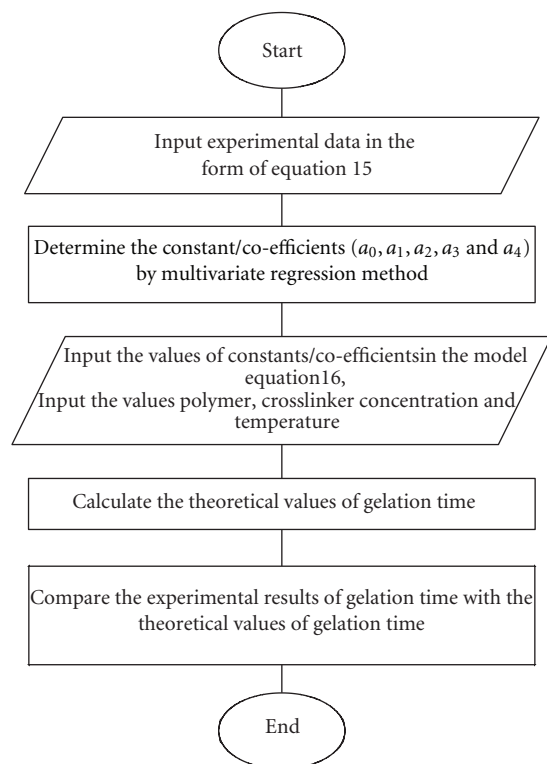
FIGURE 1: Flow chart for the solution of developed model.

HMTA/HQ: 0.5/0.4 (wt%)
pH: 7.5
Gelation time (hrs.):-
- ■ — Experimental values at PHPA 1.1 wt%
- ● — Theoretical values at PHPA 1.1 wt%
- ▲ — Experimental values at PHPA 1 wt%
- ▼ — Theoretical values at PHPA 1 wt%
- ◄ — Experimental values at PHPA 0.9 wt%
- ► — Theoretical values at PHPA 0.9 wt%
- ◆ — Experimental values at PHPA 0.8 wt%
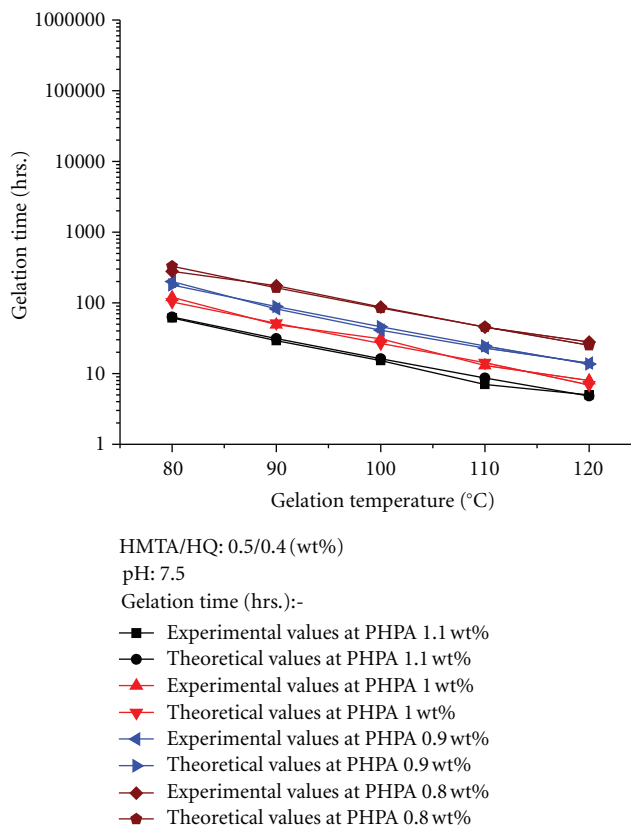- ⬠ — Theoretical values at PHPA 0.8 wt%

FIGURE 2: Plot of gelation temperature versus experimental and theoretical values of gelation time at different polymer concentration, constant crosslinker concentration (HMTA/HQ 0.5/0.4 wt%), and pH 7.5.

and temperature in case of polymer gel system used in the oil fields. For the successful design of the profile modification job the mathematical model equation consists of polymer and crosslinkers concentration as well as temperature is essential.

