Effectiveness of polymer floods in oil recovery

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An attempt has been made to describe certain features of polymer solution behaviour on a molecular scale. A model proposed for drag reduction systems is used to describe macromolecular flow encountered in typical polymer floods for improved oil recovery. Experimental results suggest that the model is acceptable as a first approximation to the physical fact.

INTRODUCTION

The use of polymer additives in improved oil recovery processes has been practised for some time[1–21]. Polymeric materials modify the mobility ratio[21] and thus improve oil recovery. However, the economic feasibility of such operations is still being questioned. Given the above it seems surprising that (among other variables) the effect of polymer concentration on the extent of oil recovery has not been studied in any detail, although the potential benefits to be derived from the economical use of polymers are obviously great. The present paper considers the effect of polymer concentration on oil recovery.

THEORY

In the authors' view, any attempt to describe the effect of polymers on oil recovery should take into account events occurring at the molecular level. The literature provides scanty information on macromolecular behaviour under the conditions of flow in oil reservoirs. An explanation of plausible polymer flow behaviour on a molecular scale is attempted by analogy with the theoretical reasoning advanced in connection with a recent study on drag reduction[22].

It is being recognized that the presence of polymeric materials in a displacing fluid forms favourable conditions for a uniform sweep in pores of the matrix[1,2]. The higher effectiveness of polymer solutions as compared with conventional water floods is usually explained in terms of polymer size and the ratio of mean macromolecular diameter to mean pore opening[1]. Thus a typical polyelectrolyte when dissolved in water expands considerably, up to 0.2–0.5 μm (2000–5000 Å), and binds a great number of solvent molecules through electrostatic interactions. As a result, a large agglomerate is formed that behaves as an independent hydrodynamic unit. The improved recovery is then related to the presence of such units, the total effect being proportional to their number. In the study on using polymers as drag-reducing agents[22], it is assumed that the maximum drag-reduction effect is achieved when the number of hydrodynamic units present is sufficient for them to just touch each other in any unit of space. Under these circumstances, the solvent ceases to move freely, but becomes entirely trapped within the network of macromolecular chains. Such a condition will be referred to as a state of 'saturation'. The relevant polymer concentration will be termed C_s, where C_s defines a population of macromolecular units sufficient to satisfy a statistical probability that each unit is contiguous with its immediate neighbours.

It is recognized *a priori* that the effect of macromolecules in improved oil recovery processes, though similar, is not identical with that in drag-reducing systems. The solution saturation condition described above does not therefore necessarily constitute optimal conditions for oil recovery efficiency. The macromolecular units referred to above are inhomogeneous in terms of their mass density at the microscopic level (density increases sharply towards the centre of gravity). The conditions under which the hydrodynamic units establish contiguity (i.e. continuous surface contact) may not provide any significant improvement in mobility control in the contacting regions. This follows because macromolecules in contact still retain appreciable independent mobility, and may permit the creation of distinct oil and aqueous layers (fingering). In order to avoid this problem, the macromolecular units need not only be contiguous, but must also have limited or no independent mobility. This situation will exist when the individual hydrodynamic units are interpenetrated by additional polymer molecules and thus 'welded' into an interpenetrating network structure. Thus, it is proposed that for optimum oil recovery performance a polymer concentration must be achieved that is characterized by a state of complete molecular entanglement, and by homogeneous physical properties of the displacing fluid, even at the local molecular level. The corresponding polymer concentration, C_c, is denoted as the 'critical' value, and no further polymer addition above this should change the oil recovery effectiveness of the fluid in any significant way. The idea of a critical concentration would become more meaningful if it could be related to molecular parameters. An attempt to describe macromolecular behaviour under reservoir conditions in such quantitative terms is presented below.

