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ORIGINAL CONTRIBUTION

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Effect of carbon dioxide on rheological properties and structure of polyacrylamide solutions

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Abstract The effect of CO_2 on rheological properties and structure of polyacrylamide solutions was studied as a function of pressure, treating time, polymer type and presence of inorganic electrolytes and natural formation rocks. It was found that the serious deterioration of the solution viscosity can be attributed mostly to the change of the solution structure, while the actual molecular degradation plays negligible role in the process. The phenomena are explained by modification of the dissociation equilibrium of polyelectrolytes in presence of high hydrogen ion concentration. The experimental results may contribute significantly to elaboration of new stabilization concepts in special enhanced oil recovery technologies based on joint application of carbon dioxide and polymers.

Key words Carbon dioxide – polyacrylamides – rheological properties – solution structure – degradation

Introduction

In Hungary, carbon dioxide as a flooding media has been extensively used in enhanced oil recovery (e.g. [1, 2]). According to the general observations, however, the crucial problem of all industrial scale projects was the poor volumetric sweep efficiency of CO_2. To overcome this problem a logical idea was the joint application of CO_2 and polymers with the aim of improving simultaneously both the sweep and the displacement efficiency. Recently, similar ideas arose in connection with the water alternating gas injection (WAG). The enhanced mobility controlling effect of water soluble polymers is, however, maintained if the long-term thermal stability of polymer solutions is not questionable in presence of CO_2. Importance of such laboratory studies is reasonable because the literature [e.g. 3–5] paid little attention to the compatibility of CO_2/polymer systems. Therefore, a detailed research program was launched in the Research Laboratory for Mining Chemistry to study the stability of polyacrylamide solutions in presence of CO_2. Partial results of that investigation, particularly the effect of CO_2 on rheological and flow properties, have already been published [6]. Aim of the present paper is to survey the effect of CO_2 on solution structure of polyacrylamide solutions and to re-evaluate the earlier conclusions concerning both the rheological properties and the feasibility of polymer applications when CO_2 is present.

Since the interpretation of degradation is often not clear the methods used for stabilization of polymer solutions fail to work under reservoir conditions. Certain confusion derives from the fact that in petroleum engineering the degradation means a deterioration of viscosity, mobility, resistance factor, sweep efficiency, etc. On the other hand, the degradation as a term in chemical engineering is always used for structural change of the dissolved chemical agents. Inadequacy of these approaches should be traced back to the fact that the transport phenomena and modification of the solution structure may also result in a comparable effect. Therefore, the later problem is in the center of the present studies, proving the close correlation between the rheological properties and the solution structure in different polymer/CO_2 systems.

Experimental

The studies were focused on partially hydrolyzed polyacrylamides. The average molecular mass and the degree of hydrolysis of polymers applied as models are listed in Table 1. The stability tests were carried out in solutions made of ion-free, NaCl and HCl containing water. The sample solutions were thermal treated at 363 K temperature in stainless steel cell. The CO_2 supplied from high pressure container was of 99.98% purity. The polymer solutions were sampled at 0-0.5-1-2-5-7-10-24-48 h frequencies. In some cases the test cell also contained crude oil and reservoir rock (sandstone). The elemental composition (trace elements) of the samples was determined by flame AAS.

The degradation process was followed by rheological measurements performed at 298 K. The flow curves were determined by Contraves Low Shear 30 rheometer and the relative viscosity – shear rate relationship was described by the Carreau model [7]:

$$\eta_r = \frac{\eta_{r,0}}{[1 + (\tau_r \gamma)^2]^m} ,$$

where η_r = relative shear viscosity, $\eta_{r,0}$ = relative zero shear viscosity, γ = shear rate, 1/s, τ_r = rotation relaxation time, s, m = shear thinning index.

The characteristic flow curves obtained in the low shear rate range (10^{-3}–10^2 1/s) could be divided into three well-defined sections. According to the "network" concept [8, 9] developed for solutions containing flexible chain-like polymers the first and the second Newtonian flow section belongs to maximal and minimal intermolecular interaction, which corresponds to a network and a particulate solution structure. Accordingly, the non-Newtonian flow behavior of polymer solutions is interpreted by the gradually ceasing intermolecular interaction or disintegration of the network structure.