The present paper involves bulk gelation studies of the polymer gelant prepared from partially hydrolyzed polyacrylamide (PHPA) and hexamine (HMTA)/hydroquinone (HQ). The gelation time determined from the bulk gelation studies at different temperatures is useful because its knowledge at reservoir temperature is required to find out the depth up to which the gel can be placed in the petroleum reservoir rock. The gelation time and gel strength mainly depend on polymer and crosslinker concentrations and reservoir temperature were also reported in this paper. On the basis of the kinetics of polymer gel system, the mathematical model for the gelation behavior is also proposed which relates the gelation time with polymer-crosslinkers concentrations and temperature. The theoretical values of gelation time obtained from the proposed model matches with the experimental data.

2. Gelation Mechanism

The hexamine on hydrolysis yields formaldehyde which then combines with hydroquinone and form 2,3,5,6-tetramethylol hydroquinone. Further, partially hydrolyzed polyacrylamide reacts with 2,3,5,6-tetramethylol hydroquinone and forms three dimensional networks of polymer gel, the different steps of which are as follows.

Step I. In the initial step, hexamine hydrolyses to yield formaldehyde

$$\underset{\text{HMTA}}{(CH_2)_6 N_4} + \underset{\text{Water}}{H_2O} \longrightarrow \underset{\text{Methane diol}}{6OH-CH_2-OH} + 4NH_3 \quad (1)$$

$$OH-CH_2-OH \longrightarrow \underset{\text{Formaldehyde}}{H-CH=O} + \underset{\text{water}}{H_2O} \quad (2)$$

Step II. Formaldehyde produced in Step I then react with hydroquinone to form a condensed structure known as 2,3,5,6-tetramethylolhydroquinone (see Scheme 1).

Step III. The condensed molecule formed in Step II then reacts with PHPA to form the 3-dimensional gel structure which helps in profile modification jobs (see Scheme 2).

3. Development of Mathematical Model

The rate of gelation process for partially hydrolyzed polyacrylamide-hexamine-hydroquinone system may be present as follows.

$\alpha A + \beta B + \Upsilon C \rightarrow$ 3D gel structure
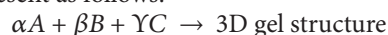
$$r_A = -\frac{dC_A}{dt} = kC_A{}^a C_B{}^b C_C{}^c, \quad (3)$$

where k is the reaction rate constant, C_A, C_B, and C_C denotes the concentration of partially hydrolyzed polyacrylamide,

Table 1: Experimental values of gelation time at different polymer concentration, temperature, and pH 7.5 (constant crosslinker concentration HMTA/HQ 0.5/0.4 wt%).

Sl. No.	Polymer PHPA (wt%)	Crosslinkers HMTA (wt%)	HQ (wt%)	Experimental values of gelation time (hrs.)	Theoretical values of gelation time (hrs.)	Temperature (°C)
1	0.8	0.5	0.4	280	328.8475	
2	0.9	0.5	0.4	200	178.3855	80
3	1.0	0.5	0.4	120	103.3145	
4	1.1	0.5	0.4	61	62.9199	
5	0.8	0.5	0.4	174.3	163.9435	
6	0.9	0.5	0.4	82.3	88.9322	90
7	1.0	0.5	0.4	49	51.4565	
8	1.1	0.5	0.4	29.3	31.3681	
9	0.8	0.5	0.4	87	84.8392	
10	0.9	0.5	0.4	41	46.0215	100
11	1.0	0.5	0.4	31	26.6282	
12	1.1	0.5	0.4	15.3	16.2326	
13	0.8	0.5	0.4	45.3	45.4394	
14	0.9	0.5	0.4	23	24.6489	110
15	1.0	0.5	0.4	13	14.2619	
16	1.1	0.5	0.4	7	8.6941	
17	0.8	0.5	0.4	28	25.1225	
18	0.9	0.5	0.4	14	13.6278	120
19	1.0	0.5	0.4	8	6.8917	
20	1.1	0.5	0.4	5	4.80681	

hexamine and hydroquinone and a, b, and c are the order with respect to A, B, and C, respectively. If the reactants are present in their stoichiometric ratios, they will remain at that ratio throughout the reaction [19]. Thus for reactants A, B, and C at any time,

$$\frac{C_B}{C_A} = \frac{\beta}{\alpha} \implies C_B = \frac{\beta}{\alpha} C_A, \qquad \frac{C_C}{C_A} = \frac{\gamma}{\alpha} \implies C_c = \frac{\gamma}{\alpha} C_A,$$
(4)

where α, β, and γ = reactant of species A, B, and C present in the reaction, respectively

$$r_A = -\frac{dC_A}{dt} = kC_A{}^a \cdot \left(\frac{\beta}{\alpha} C_A\right)^b \cdot \left(\frac{\gamma}{\alpha} C_A\right)^c$$

$$= k\left(\frac{\beta}{\alpha}\right)^b \left(\frac{\gamma}{\alpha}\right)^c \cdot C_A{}^{a+b+c}.$$
(5)

