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Study on the Hydrolysis Degree of Polyacrylamide with High Temperature and High Salinity Reservoir

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Abstract: Polyacrylamide solution will have a stronger hydrolysis under the condition of high temperature, then hydrolysis degree increasing, when the degree of hydrolysis exceeds a certain value, the viscosity of the solution is on the decline. If the solution of high salinity, especially with high bivalent cation content (hardness), the viscosity declines substantially, even will produce precipitation which will make polymer lose oil displacement ability. The hydrolysis degree of polyacrylamide is an important factor affecting and limiting the use of polymer in high temperature reservoirs. By studying the theory of chemical reaction dynamics, the mathematical model of the hydrolysis degree of polymer has been established theoretically, influencing factors such as temperature, salinity, polymer solution concentration on hydrolysis degree of polymer have been simulated which provided the effective guidance for polymer under high temperature and high salinity reservoir.

Key words: Hydrolysis degree, salinity, high temperature and high salinity, mathematical model, polymer

INTRODUCTION

Polyacrylamide is linear organic synthetic polymer which has excellent flocculating performance, usually as a tackifier to use, is widely used in chemical, pharmaceutical, food, oil and other industries, especially for the three oil recovery technology in the petroleum industry, can improve the oil recovery (Reed and Healy, 1977; Soo and Slattery, 1978). Hydrolysis degree of polymer is an important parameter in determining the rheological behavior of polymer, adsorption and flocculation performance, directly influence the flocculation effect, anions produced by hydrolysis in aqueous solution can generate strong electrostatic repulsion, resulting in the coil expansion, causing the larger thickening effect (Hester *et al.*, 1994; Mei, 1982). But this anion radical repulsion significantly depends on the mineralization of water, especially the divalent ions in the water, the association of bivalent ions and carboxylic acid groups reduces the polymer water soluble which will precipitate when the degree of hydrolysis is high. The polymer has strong hydrolysis at high temperature conditions. When the degree of hydrolysis exceeds a certain value, the viscosity decreased. If the solution of high mineralization, especially with high bivalent cation content hardness, the viscosity declines substantially, even will produce precipitation which will make

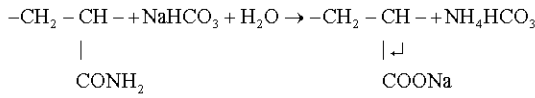
polymer lose oil displacement ability (Yang *et al.*, 1997; Zhang *et al.*, 1998). Hydrolysis is an important factor to influence and limit the polymer used in high temperature reservoirs. Therefore, the accurate determination of polymer hydrolysis degree of polymer is very important in the application. The hydrolysis degree of poly model of acrylamide has been deduced according to chemical reaction dynamics, influencing factors such as temperature, mineralization on hydrolysis degree of polymer have been simulated which provided an important reference value for polymer under high temperature and high salinity reservoir.

A MATHEMATICAL MODEL OF POLYMER HYDROLYSIS

The hydrolysis degree of polymer is defined as: In the hydrolysis of polymer molecules, the ratio of the number of carboxyl group m to n the total number of amide group before the hydrolysis expressed as a percentage. Using h to represent the degree of hydrolysis:

$$h = m/n \quad (1)$$

The polymer expressed with acrylamide monomer, the hydrolysis reaction equation can be simplified as:



The reaction was a second order reaction.

M stands for acrylamide monomer, N stands for NaHCO₃; The reaction initial concentration of M, N, respectively is C_{M0}, C_{N0}, after t time the concentration, respectively is C_M and C_N. By chemical reaction kinetics, the secondary reaction kinetics equation of the equation can be obtained:

$$-\frac{dC_M}{dt} = kC_M C_N \quad (2)$$

$$kt = \frac{1}{C_{M0} - C_{N0}} \ln \frac{C_{N0} C_M}{C_{M0} C_N} \quad (3)$$

The k in the formula is the reaction rate constant, each concentration is quality molarity (mol kg⁻¹).