One of the greatest advantage of the Carreau model is that its characteristic parameters (rotation relaxation time and shear thinning index) can be easily determined by graphical technique [10]. Since the rotational relaxation time is a sensitive indicator of the solution structure, it can also be used to detect any changes in the molecular interaction. In this way, we may firmly say that at 1 g/l concentration used through the tests the polymer solutions represent quite different structured systems. Thus, the polymer AN-34 forms a typical network solution with a relaxation time of ≈ 10 s, while the polymer NP-10 remains basically in particulate state having a relaxation time close to 0.01 s (Fig. 1.). Since the absolute value of the relaxation time and its change within orders of magnitude is in direct connection with the solution structure, it might be used for characterization of the actual solution structure and the processes considered earlier exclusively as degradation.

Table 1 Molecular weight and degree of hydrolysis of polymers used as models

Polymer	Molecular weight 10^6 g/mol	Degree of hydrolysis %
NP-10	1.0	5–7
AP-30	3.5	30
AN-34	9.5	17

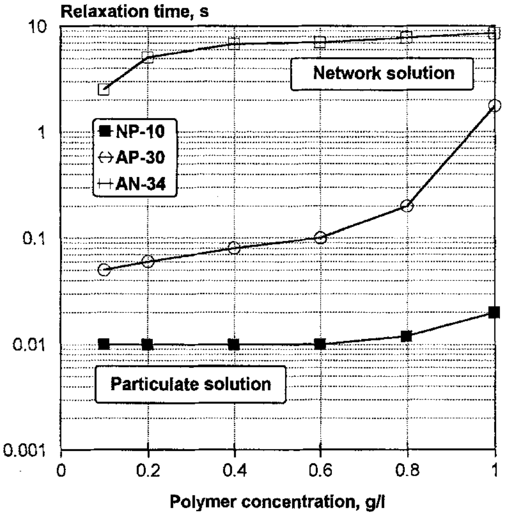


Fig. 1 Effect of polymer concentration on rotation relaxation time

Results and discussion

General features of degradation in presence of CO_2

On the basis of the earlier results [7] obtained under similar experimental condition the following conclusions were drawn:

1) In presence of CO_2 the partially hydrolyzed polyacrylamides apparently undergo a very serious degradation and surprisingly, its extend exceeds the measure found even in oxidative environment.

2) Deterioration of the flow properties in porous media is higher than the value predicted by the viscosity lowering.

3) The apparent degradation is increasing with the CO_2 pressure in range of 10–100 bar, but the change is relatively small.

4) The stability of polymer solutions deteriorates with the temperature. It is worthy mentioning, however, that there is no significant difference among the polymers as far as the tendency is concerned and the effect of temperature remains tolerable between 323 and 363 K.

Further, it was also indicated that during the thermal treatment dissolution of heavy metal ions (Fe, Cr, Ni, etc.) from the stainless steel container was negligible, viz. structural change or precipitation of polymers caused by the presence of these cations did not interfere with the actual processes.

Completing the rheological measurements in the entire shear rate range and plotting the $\lg\eta$–$\lg\gamma$ curves as a function of time the response surfaces shown in Fig. 2 were found. Analyzing these experimental results additional conclusions can be drawn:

5) Deterioration of viscosity depends significantly on shear rate. The greatest change is observed at the zero shear viscosity (first Newtonian section).

6) The apparent degradation is increasing with the degree of hydrolysis, while the molecular weight has a negligible effect on the process.

7) The rate of degradation is unexpectedly fast in the initial period, practically within 1–2 h and later on the changes become relatively small.

8) The most striking effect of CO_2 is that the non-Newtonian flow character of the polymer solutions almost completely disappear after 2 h thermal treatment.