The above equation can be also written as

$$r_A = -\frac{dC_A}{dt} = k' C_A{}^n.$$
(6)

Taking integration both side w.r.t. time, we have

$$t = \frac{1}{(n-1)\, k'} \left\{ \frac{1}{C_A{}^{n-1}} - \frac{1}{C_{Ao}{}^{n-1}} \right\}.$$
(7)

Rearranging the above equation and putting the value of k' and n,

$$t = \frac{1}{k\{(a+b+c)-1\}} \left\{ \frac{C_A}{C_A{}^a \cdot C_A{}^b (\beta/\alpha)^b \cdot C_A{}^c (\gamma/\alpha)^c} \right.$$

$$\left. - \frac{C_{Ao}}{C_{Ao}{}^a \cdot C_{Ao}{}^b (\beta/\alpha)^b \cdot C_{Ao}{}^c (\gamma/\alpha)^c} \right\}.$$
(8)

Rearranging the above equation, we get

$$t = \frac{1}{k\{(a+b+c)-1\}} \left\{ \frac{C_A}{C_A{}^a C_B{}^b C_C{}^c} - \frac{C_{Ao}}{C_{Ao}{}^a C_{Bo}{}^b C_{Co}{}^c} \right\},$$
(9)

where C_{Ao}, C_{Bo}, and C_{Co} = initial concentrations of polymer, hexamine & hydroquinone.

By generalizing the above equation, it can be written as

$$t \propto \frac{1}{C_A{}^a C_B{}^b C_C{}^c}.$$
(10)

The effect of temperature (T in degree kelvin) can also be incorporated in (8) and Arrhenius model [19] can be utilized to connect k with T which is as follows:

$$k = A \exp\left(\frac{-E_a}{RT}\right),$$
(11)

TABLE 2: Experimental values of gelation time at different polymer concentration, temperature, and pH 7.5 (constant crosslinker concentration HMTA/HQ 0.5/0.3 wt%).

Sl. No.	Polymer PHPA (wt%)	Crosslinkers HMTA (wt%)	HQ (wt%)	Experimental values of gelation time (hrs.)	Theoretical values of gelation time (hrs.)	Temperature (°C)
1	0.8	0.5	0.3	312	376.7173	
2	0.9	0.5	0.3	230	204.3528	80
3	1.0	0.5	0.3	134	118.2393	
4	1.1	0.5	0.3	68	72.0791	
5	0.8	0.5	0.3	207	187.8085	
6	0.9	0.5	0.3	91	101.8779	90
7	1.0	0.5	0.3	55.3	58.9469	
8	1.1	0.5	0.3	33.3	35.9343	
9	0.8	0.5	0.3	101	97.1891	
10	0.9	0.5	0.3	55.3	52.7208	100
11	1.0	0.5	0.3	34	30.5045	
12	1.1	0.5	0.3	19	18.5956	
13	0.8	0.5	0.3	50	52.0539	
14	0.9	0.5	0.3	25.3	28.237	110
15	1.0	0.5	0.3	14.3	16.338	
16	1.1	0.5	0.3	8	9.9597	
17	0.8	0.5	0.3	32	28.7795	
18	0.9	0.5	0.3	14.3	15.6116	120
19	1.0	0.5	0.3	8.3	9.0329	
20	1.1	0.5	0.3	6.3	5.5065	

where E_a is an apparent activation energy and R is the gas constant. Therefore, the combination of (10) and (11), then we get

$$t \propto \frac{1}{C_A{}^a C_B{}^b C_C{}^c} \times \exp\left(\frac{E_a}{RT}\right). \tag{12}$$

The above equation can be written as follows, k'' is the proportionality constant:

$$t = k'' \frac{1}{C_A{}^a C_B{}^b C_C{}^c} \times \exp\left(\frac{E_a}{RT}\right). \tag{13}$$