By the definition of hydrolysis degree, in equation of the reaction, degree of hydrolysis at time t is:

$$h = \frac{C_{M0} - C_M}{C_{M0}} \quad (4)$$

$$C_M = C_{M0}(1 - h) \quad (5)$$

From equation(1-1), M and N is the reaction of the 1:1, namely:

$$C_{M0} - C_M = C_{N0} - C_N \quad (6)$$

$$C_N = (C_{N0} - C_{M0}) + C_M \quad (7)$$

Put Eq. 1-5, 1-7 into 1-3, get:

$$kt = \frac{1}{C_{M0} - C_{N0}} \ln \frac{C_{N0}(1-h)}{C_{N0} - C_{M0}h} \quad (8)$$

The mass ratio of sodium bicarbonate to polyacrylamide quality, expressed in b, set the mass percent concentration of polymer in the solution for c, the proportion of solution for γ. The molar mass of polyacrylamide known as 71 g mol⁻¹, sodium bicarbonate as 84 g mol⁻¹, there are:

$$C_{M0} = \frac{1000c(1-h_0)\gamma}{71} = 14.1c(1-h_0)\gamma \quad (9)$$

$$C_{N0} = \frac{1000c(1-h_0)b\gamma}{84} = 11.9c(1-h_0)b\gamma \quad (10)$$

Put Eq. 9-10 into 8, can get:

$$\ln \frac{11.9b - 14.1h}{1-h} = \ln(11.9b) + (11.9b - 14.1)c(1-h_0)\gamma kt \quad (11)$$

Order:

$$y = \ln \frac{11.9b - 14.1h}{1-h}$$

$$A = \ln(11.9b) \quad B = (11.9b - 14.1)c(1-h_0)\gamma k$$

Then:

$$h = \frac{e^y - 11.9b}{e^y - 14.1} \quad (12)$$

$$Y = A + Bt \quad (13)$$

Equation A and B have relations with the mass ratio of the sodium bicarbonate to polymer hydrolysis polymer solution concentration and the hydrolysis conditions such as hydrolysis temperature etc., when the hydrolysis conditions are fixed, A and B are constants.

According to the chemical kinetics, the reaction rate constant K depends only on the temperature, there is Arrhenius equation as follow:

$$\ln k = \frac{C}{T} + D \quad (14)$$

$$k = e^{\frac{C}{T} + D} \quad (15)$$

Among them, T is the absolute temperature, C and D is a constant. So, we can calculate the value of B. The degree of hydrolysis caused by alkali is:

$$h = \frac{e^{A+Bt} - 11.9b}{e^{A+Bt} - 14.1} \quad (16)$$

The total hydrolysis degree is equal to the sum of initial hydrolysis degree h₀ and hydrolysis degree h caused by alkali, then can get:

$$h = \frac{e^{A+Bt} - 11.9b}{e^{A+Bt} - 14.1} + h_0 \quad (17)$$

Wherein: A = ln(11.9b)

$$B = (11.9b - 14.1)c(1-h_0)\gamma e^{\frac{C}{T} + D}$$

- h = The hydrolysis degree of polyacrylamide caused by alkali, decimal
- b = The mass ratio of the sodium bicarbonate to polyacrylamide, decimal
- c = Mass percent concentration of polymer in the solution (%)
- γ = The proportion of solution, constant
- T = Temperature, K
- h_0 = The initial hydrolysis degree of polyacrylamide, decimal
- C, D = The experimental parameters

EXAMPLE ANALYSIS

When $T = 85$, $h_0 = 0.22$, $\gamma = 1.2$, $b = 0.3$, the relation curve of polymer hydrolysis degree along with the change of hydrolysis time is obtained by calculation of hydrolysis degree mathematical model under different concentrations, as shown in Fig. 1.

Figure 1 shows that polymer hydrolysis degree is gradually increasing with the increase of hydrolysis time, at the beginning of the hydrolysis, generally within 40–60 days, the increase amplitude of the hydrolysis degree is larger, in the following period of time, although the degree of hydrolysis also increases with the increase of hydrolysis time, but the increase amplitude is small, for example, when concentration of the polymer solution was 0.2%, Hydrolysis time is 60 days, hydrolysis degree increased to 47% and the final hydrolysis degree of the solution under this concentration is only 58%; Also can be seen from the figure, the hydrolysis degree of the high concentration polymer solution in the same time is higher than low concentration of polymer solution, such as hydrolysis time is 60 days, the hydrolysis degree of the largest concentration of polymer solution reached 47%, with minimal concentration of polymer solution hydrolysis degree was only 30%.

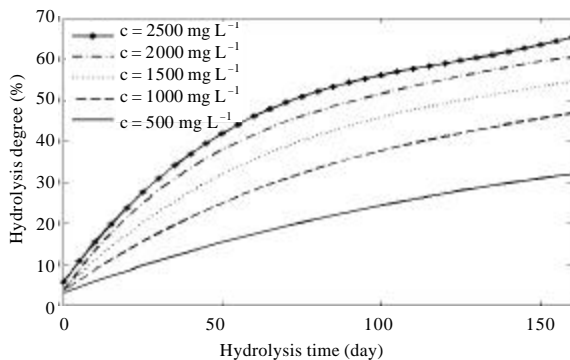


Fig. 1: Relation curve of polymer hydrolysis degree along with the change of hydrolysis time to under different concentrations

When $c = 1500 \text{ mg L}^{-1}$, $h_0 = 0.22$, $\gamma = 1.2$, $b = 0.3$, the relation curve of polymer hydrolysis degree along with the change of hydrolysis time is obtained by calculation of hydrolysis degree mathematical model under different temperatures (Fig. 2).