The later observations seem to contradict the general experiences in degradation studies and they may suggest that not only a simple molecular fragmentation is in the background of the phenomena. To make evident this idea, additional arguments were tried by studying the salt effect. It is well known that the inorganic electrolytes through the salt effect influence drastically the structure and hence the viscosity of solutions containing ionized polymers. Therefore, the same polymer solutions having different NaCl content were thermal treated under identical conditions. As representative results of these test series the response surfaces obtained for NP-10 and AP-30 polymers are shown in Fig. 3. The new conclusions which we may draw are the following:

9) The stability of polymers and the polymer solutions improve significantly with increasing salt concentration.

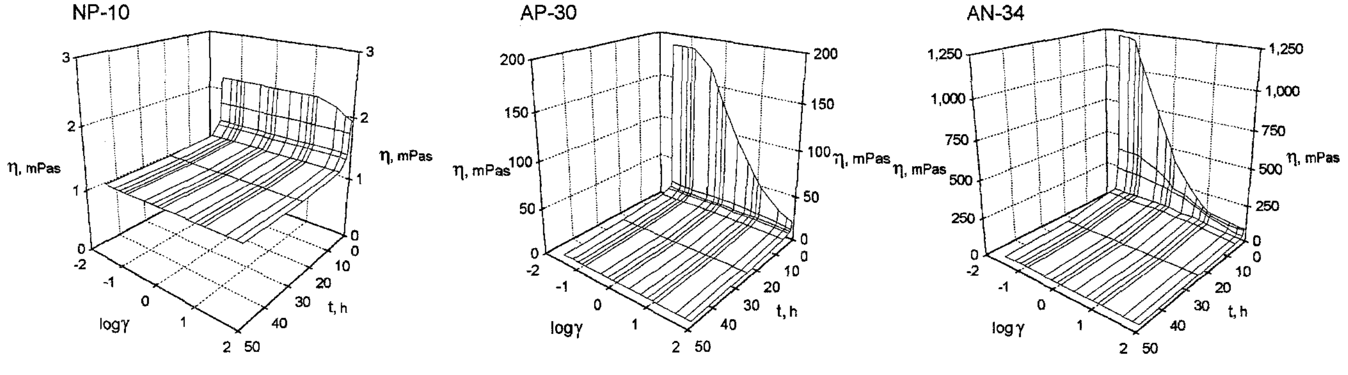
10) The partially hydrolyzed polyacrylamides show much higher improvement in stability than the slightly hydrolyzed ones do. Consequently, the non- or slightly hydrolyzed polyacrylamides are less sensitive to degradation than the highly hydrolyzed ones is.

The drastic effect of monovalent cations on viscosity of polyelectrolyte solutions logically raises an issue on similar influence of H^+ ions. The firm basis of such a suggestion is that dissolution of CO_2 in the aqueous phase leads to substantial increase of H^+ concentration. Consequently, a systematic study of the pH dependence of solution viscosity was necessary. The response surfaces obtained for viscosity-shear rate-H^+ concentration relationships are shown in Fig. 4 and they provide the following information:

11) An obvious parallelism between the effect of CO_2 and H^+ ion concentration.

12) Comparing the final results of thermal treatment in CO_2 atmosphere and setting the pH < 5.0 it was found that the absolute viscosities and depression of the non-Newtonian flow behavior are nearly identical.

Fig. 2 Dependence of the dynamic viscosity of different polymer solutions on shear rate and time of thermal treatment in presence of CO_2 ($c_p = 1$ g/l; $T = 363$ K; $p_{CO_2} = 100$ bar)



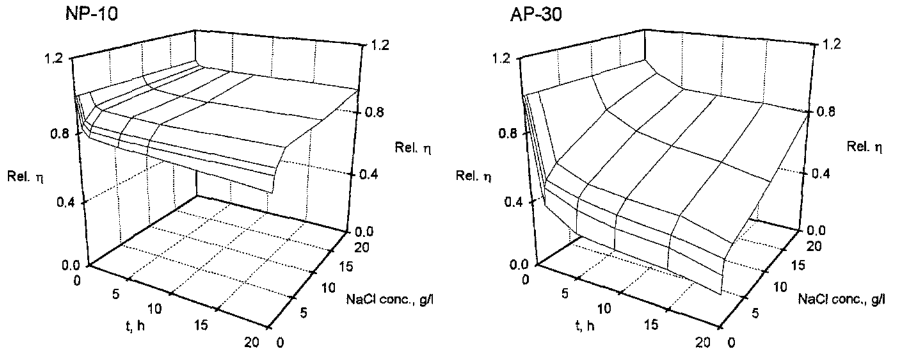


Fig. 3 Dependence of the relative zero shear viscosity of different polymer solutions on NaCl concentration and time of thermal treatment in presence of CO_2 ($c_p = 1$ g/l; $T = 363$ K; $p_{CO_2} = 100$ bar)