Taking natural logarithm and introducing the coefficients a, b, c then we get,

$$\ln t = \ln\left\{k'' \frac{1}{C_A{}^a C_B{}^b C_C{}^c} \times \exp\left(\frac{E_a}{RT}\right)\right\}, \tag{14}$$

$$\ln t = a_0 + a_1 \ln C_A + a_2 \ln C_B + a_3 \ln C_C + \frac{a_4}{T}. \tag{15}$$

Taking antilog both sides and assume t then we get

$$t = C_A{}^{a_1} \times C_B{}^{a_2} \times C_C{}^{a_3} \times \exp\left(a_0 + \frac{a_4}{T}\right). \tag{16}$$

Equation (16) is the general equation for the gelation behavior of partially hydrolyzed polyacrylamide-hexamine-hydroquinone gel system. The value of constant depends upon the polymer and crosslinkers composition and temperature.

4. Solution Procedure of the Developed Model

The mathematical model for gelation time consists of four variable parameters (C_A, C_B, C_C, and T) and five constants (a_0, a_1, a_2, a_3, and a_4). For the determination of these constants, five simultaneous equations are generated by multiplying the variables in both side of the model equation and utilizing the experimental data, the flow diagram for solution of proposed model is shown in Figure 1. Further, these equations are solved by multivariate regression method and values of the constants a_0, a_1, a_2, a_3, and a_4 are determined. After putting these values in the model equation, the gelation time are calculated by varying the different parameters (C_A, C_B, C_C, and T). Finally, these calculated values are compared with the actual values obtained from the laboratory work.

5. Experimental Work

5.1. Material Used. The materials used for this work are partially hydrolyzed polyacrylamide, hexamine, hydroquinone, sodium chloride, hydrochloric acid, and sodium hydroxide. Partially hydrolyzed polyacrylamide is procured from Oil and Natural Gas Corporation Limited, Mumbai, India. Hexamine is purchased from Otto Kemi Mumbai, India and hydroquinone is procured from Ranbaxy Fine Chemicals Ltd., New Delhi, India. Hydrochloric acid is purchased from Central Drug house (P) Ltd. New Delhi, India. Sodium chloride is purchased from Nice Chemical Pvt. Ltd. Cochin, India and

TABLE 3: Experimental values of gelation time at different polymer concentration, temperature, and pH 7.5 (constant crosslinker concentration HMTA/HQ 0.4/0.4 wt%).

Sl. No.	Polymer PHPA (wt%)	Crosslinkers HMTA (wt%)	HQ (wt%)	Experimental values of gelation time (hrs.)	Theoretical values of gelation time (hrs.)	Temperature (˚C)
1	0.8	0.4	0.4	331	411.5734	
2	0.9	0.4	0.4	243	223.2606	80
3	1.0	0.4	0.4	140	129.1795	
4	1.1	0.4	0.4	77	78.7483	
5	0.8	0.4	0.4	226	205.1856	
6	0.9	0.4	0.4	105	111.3043	90
7	1.0	0.4	0.4	71	64.4011	
8	1.1	0.4	0.4	37.3	39.2591	
9	0.8	0.4	0.4	115	106.1816	
10	0.9	0.4	0.4	61	57.5989	100
11	1.0	0.4	0.4	37	33.3269	
12	1.1	0.4	0.4	23	20.3162	
13	0.8	0.4	0.4	56	56.8703	
14	0.9	0.4	0.4	30	30.8496	110
15	1.0	0.4	0.4	17	17.8497	
16	1.1	0.4	0.4	10	10.8812	
17	0.8	0.4	0.4	36	31.4424	
18	0.9	0.4	0.4	17	17.0561	120
19	1.0	0.4	0.4	9	9.8687	
20	1.1	0.4	0.4	7	6.016	

sodium hydroxide is purchased from S. D. Fine-Chem Ltd. Mumbai, India.

5.2. Experimental Procedure. Initially stock solution of partially hydrolyzed polyacrylamide was prepared in brine solution and kept for aging at ambient temperature for 24 hrs and further fresh solution of hexamine and hydroquinone were also prepared in brine. The appropriate solution of partially hydrolyzed polyacrylamide, hexamine, hydroquinone, and brine were thoroughly mixed at room temperature by magnetic stirrer. The pH of the gelant solution was measured by Century CP-901 digital pH meter and the pH of the gelant solution was adjusted by using 1 N sodium hydroxide and 1 N hydrochloric acid. Finally, the gelant solution was transferred into small glass bottle and kept at the desire temperature in the hot air oven (temperature ranges from 80˚C to 120˚C). Due to the increased temperature and the crosslinking reaction, gel formation takes place. The quality of gel was visually inspected at regular intervals and gelation time was noted. Here, the time for the formation of stiff/rigid gel was only considered.