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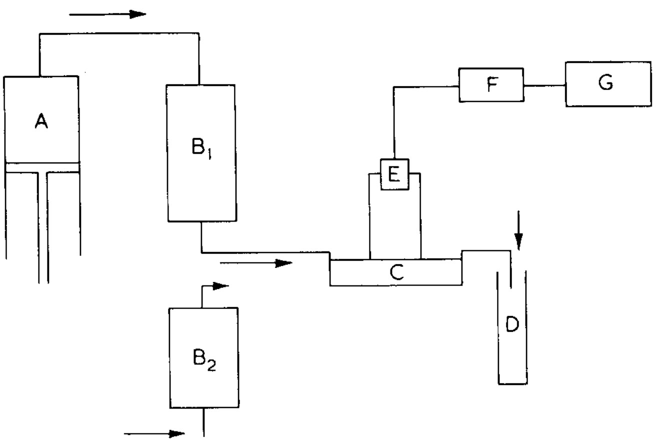

Figure 1 Schematic diagram of flow apparatus. A, Ruska proportioning pump (Ruska Instrument Corporation, Houston); B_1 hydraulic accumulator (fibre glass); B_2, hydraulic accumulator (steel) with plastic bag; C, Berea consolidated sandstone core encased in epoxy; D, graduated cylinder; E, pressure transducer (Validyne); F, transducer indicator (Validyne); G, strip chart recorder (Philips)

In spite of undeniable conceptual difficulties, the number of macromolecules accounting for the saturation state (C_s) defined above, can be estimated quantitatively. At saturation, it is assumed that any unit of volume, for example that of a pore, is entirely filled with the polymer-bearing solution. Were the carrier solvent not present, the number of macromolecules at saturation would be given by C_s/M_w and by their respective molecular volume V_m. The polymer agglomerates, however, are penetrated and swollen by the solvent; as a result the actual number of polymer molecules in a unit of volume will be reduced. This reduction is expressed as an efficiency factor characterizing the amount of solvent trapped within a macromolecule $\xi \leqslant 1$, leading to the concept that

$$\frac{(C_s)^{1/3}}{M_w} V_m \xi = \text{constant} \tag{1}$$

Following a line of reasoning similar to that presented in connection with drag reducing systems[22],

$$(C_s)^{1/3} |\eta| = \text{constant} \tag{2}$$

where $|\eta|$ is the intrinsic viscosity. In terms of equation (2), the product of intrinsic viscosity and the third root of polymer concentration corresponding to the state of saturation, and thus to optimum drag reduction, is constant for various polymeric materials and solvents. As previously explained, in oil recovery the most effective use of displacing fluids is observed at polymer concentration above the saturation level. By analogy with equation (2), the expression is rewritten

$$(C_c)^{1/3} |\eta| = \text{constant} \tag{3}$$

Note that the critical concentration, C_c, must be greater than the saturation concentration, C_s, although the ratio C_c/C_s cannot at this stage be expressed numerically. It will, at any rate, vary with the chemical composition and the morphology of the polymer, and with its molecular weight.

The main objective of the study is to determine whether or not the concept of critical polymer concentration, C_c, can be established experimentally. Any such evidence would support the reasoning leading to the suggested, complete penetration by polymer networks of the solvent matrix. Thus, experiments were designed to investigate the relationship between the amount of oil recovered and the concentration of various polymer solutions currently used in improved recovery schemes.

Experimental apparatus

Figure 1 shows main features of our apparatus: it consisted of a fibreglass cylinder containing a polymer solution, which was placed between the Ruska proportioning pump and the porous medium. All tubing was made of polyethylene to avoid metal contamination of polymer solutions. The pressure drop across the core was registered by a differential pressure transducer and was continuously monitored on a strip chart recorder. The study used a consolidated Berea sandstone core of rectangular shape (size 150 x 48.5 x 25 mm, permeability 766 md).

The core was heated up to 650°C initially, and kept at that temperature for several hours to deactivate clays and oxidize whatever organic materials might have been present. After thermal treatment, the core was encased in an epoxy resin core holder and subjected to further cleaning by the successive use of hydrochloric acid, brine, ethanol, and heptane.

A Cannon–Fenske viscometer (size 100, N 738) was used to determine the kinematic viscosities of polymer solutions; for the determination of oil viscosity, a Brookfield microviscometer (model LVT-CIP) was employed.