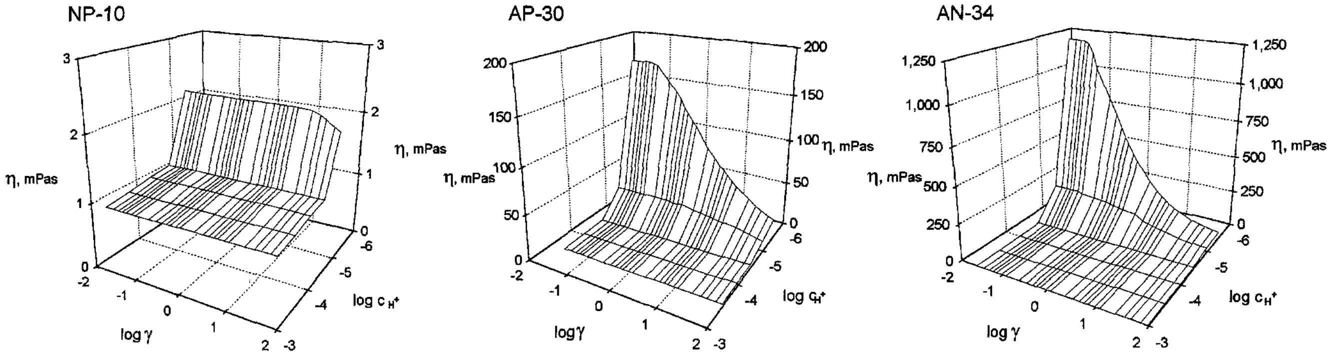


Fig. 4 Dependence of the dynamic viscosity of different polymer solutions on shear rate and H^+ concentration ($c_p = 1$ g/l; $T = 298$ K)

13) The sharp deterioration of viscosity in the initial period of thermal treatment may be attributed exclusively to dissolution of the gas and the tendencies reflect the kinetics of H^+ formation.

Degradation of polymers in highly acidic media is well known. However, in pH = 4–7 range an enhanced degradation of polymers is not probable. Rather, the pronounced influence of H^+ ions on dissociation equilibrium of ionized polymers is predominant. Accordingly, the effect of CO_2 on rheological properties of polyelectrolyte solutions should actually be explained by the later effect.

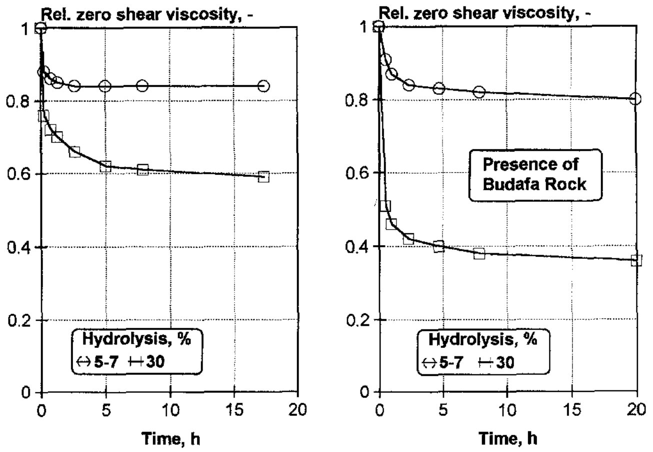


Fig. 5 Dependence of the zero shear viscosity on time of thermal treatment and degree of hydrolysis in rock-free and rock-containing system (polymer = NP-10 and AP-30; $c_p = 1$ g/l; $T = 363$ K; $p_{CO_2} = 100$ bar)