6. Results and Discussions

The gelation behavior of the polymer gel system largely depends on the polymer-crosslinker concentrations and the temperature. The effects of these parameters on gelation time are described below.

6.1. Effect of Temperature on Gelation Time. Different gelling solutions were prepared with different concentrations of polymer and crosslinking agent at pH 7.5 and kept for gelation at different temperature. The reaction rate between amide group and methylol group was accelerated by increasing temperature and the gelation time decreased. Increasing the gelation temperature results in a decrease in gelation time since at higher temperature gels are formed in lesser time due to rapid crosslinking as is depicted in Figures 2 and 3 and Tables 1, 2, 3, 4, and 5. A possible explanation for rapid cross-linking is either due to an increase in molecular mobility or formation of new cross-linking sites as a result of gelation reaction. It is a known fact that degree of hydrolysis of the polymer increases at elevated temperatures which in turn increases the number of cross-linking sites that is found increasing the reaction rate and decreasing the gelation time.

6.2. Effect of Polymer Concentration on Gelation Time. The polymer concentration has a significant effect on the physical properties of gel. The polymer concentration increases and gelation time decreases were shown in Figure 4. The polymer concentration ranges from 0.8 to 1.1 wt% and constant concentration of crosslinker (0.5 to 0.3 wt% HMTA and 0.4 to 0.3 wt% HQ) at pH 7.5 are depicted in Tables 1 to 5. As the

TABLE 4: Experimental values of gelation time at different polymer concentration, temperature, and pH 7.5 (constant crosslinker concentration HMTA/HQ 0.4/0.3 wt%).

Sl. No.	Polymer PHPA (wt%)	Crosslinkers HMTA (wt%)	HQ (wt%)	Experimental values of gelation time (hrs.)	Theoretical values of gelation time (hrs.)	Temperature (°C)
1	0.8	0.4	0.3	370	471.4855	
2	0.9	0.4	0.3	286	255.7604	80
3	1.0	0.4	0.3	168	147.9839	
4	1.1	0.4	0.3	84	90.2116	
5	0.8	0.4	0.3	266	235.0542	
6	0.9	0.4	0.3	135.3	127.5067	90
7	1.0	0.4	0.3	78	73.7758	
8	1.1	0.4	0.3	42.3	44.974	
9	0.8	0.4	0.3	133	121.6383	
10	0.9	0.4	0.3	71	65.9835	100
11	1.0	0.4	0.3	42	38.1783	
12	1.1	0.4	0.3	27	23.2736	
13	0.8	0.4	0.3	60	65.1488	
14	0.9	0.4	0.3	35	35.3404	110
15	1.0	0.4	0.3	20.3	20.4481	
16	1.1	0.4	0.3	12	12.4652	
17	0.8	0.4	0.3	39	36.0194	
18	0.9	0.4	0.3	19	19.539	120
19	1.0	0.4	0.3	10	11.3053	
20	1.1	0.4	0.3	8	6.8917	

polymer concentration increases, it means more crosslinking sites are available for the fast crosslinking reaction takes place. Thus, the gel formation reaction increases, which leads to the decreases of gelation time. This trend is expected to be the same at all gelation temperatures under study. Thus, the required time to obtain a non-flowing polymer gel with a tolerable strength decreased when the polymer concentration was increased.

6.3. Effect of Cross-Linker Concentration on Gelation Time. Hexamine and hydroquinone crosslinkers are a multifunctional group which can build a complex network with amide groups of partially hydrolyzed polyacrylamide and form a 3-dimentional gel network structure. Crosslinker concentration has a significant effect on the gel strength. The crosslinker concentration increases and gelation time decreases were shown in Figure 5. The several samples were prepared to investigate the effect of crosslinker concentration on the network strength. Bottle testing results shown in Tables 1 to 5 indicate that when the concentration of both crosslinker was decreased the gelation rate and gel quality is also decreased. In other words, when crosslinking agent concentration was increased, the stage of polymer gel changed from a state of flowing gel to one of deformable non-flowing gel, because crosslinking sites are increased for the formation of gel in lesser time intervals.