Viscosity against concentration plots for polyelectrolytes tend to be linear at low to moderate concentrations, but then viscosities increase strongly at very low polymer concentrations. Intrinsic viscosities $|\eta|$ were determined by extrapolating the linear portions of viscosity/concentration relationships to the limit of vanishing concentration. Screen factor[21] and pH measurements were made with the aid of a screen viscometer supplied by Dow Chemical Co and a Corning Model 12 pH meter, respectively.

Polymers and preparation of solutions

The polymeric materials that were used are identified in *Table 1*, which also lists their weight average molecular weight and some physical properties. M_w values are given as, in most cases, they were the only experimentally reliable characterization parameters available.

Table 1 Polymers used in experiments

Chemical type	Trade name	Manufacturer	Ionic type	Weight-average molecular weight, $M_w \times 10^{-6}$
Polyacrylamide	Pusher 500	Dow	Anionic	4.5–5.5
Polyacrylamide	Pusher 700	Dow	Anionic	3.0–4.0
Polyacrylamide	Reten 421	Hercules	Anionic	8.0–9.0
Polyacrylamide	Reten 425	Hercules	Anionic	6.0–7.0
Polyethyleneoxide	Polyox WSR-301	Union Carbide	Nonionic	4.0
Polysaccaride	Xanflood	Kelco	Slightly anionic	2.0

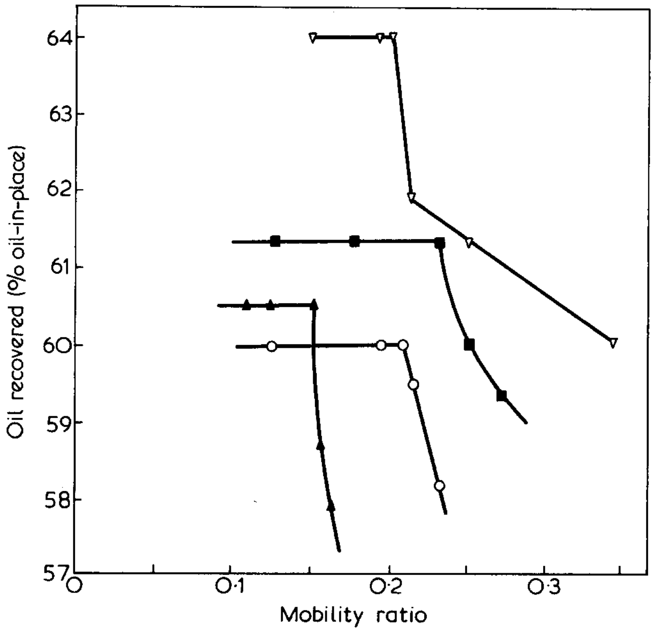

Figure 2 Variation of oil recovered with mobility ratio: effect of different polymers. ▽, Pusher 700 in 2% NaCl; ■, pusher 500 in 2% NaCl; ○, Reten 425 in 2% NaCl; ▲, Reten 421 in 2% NaCl

Fresh solutions were used in all experimental runs to avoid any possible degradation due to bacterial action. Solutions were prepared by using the standard laboratory technique as devised by Dow Chemical Co and Kelco Co[23]. In recognition of the high sensitivity towards shear degradation, special care was taken in preparing polyacrylamide and polyethylene-oxide solutions. Detailed procedures of preparation, given in Reference 23.

Hydrocarbon oil

In all experiments a refined hydrocarbon oil, Soltrol 130, was employed. This is a low viscosity oil that could be recovered efficiently without adjusting the mobility ratio.

Experimental procedure

The dry and clean core was initially saturated with the refined oil. A polymer solution was then introduced continuously at a constant volumetric flow rate of 8.9 ml/s. After polymer breakthrough had occurred, the pressure taps were connected to the pressure transducer to register the differential pressure drop. Polymer injection was continued until a constant differential pressure drop was attained.

After each run, the core was regenerated in a series of sequential steps. The regeneration procedure was designed so as to avoid changing the basic permeation characteristics of the core owing to residual sorption of polymer on pore surfaces. A 2.5% sodium hyprochlorite solution in 2% sodium chloride was injected into the core. Floods of isopropanol and heptane then followed, to ensure complete cleaning. The core was dried by a flow of nitrogen. Finally, the permeability was measured to check on differences from the initial state. A maximum variation of 4% from the original permeability was tolerated, otherwise the whole cleaning process was repeated. The detailed procedure is reported elsewhere[23].