The laboratory investigations were also extended to analyze the effect of crude oil and formation rock on degradation. These materials were obtained from a Hungarian (Budafa) oil field. As expected, the presence of crude oil does not influence the stability of polymer solutions in CO_2 atmosphere. As far as the effect of formation rock is concerned it was found that deterioration of the solution viscosity is, however, more severe if formation rock is present in the system (Fig. 5). In addition, it was observed that the higher the degree of hydrolysis, the greater the influence of rocks on degradation. Simultaneously, with the rheological measurements the test solutions were also analyzed for the cation content by AAS. As illustrated in Fig. 6, the total concentration of bivalent cations (Ca^{2+} and Mg^{2+}) increases considerably in time and their similar but stronger effect on dissociation equilibrium of

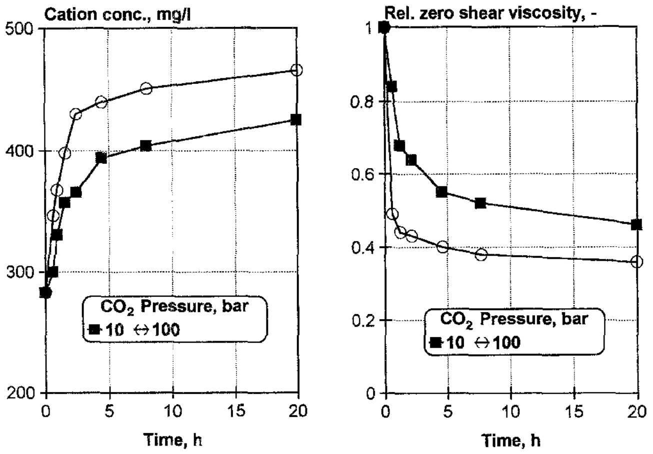


Fig. 6 Dependence of the zero shear viscosity and total cation ($Ca^{2+} + Mg^{2+}$) concentration on time of thermal treatment and CO_2 pressure (polymer = AP-30; $c_p = 1$ g/l; $T = 363$ K)

polyelectrolytes may sufficiently explain the experimental findings. It was also observed that the greater the CO_2 pressure, the higher the cation production in the cell and hence, more significant was the apparent deterioration of viscosity.

Effect of CO_2 on solution structure

As mentioned earlier, the model solutions having 1 g/l polymer concentration can be characterized by different structures. Therefore, it may be interesting to analyze the structural changes taking place under the thermal treatment in presence of CO_2. First, the effect of treatment time on relaxation time is illustrated in Fig. 7. The curves make possible to draw the following conclusions:

1) The rotation relaxation time decreases with the thermal treatment and approaches a limiting value.

2) Similarly to behavior of the viscosities the relaxation time drops down within the initial period of treatment.

3) Taking the absolute values into account the final relaxation times imply that at the end of treatment all polymer solutions have nearly particulate structure.

It might be interesting to compare the previous results with those obtained by NaCl, HCl and $CaCl_2$ addition (Figs. 8–10). The converging findings definitely prove the following statements:

4) The structure of polymer solutions is very close to the particulate state when $c_{NaCl} > 2\,10^{-2}$ mol/l (1.0 g/l), $c_{H^+} > 1\,10^{-3}$ mol/l, $c_{CaCl_2} > 4\,10^{-3}$ mol/l (0.5 g/l).

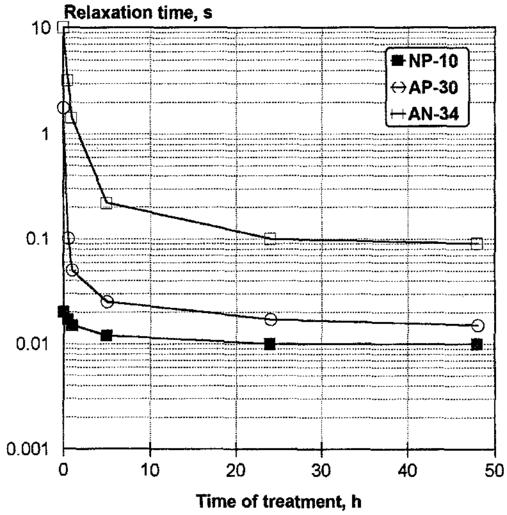


Fig. 7 Dependence of the rotation relaxation time on time of thermal treatment ($c_p = 1$ g/l; $T = 363$ K; $p_{CO_2} = 100$ bar)