7. Model Discussion

Equation (12) shows the relation of gelation time with polymer concentration, cross linker concentrations and temperature. Here, C_A, C_B, and C_C are polymers, HMTA and hydroquinone concentrations, respectively, in gm/litre and temperature, are taken in degree kelvin. This equation indicates that the gelation time is inversely proportional to the concentrations of polymer and crosslinking agent, which reflects that the increasing the concentration of polymer and crosslinking agent decreases the gelation time. The proposed model for the study of the gelation behavior of partially hydrolyzed polyacrylamide-hexamine-hydroquinone polymer gel system is shown in (15)-(16). The values of the constants/coefficients a_0, a_1, a_2, a_3, and a_4 are determined by multivariate regression method.

Equation (15) can be rewritten as follows:

$$y = a_0 + a_1 \cdot x_1 + a_2 \cdot x_2 + a_3 \cdot x_3 + a_4 \cdot x_4, \quad (17)$$

where

$$y = \ln t; \qquad x_1 = \ln C_A; \qquad x_2 = \ln C_B,$$
$$x_3 = \ln C_C, \qquad x_4 = \frac{1}{T}. \quad (18)$$

The above equation solved by multivariate regression method and the values of constants a_0, a_1, a_2, a_3, and a_4 are calculated.

TABLE 5: Experimental values of gelation time at different polymer concentration, temperature, and pH 7.5 (constant crosslinker concentration HMTA/HQ 0.3/0.3 wt%).

Sl. No.	Polymer PHPA (wt%)	Crosslinkers HMTA (wt%)	HQ (wt%)	Experimental values of gelation time (hrs.)	Theoretical values of gelation time (hrs.)	Temperature (°C)
1	0.8	0.3	0.3	451	629.6609	
2	0.9	0.3	0.3	362	341.5637	80
3	1.0	0.3	0.3	216	197.63	
4	1.1	0.3	0.3	111	120.476	
5	0.8	0.3	0.3	311	313.9109	
6	0.9	0.3	0.3	158	170.283	90
7	1.0	0.3	0.3	102	98.5264	
8	1.1	0.3	0.3	55.3	60.0621	
9	0.8	0.3	0.3	170	162.4459	
10	0.9	0.3	0.3	82	88.1198	100
11	1.0	0.3	0.3	58	50.9864	
12	1.1	0.3	0.3	30	31.0815	
13	0.8	0.3	0.3	86	87.0051	
14	0.9	0.3	0.3	66	57.1604	110
15	1.0	0.3	0.3	24.3	27.308	
16	1.1	0.3	0.3	15	16.6471	
17	0.8	0.3	0.3	45	48.1034	
18	0.9	0.3	0.3	23	26.094	120
19	1.0	0.3	0.3	14	15.098	
20	1.1	0.3	0.3	10	9.2038	

TABLE 6: Comparison of gelation time of developed model and Arrhenius type equation.

Temperature (°C)	Experimental gelation time (hrs.)	Theoretical gelation time (hrs.) by Arrhenius type equation {Civan et al. [18]} $\ln(t) = 8288.47281/T\ (°K) - 17.63044$ (0.8 wt% PHPA, 0.5 wt% HMTA and 0.3 wt% hydroquinone)	Theoretical gelation time (hrs.) by Developed Model (0.8 wt% PHPA, 0.5 wt% HMTA and 0.3 wt% hydroquinone)
80	312	343.66928	376.66426
90	207	180.07746	187.78207
100	101	97.68365	97.17542
110	50	54.70794	52.04664
120	32	31.55635	28.77554

The values of the constants a_0, a_1, a_2, a_3, and a_4 are found to be 1.77831, −5.19301, −1.00564, −0.47246 and 8926.87612, respectively and finally the gelation time is calculated from the following equation:

$$t = C_A^{-5.19301} \times C_B^{-1.00564} \times C_C^{-0.47246} \\ \times e^{(1.77831+(8926.87612/T))}. \tag{19}$$

The value of R^2 is 0.99122, which shows the good agreement between experimental and theoretical values of gelation time. This study reveals that the developed model may be used for the study of gelation behavior of partially hydrolyzed polyacrylamide-hexamine-hydroquinone gel system for its application in profile modification jobs. The theoretical

values calculated from above equation are shown in Tables 1–5 at different polymer-crosslinker concentration and temperature.