Figure 2 shows that polymer hydrolysis degree is gradually increasing with the increase of hydrolysis time, The higher the temperature, at the same hydrolysis time, the greater the hydrolysis degree of polymer solution; The lower the temperature, the smaller the hydrolysis degree of the polymer solution. As in the hydrolysis of 60 days, temperature, respectively in 55, 65, 75, 85 and 95, hydrolysis degree of polymer solution was 23.8, 27.4, 34.2, 41.3 and 49.6%, respectively.

When $c = 1500 \text{ mg L}^{-1}$, $h_0 = 0.22$, $\gamma = 1.2$, $T = 85$, the relation curve of polymer hydrolysis degree along with the change of hydrolysis time is obtained by calculation of hydrolysis degree mathematical model under different concentration of sodium bicarbonate as shown in Fig. 3.

Figure 3 shows under different mass ratio of sodium bicarbonate to polyacrylamide, hydrolysis degree

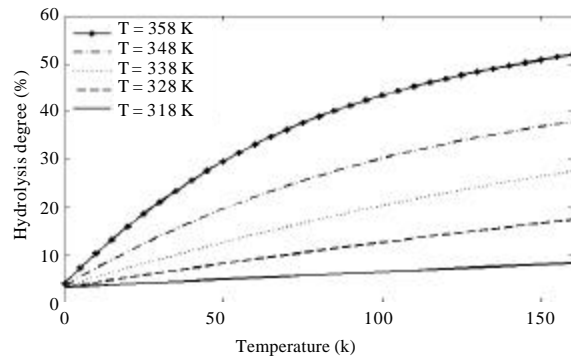


Fig. 2: Relation curve of polymer hydrolysis degree along with the change of hydrolysis time to under different temperatures

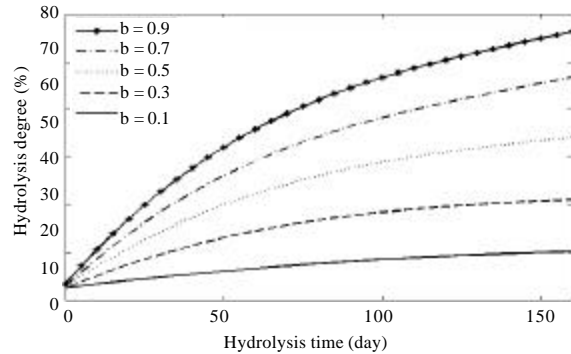


Fig. 3: Relation curve of polymer hydrolysis degree along with the change of hydrolysis time to under different concentration of sodium bicarbonate

increasing with the increase of hydrolysis time, the greater of the mass ratio of sodium bicarbonate to polyacrylamide, at the same hydrolysis time, the greater the hydrolysis degree of polymer solution; the smaller of the mass ratio of sodium bicarbonate to polyacrylamide, the smaller the degree of hydrolysis of the polymer solution. Such as hydrolysis in 60 days, under the condition of the mass ratio of the solution of sodium bicarbonate to polyacrylamide is 0.1, 0.3, 0.5, 0.1, 0.9, the degree of hydrolysis of polymer solution is 23.8, 32.2, 39.5, 47.4 and 54.3%, respectively.

CONCLUSION

This study established a mathematical model of the hydrolysis degree of polymer solution, simulation results of the model show that the longer the hydrolysis time, the greater the hydrolysis degree of the polymer solution. The initial hydrolysis rate is high, when hydrolyzed to a certain degree the hydrolysis rate at a slower pace, growth is leveling off. Under the same hydrolysis time, the lower the temperature, the lower the hydrolysis degree of polymer relatively, with the increase of temperature, hydrolysis rate accelerating, polymer hydrolysis degree increases; Mineralization degree is smaller, the lower the hydrolysis degree of polymer relatively, with the increase of mineralization degree, hydrolysis rate accelerating, polymer hydrolysis degree increases; hydrolysis degree of the polymer solution is proportional to the concentration, the higher concentration, the greater the degree of hydrolysis.

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