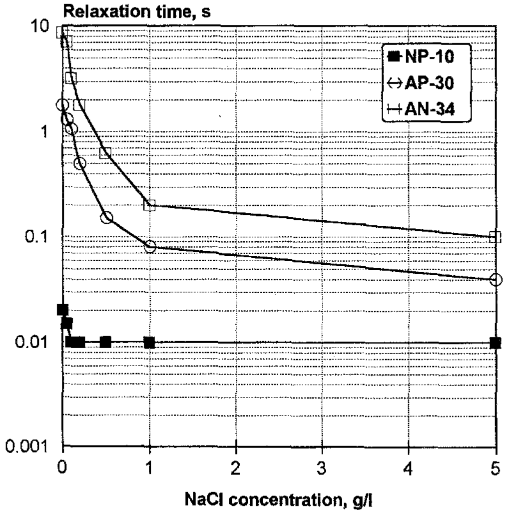


Fig. 8 Dependence of the rotation relaxation time on NaCl concentration ($c_p = 1$ g/l; $T = 298$ K)

5) Differences among the values above can be explained well by the dissociability of carboxyl group-cation bonds and the valency of cations.

6) The so-called "salt effect", namely the higher apparent stability of polymer solutions in presence of CO_2 must be attributed to the fact that the solutions to be tested are mostly in particulate state when the NaCl concentration exceeds 0.5 g/l. Thus, the H^+ ion concentration increasing gradually during the thermal treatment may have only a negligible influence on solution structure.

7) The effect of formation rock can be explained similarly as the influence of NaCl. The only difference is that

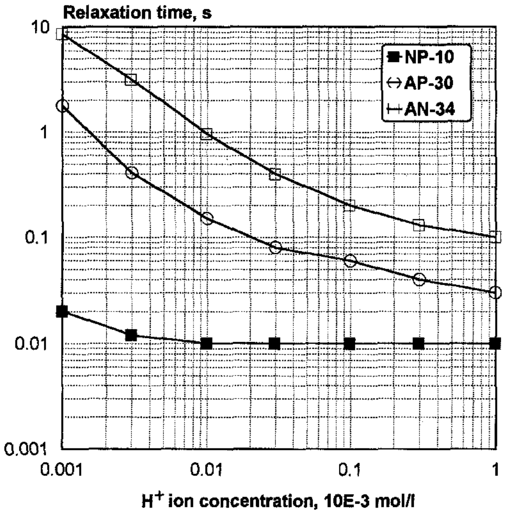


Fig. 9 Dependence of the rotation relaxation time on H^+ ion concentration ($c_p = 1$ g/l; $T = 298$ K)

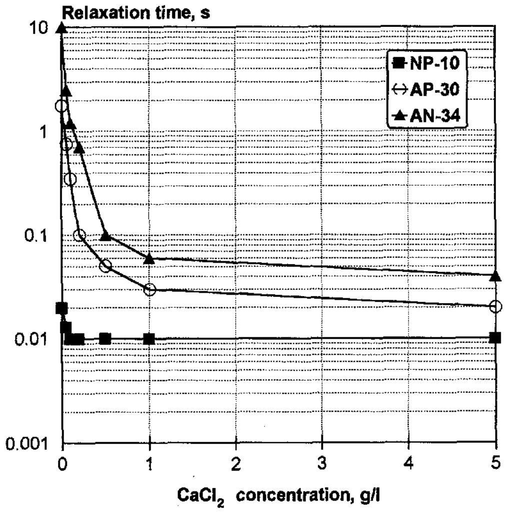


Fig. 10 Dependence of the rotation relaxation time on $CaCl_2$ concentration ($c_p = 1$ g/l; $T = 298$ K)

the structural change of polymer solutions is more pronounced on account of the higher valency and poorer dissociability of calcium cations attached to anionic groups of the polymer chain.