7.1. Comparison between Developed Model and Civan et al. [18]. The developed model in the present study relates stoichiometric relation between reactants involved in the gelation reaction as well as Arrhenius equation. In this case, gelation time is dependent on polymer and crosslinker concentration as well as temperature. However, model proposed by Civan et al. is simply Arrhenius type equation which is dependent on temperature only. Figure 3 shows the theoretical values of gelation time for different concentration of polymers. It was found that there are several variations
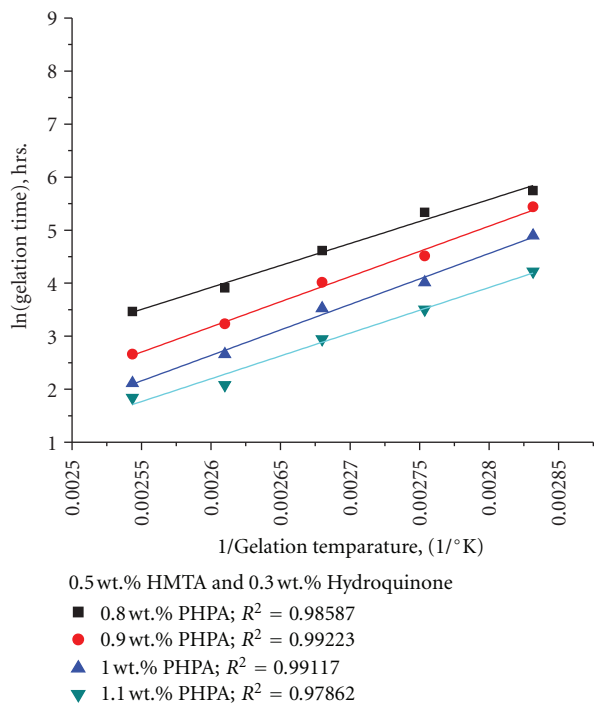
FIGURE 3: Plot for the temperature dependence of gelation time according to Arrhenius-type equation.
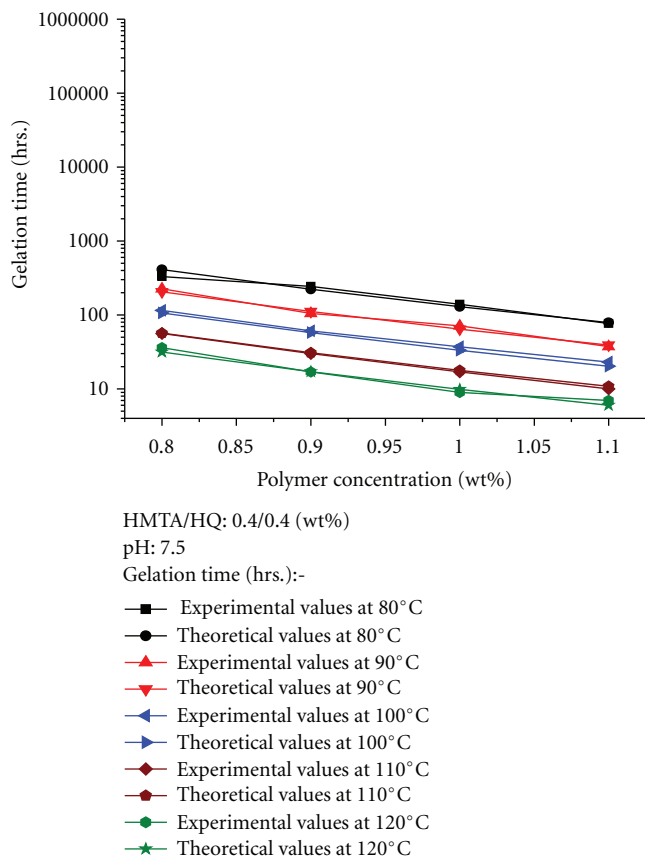

