Role of Molecular Parameters during Flow of Polymer Solutions in Unconsolidated Porous Media

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Synopsis

In order to understand the molecular behavior of polymers during flow through porous media, five polymers with varying degree of amide-carboxylate group ratio in partially hydrolyzed polyacrylamides were selected, and the flow properties of their dilute solutions were measured in unconsolidated porous media. It has been found that adsorption of the polymers at the surface during flow, which plays an important role in permeability reduction, largely depends on the flexibility of the linear chains and electrostatic nature of the porous matrix. The flexibility of the chain is explained on the nature and ratio of groups attached on linear —C—C— chains, e.g., varying degree of NH_2 and COOH groups in partially hydrolyzed polyacrylamides in the experiment.

INTRODUCTION

In recent years, considerable interest has been generated in understanding the mechanism of permeability reduction by flow of dilute solution of high molecular weight polymers in porous media.[1-5] This is mainly due to the fact that one can recover a higher amount of oil from a reservoir by polymer flooding than by conventional water flooding through mobility control of the displacing fluid.[6-9]

Partially hydrolyzed polyacrylamide polymers control the mobility of the flooding solution not only by increasing the viscosity of the solution but also by reducing permeability of the porous media.[8-11] It has been reported that permeability reduction is mainly due to adsorption and/or mechanical entrapment of the polymer molecules within the void space of the porous media.[12-14] However, the role of molecular–surface interaction creates further resistance in the flow of polymer solution through porous media, the mechanism of which has not been fully investigated so far.

Therefore, in order to understand the role of polymer molecules, polymers with different chemical structures were selected in the measurement of flow properties in unconsolidated porous media. As the surface of porous matrix also exerts its influence in the interaction with the molecule, the study was conducted with the same porous materials having one of the surfaces changed by physical treatment. The results are given in this paper.

EXPERIMENTS

In the present study, flow experiments were conducted on unconsolidated silica sands of (−100 + 200) mesh size with solutions of five partially hydrolyzed polyacrylamides, viz., polyacrylamide, Separan MG-200, Pusher 700, Pusher 500, and polyacrylic acid in an air-circulated bath maintained at 38°C.
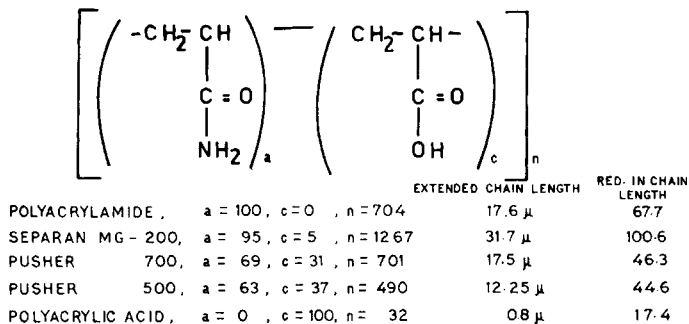
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$$\left[\left(\begin{array}{c} -CH_2-CH \\ | \\ C=O \\ | \\ NH_2 \end{array} \right)_a - \left(\begin{array}{c} CH_2-CH- \\ | \\ C=O \\ | \\ OH \end{array} \right)_c \right]_n$$

				EXTENDED CHAIN LENGTH	RED. IN CHAIN LENGTH
POLYACRYLAMIDE,	a = 100,	c = 0	, n = 704	17.6 μ	67.7
SEPARAN MG - 200,	a = 95,	c = 5	, n = 1267	31.7 μ	100.6
PUSHER 700,	a = 69,	c = 31	, n = 701	17.5 μ	46.3
PUSHER 500,	a = 63,	c = 37,	n = 490	12.25 μ	44.6
POLYACRYLIC ACID,	a = 0	, c = 100,	n = 32	0.8 μ	17.4

Fig. 1. Structure of partially hydrolyzed polyacrylamides. Length of 1 mer unit $CH_2CHCONH_2$ or $CH_2CHCOOH$ is 2.5 Å.

The porous media was prepared by carefully packing the unconsolidated sands of (−100 + 200) mesh size in a long glass tube (50 cm long and 3.5 cm internal diameter) by displacement of brine. To ensure informity in packing, the sands were added by a small amount at a time into the tube filled with brine. The tube was placed vertically and the lower outlet displaced the excess brine due to addition of sands. This wet packing method was found very suitable, and any fracturing or channeling in the packing was avoided.[15]

The sands were obtained by grinding iron-free sandstones and further purified for iron impurities by washing with hot hydrochloric acid. The size of the particles were assessed by dry sieving. The clay particles were removed by repeated washing with tap water and then finally with distilled water. The sands were analyzed and found to be 99.24% silica, 0.5% alumina, and 0.26% ferric oxide.