RESULTS AND DISCUSSION

Figures 2 and *3* represent oil displacement efficiency as a function of mobility ratio (M) for all tested solutions (the low values of M should be noted). It is observed that increasing the polymer concentration lowers M, and results to some extent in increasing oil displacement efficiency. Apparently, the theory of mobility ratio reduction cannot by itself explain the mechanism of improved oil recovery at very low levels of M.

The pertinence of the concept of critical polymer concentration to oil-recovery as introduced above is indicated by *Figure 4*, which shows the relationship between polymer concentration and the displacement efficiency of oil recovery. Inspection of *Figure 4* suggests that, as expected, increasing efficiency is achieved at higher polymer concentrations. Moreover, the critical concentration is clearly defined by all the experimental curves; further increase in polymer concentration above the critical level does not result in any improvement of oil recovery. These results therefore follow closely the patterns of behaviour called for by the proposed theory, and establish convincingly the existence of the critical concentration. In turn, this lends credence to the concept of describing the role of polymers in the oil-recovery process in terms of effects occurring at a molecular level. No claim is made, of course, as to the completeness of the present working hypothesis as other factors, notably the question of interfacial tensions in the pore/oil/water-flood system, must play important parts in determining oil-recovery performance. A number of these additional problems is currently under active study.

Experiments with polyacrylamide confirmed that higher efficiency in oil recovery at any given polymer concentration is achieved with solutions of lower ionic strength. The phenomenon is attributed to variations in the degree of

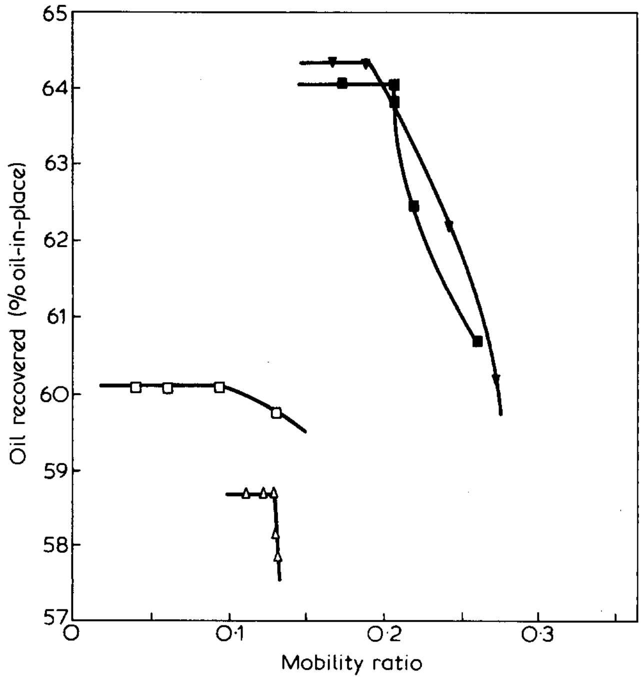

Figure 3 Variation of oil recovered with mobility ratio: effect of salt concentration and polymer type. △, Polyox WSR 301 (in 2% NaCl; ■, Pusher 700 in 6% NaCl; ▼, Pusher 700 in 1% NaCl; □, Xanflood in 2% NaCl