The experimental program was completed with thermal treatment of solutions having 0.3-0.5-0.7-1.0 g/l polymer and uniformly 1 mol/l $NaNO_3$ concentration. Then, using the Mark–Kuhn equation valid for polyacrylamides at 303 K temperature, the average molecular weight was calculated by the intrinsic viscosities. The final outcome of these studies can be summarized so that deterioration of the molecular weight is relatively great for high molecular weight and highly hydrolyzed polymers (AP-30 and AN-34), but its extent was always less than 40%. That value should be considered as an upper limit of real degradation. Since the rheological (and flow) properties of polyacrylamide solutions depend primarily on chain ionization, we may conclude that contribution of the actual chemical degradation to the final effect is secondary.

Classification of degradation phenomena

On the basis of the detailed studies, it can be concluded that the experimental findings are converging with the statements of Tolstikh et al. [11]. Namely, the following elements of the process can be differentiated:

1) Chemical degradation consisting of two parts:

a) Minimal chemical degradation which is independent of the salt content of the aqueous phase.

b) Excess chemical degradation depending mainly on the salt content and which is in an inverse ratio to the cation concentration.

2) Apparent degradation, which can be attributed to the dissolution of CO_2 into the aqueous phase leading to high concentration of hydrogen ions (and other rock constituents), deteriorating in this way the solution properties through alteration of the dissociation equilibrium of the partially hydrolyzed polyacrylamides.

The surprising phenomena proved satisfactorily is that the real chemical degradation represents usually a minor and constant share (~ 35–40%) in the total degradation. Consequently, the major part of the degradation can be classified as an apparent one deriving from the reversible structural change of polymer solutions.

As the practical application of polymer flooding is concerned it is concluded that high molecular weight unhydrolyzed or slightly hydrolyzed polyacrylamides must be used if the polymer may contact with CO_2. Another possibility is the use of large, CO_2-free spacers in flooding or in polymer assisted WAG. In heterogeneous porous systems the deeply penetrating and systematic local profile corrections using self-conforming gels also represent alternative techniques to cure the poor sweep efficiency of inmiscible gas flooding.

Conclusions

Effect of CO_2 on rheological properties and structure of different polymer solutions was studied with the aim of evaluating the joint application of CO_2 and partially hydrolyzed polyacrylamide in enhanced oil recovery.

On the basis of the experimental results the following conclusions were drawn:

1) The terms of degradation used in petroleum and chemical engineering are different and that fact may cause some confusion in both the interpretation of the phenomena and the technological concept applied for prevention of deterioration in flow properties of polymer solutions.

2) In presence of CO_2 the drastic worsening of the rheological and the flow properties can be attributed partially to real chemical degradation, however, the major factor is the reversible modification of the solution structure.

3) The network type polymer solutions become particulate systems if the polymer solutions get into a new chemical environment where the dissociation equilibrium of polyelectrolytes is significantly influenced by the mono- and bivalent cations (H^+, Na^+, Ca^{2+}, etc.).

4) In presence of CO_2 the effect of pressure, formation rocks, inorganic electrolytes and molecular structure of polymers can be explained correctly through the modification of the solution structure induced by the increased H^+ ion concentration and the excess dissolution of rock constituents.

5) The real chemical degradation represents a minor share (~35–40%) in deterioration of solution viscosities. Consequently, the major part of the unfavorable change can be classified as an apparent "degradation" deriving from the reversible structural modification of polymer solutions.

As the practical applications of polymers are concerned, it is concluded that high molecular weight unhydrolyzed or slightly (5–10%) hydrolyzed polyacrylamides must be used if the polymer may contact with CO_2. Another possibility is the use of large, CO_2-free spacers in flooding or in polymer assisted WAG. In highly heterogeneous porous systems a deeply penetrating and systematic local profile correction is also an alternative technique to cure the poor sweep efficiency of inmiscible gas flooding.

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