Another sand pack was prepared with silica sands of same mesh size but pretreated with crude oil to understand its effect on sand surface. Silica sands, after keeping in contact with crude oil for a week, were washed several times with tap water, hot dilute hydrochloric acid, and then ringed again with tap water and finally with distilled water. The length and diameter of the pretreated sandpack was 45 cm and 3.4 cm, respectively.
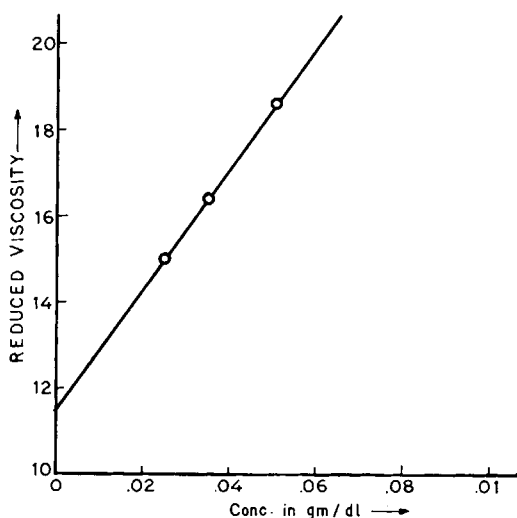

Fig. 2. Reduced viscosity vs. conc of Pusher 500 in 1% brine at 38°C. $[\mu] = 11.5$ dL/gm; $\sqrt{r^2} = 8(M[\mu])^{1/3} = 8(3.5 \times 10^6 \times 11.5)^{1/3} = 0.2744$ μm.

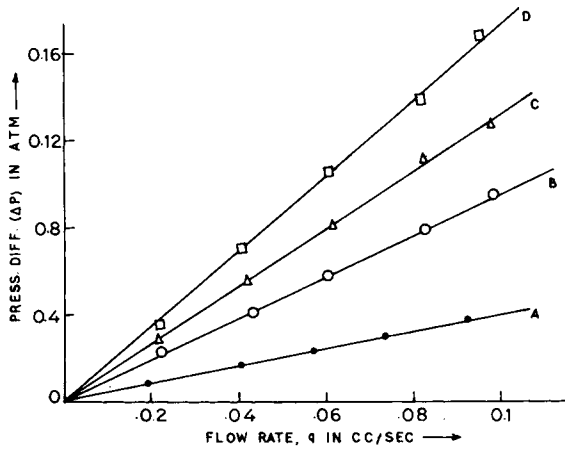Fig. 3. Flow of Pusher 500 soln through (−100 + 200) mesh sand pack.

		μ	R	k
A	brine	0.6931	—	8.79
B	250-ppm polymer soln	0.9519	2.35	5.16
C	350-ppm polymer soln	1.0899	3.25	4.26
D	500-ppm polymer soln	1.3351	4.24	3.99

Fresh solution of the polymers were prepared in 1% NaCl water by slowly stirring with a magnetic stirrer over 24 h in a dark environment to achieve complete hydration. Before using, the polymer solutions were filtered through hundred mesh screen. A small amount (0.5 cc) of 37% formaldehyde was added per liter of the solution to prevent oxidative degradation.[16] 1% brine was used as solvent throughout the experiment.

Five polymer solutions with different concentrations were injected by a mini reciprocating pump at a constant flow rate, and the rate of injection was measured by noting the volume of effluent solution and time of collection. The pressure difference across the tube was noted with the help of a manometer. To minimize the end effect, two ends of the manometer were placed at the two points approximately 10 cm away from the ends.

Permeability of the porous packs were restored after each run of polymer flow by flushing several pore volumes of brine, chlorox solution, and brine subsequently. 4% chlorox solution was adopted for cleaning the porous matrix.[17]