FIGURE 4: Plot of polymer concentration versus experimental and theoretical values of gelation time at different temperature, constant crosslinker concentration (HMTA/HQ 0.4/0.4 wt%) and pH 7.5.
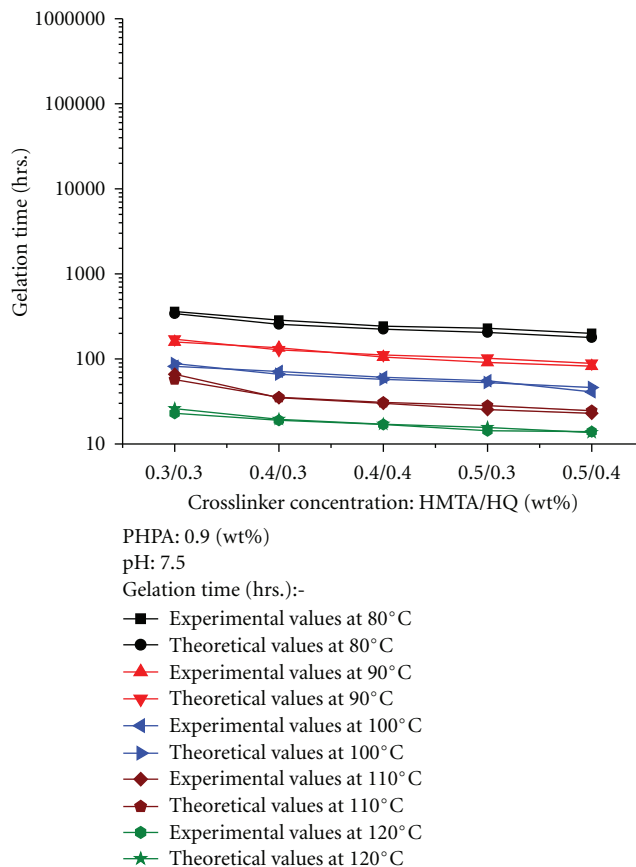

FIGURE 5: Plot of crosslinker concentration versus experimental and theoretical values of gelation time at different temperature, constant polymer concentration (PHPA 0.9 wt%), and pH 7.5.

in the values of slopes and intercepts as well as R^2 and may have different activation energy for different concentrations of polymers. The comparison of theoretical gelation time calculated using Civan et al. model and our developed model at the concentration (0.8% polymer) are approximately the same which is shown in Table 6 and have good agreement with that particular experimental data. But, the developed model presents the same values of coefficients and activation energy for whole experimental study and all data are fitted in that mathematical equation. Hence, it may be more realistic in nature.

8. Conclusion

The following conclusions are drawn from the present study.

(1) The gelation time of partially hydrolyzed poly-acrylamide-hexamine-hydroquinone gel system decreases with increasing the cross linker concentration and temperature.

(2) On the basis of kinetics of gelation behavior the mathematical model for the partially hydrolyzed

polyacrylamide-hexamine-hydroquinone gel system is the following:

$$t = C_A{}^{a_1} \times C_B{}^{a_2} \times C_C{}^{a_3} \times e^{(a_0 + (a_4/T))}. \tag{20}$$

(3) The values of constants a_0, a_1, a_2, a_3, and a_4 for this study are found to be 1.77831, -5.19301, -1.00564, -0.47246, and 8926.87612, respectively.

(4) The final mathematical model for the present study is as follows:

$$
\begin{aligned}
t = C_A{}^{-5.19301} \times C_B{}^{-1.00564} \times C_C{}^{-0.47246} \\
\times e^{(1.77831 + (8926.87612/T))}.
\end{aligned}
\tag{21}
$$

(5) A values show good agreement between experimental and theoretical values of gelation time. This study reveals that the developed model may be used for the study of gelation behavior of partially hydrolyzed polyacrylamide-hexamine-hydroquinone gel system for its application in profile modification jobs.

Nomenclature

C_A:	Concentration of partially hydrolyzed polyacrylamide (PHPA) (gm/liter)
C_B:	Concentration of hexamine (HMTA) (gm/liter)
C_C:	Concentration of hydroquinone (gm/liter)
t:	Gelation time (second)
T:	Temperature (°K)
k, k', k'':	Reaction rate/proportionality constants
C_{Ao}:	Initial concentrations of polymer
C_{Bo}:	Initial concentrations of hexamine
C_{Co}:	Initial concentrations of hydroquinone
E_a:	Activation energy
R:	Gas constant
a_0, a_1, a_2, a_3 and a_4:	Constants
a, b and c:	Reaction order with respect to A, B, and C
α, β and γ:	Reactant of species A, B and C present in the reaction respectively.

Acknowledgment

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