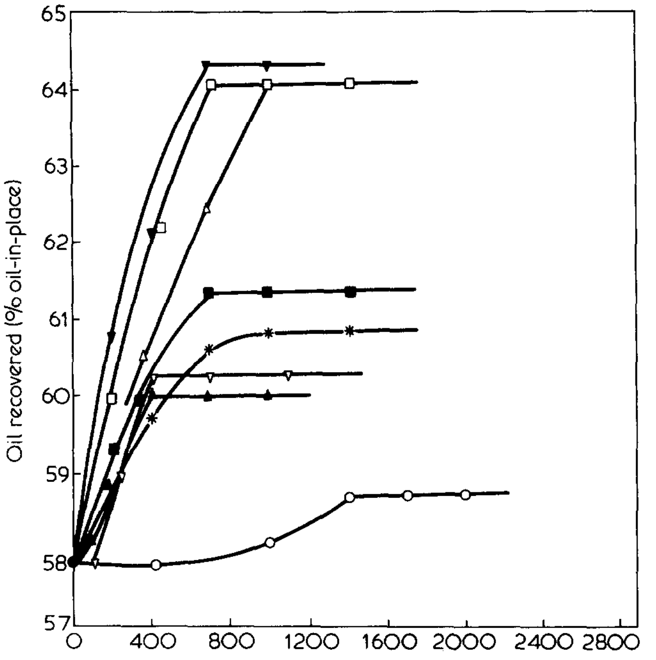

Figure 4 Effect of polymer concentration on displacement efficiency of polymer floods. ●, 2% NaCl; □, Pusher 700 in 2% NaCl; ■, Pusher 500 in 2% NaCl; ▲, Reten 425 in 2% NaCl; ▽, Reten 421 in 2% NaCl; ○, Polyox WSR 301 in 2% NaCl; △, Pusher 700 in 6% NaCl; ▼, Pusher 700 in 1% NaCl; *, Xanflood in 2% NaCl

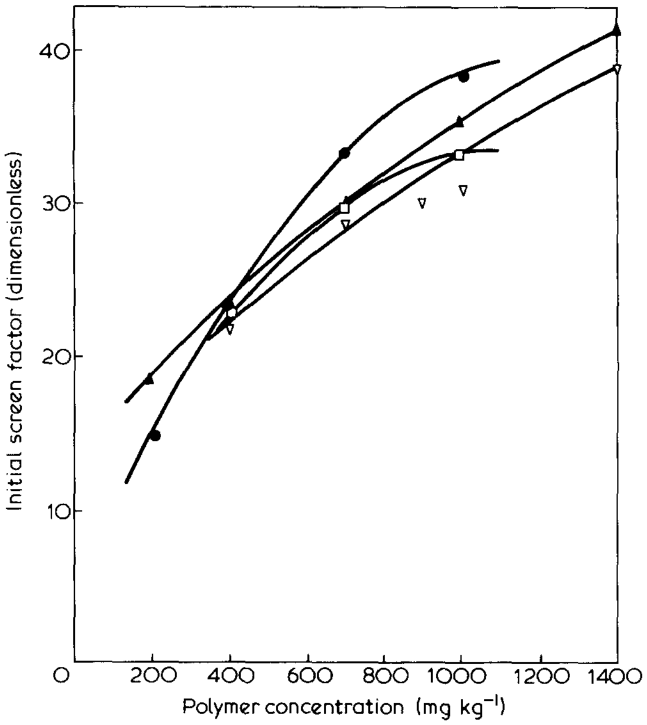

Figure 5 Effect of ionic strength on screen factor performance of polyacrylamide solutions. ●, Pusher 700 in 1% NaCl; ▲, Pusher 700 in 2% NaCl; ▽, Pusher 700 in 6% NaCl; □, Pusher 700 in 10% NaCl

molecular expansion. Overlapping of the curves for 2% and 6% NaCl solutions at polymer concentration equal to, or higher than, 1000 mg Kg^{-1} (*Figure 5*) suggests that there is no difference between the two in terms of the degree of molecular coiling. The higher efficiency of Pusher 700 seems to be linked to the high screen factors (*Figures 5* and *6*) of this particular polymer solution as compared with other tested materials. As the screen factors are qualitative indicators of normal stresses[10], it appears that solution elasticity is also an important parameter to be considered in designing a successful polymer flood.

The second objective of this study was to examine the validity of equation (3). The only parameters which could be (at least partly) controlled to influence $[\eta]$, were the macromolecular size, and brine concentrations. A variety of polymeric materials in solutions of different brine concentration were therefore used, so as to produce variations in intrinsic viscosity of the order of 3. The results are presented in *Table 2*. The other component of equation (3), the critical concentration, varied by as much as a factor of ten, depending on the conditions of experimentation. The variations in C_c and $[\eta]$ would allow for possible variations in the product by a factor of 6. In fact the products listed in *Table 2* show only a small scatter and may be judged as roughly constant near a value of 6.

The range of $[\eta]$ values was relatively small; in the analogous drag-reduction study[22] a more plentiful literature allowed the use of a wide $[\eta]$ range, with the similar result of confirming the validity of equation (2). Considering the simplicity of reasoning which leads to equations (2) and (3), the results are encouraging and the proposed mechanism of polymer behaviour under the given conditions is acceptable at least as a first approximation to the physical fact. Any attempt to use equation (3) for estimating critical polymer concentrations is limited by the present conditions of experiments, namely low M and the physical characteristics of the model porous medium.

Comparison of the given data with those obtained with drag reducing systems[22] shows that the ratio C_c/C_s is approx-

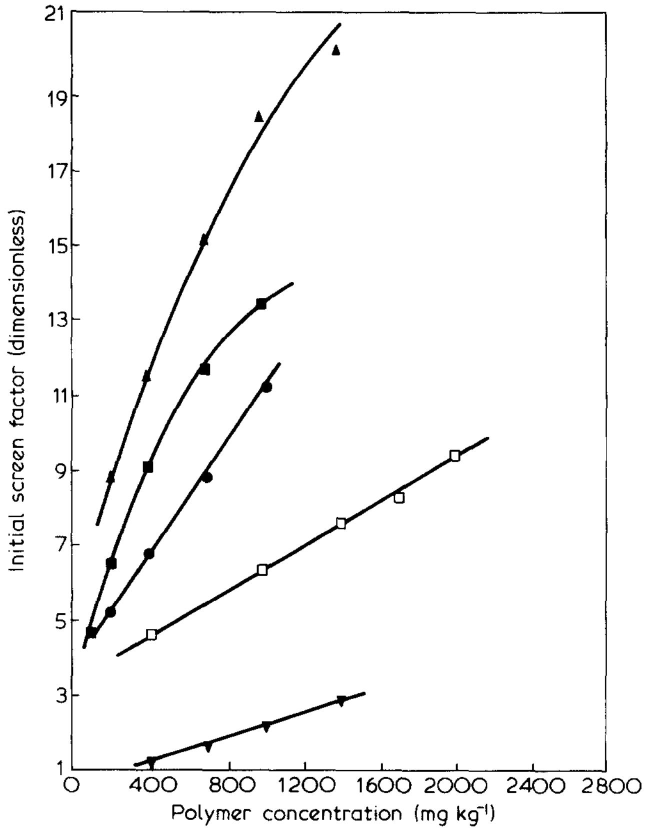

Figure 6 Comparison of screen factor vs. concentration relationships for selected polymer candidates. ▼, Xanflood; □, Polyox WSR 301; ■, Reten 421; ●, Reten 425; ▼, Pusher 500

Table 2 Values of $C_s^{1/3}\eta$ for different polymers in porous media

Polymer type	Critical concentration C_c (wt %)	$C_c^{1/3}$ (mg/kg)$^{1/3}$	Intrinsic viscosity η (dl/g)	$C_s^{1/3}\eta$
Pusher 700 (in 2% NaCl)	0.07	0.41	18.25	7.5
Pusher 500 (in 2% NaCl)	0.07	0.41	14.00	5.7
Pusher 700 (in 1% NaCl)	0.07	0.41	22.30	9.1
Pusher 700 (in 6% NaCl)	0.10	0.46	14.00	6.4
Reten 425 (in 2% NaCl)	0.04	0.34	14.50	5.0
Reten 421 (in 2% NaCl)	0.04	0.34	10.40	3.5
WSR 301 (in 2% NaCl)	0.14	0.52	7.50	3.9
Xanflood	0.10	0.46	19.00	8.7

Arithmetic average $C_s^{1/3}\eta = 6.3$
Standard deviation $s = 1.98$
Coefficient of variation $\nu = 31.6\%$

imately constant at a value of 3. While this value could not be predicted, it is reasonable since, as already noted, concentration in oil recovery must exceed the saturation value and thus contribute to a higher constant in the corresponding equation.

CONCLUSION

The existence of a critical concentration was established for all three main groups of polymers used in improved oil recovery schemes.

Experimental results warrant the further pursuit and development of ideas presented here into a more complete theory.

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