TABLE I
Characteristic Properties of Polymers Used

Polymers	Molecular weight	Degree of hydrolysis (%)	Intrinsic viscosity (dL/gm)	Molecular diameter in solution (μm)
Polyacrylamide	5×10^6	0	7.0	0.26
Separan MG-200	9×10^6–10×10^6	5	6.8	0.315
Pusher 700	4.5×10^6–5.5×10^6	31	21.0	0.3776
Pusher 500	3×10^6–4×10^6	37	11.5	0.2744
Polyacrylic acid	0.23×10^6	100	0.82	0.046
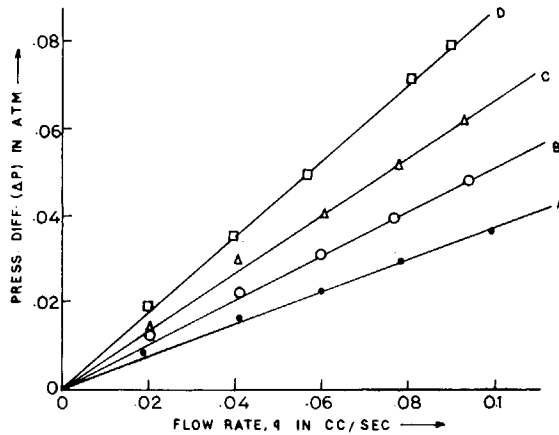
Fig. 4. Flow of Pusher 500 soln through (−100 + 200) mesh pretreated sand pack.

		μ	R	k
A	brine	0.6931	—	9.28
B	250 ppm	0.9519	1.36	8.58
C	350 ppm	1.0899	1.80	8.12
D	500 ppm	1.3351	2.35	7.61

RESULTS AND CALCULATIONS

Molecular characteristics of the five partially hydrolyzed polyacrylamides are given in Table I and their structures are shown in Figure 1. The molecular diameter, or more correctly, root-mean-square end-to-end distance, of the polymers was determined using Flory's equation[18]:

$$d_p = \sqrt{\bar{r}^2} = 8(M[\mu])^{1/3} \tag{1}$$

Though the equation is valid for noncharged polymers, it can be used satisfactorily for partially hydrolyzed polyacrylamides in brine since the charge on the polymer chain is screened at least partially by oppositely charged ions of the electrolyte.[15] For the purpose, intrinsic viscosity was determined by plotting reduced viscosity vs. polymer concentration. One typical curve is shown in Figure 2.

Permeability of the porous media was determined by Darcy's equation for laminar and linear flow of noncompressible fluids through homogeneous porous media under the steady state condition[19]:

$$\Delta P = \frac{\mu}{k} \cdot \frac{L}{A} \cdot q \tag{2}$$

Permeability was determined from the slope of the ΔP vs. q plot for the flow of a particular liquid when the steady state condition was achieved. Two typical curves of polymer flow in fresh and pretreated sandpacks are given in Figures 3 and 4.

Viscosity of the liquid was determined by using an Ostwald Viscometer kept in a water bath at 38°C. Porosity of the pack was determined from the volume of brine displaced by the addition of sand during packing in the brine-filled tube and from the total volume of tube used.[14]

The pore diameter (more correctly, mean hydraulic diameter) of the porous media was calculated using the Kozeny–Carman equation[19]:

$$d_h = 2r_h = 2\left(\frac{kK_z}{\phi}\right)^{1/2} \tag{3}$$

The resistance factor was determined from the ratio of the pressure drop for the polymer solution flow to that of the brine flow at the same rate of injection in the same sand pack, i.e.,

$$R = (\Delta P)_p/(\Delta P)_b \tag{4}$$

Similarly, the residual resistance factor was calculated from the ratio of the pressure drop for the brine flow after and before polymer treatments.[14] All these flow parameters for fresh and pretreated sandpacks are given in Tables II and III.

DISCUSSION

Porous media, for simplicity's sake, have been regarded as a bundle of capabilities forming the flow path of the media.[19] The pore diameter of the unconsolidated packings of our porous matrix are found to be about 20 μm. So, there is a considerable difference between average pore diameter of the porous media and average diameter of the polymer molecule, but still there is an appreciable reduction of permeability of porous media during the flow of the polymer solution. On subsequent flow of several pore volumes of brine it is observed that the permeability reduction of porous media persists.[5] This reduction in permeability may be interpreted as a reduction of effective pore diameter of the porous media, and this can be explained by mechanical entrapment and physical adsorption of the polymer molecules.[12–14]

As the pore diameter obtained by the Kozeny–Carman equation is only the average value, it is reasonable to assume that there might be some pores that have very small sizes compared to the average value. These small pores form small channels that are almost blocked when the polymer front penetrates into the small channels. Also there are pores that have inlets large enough to allow polymer molecules to enter, but outlet openings are small enough to trap the polymer molecules. With higher polymer concentrations, the entrapment is also increased, causing greater reduction of permeability. Reasoning in the same fashion, the greater reduction of permeability in the media can be explained with higher molecular size of the polymer. This "pore throat entrapment" theory[12,20] is in harmony with our experimental data. Pusher 700 is found to decrease the permeability to a greater extent than the other polymers mainly due to its bigger size of molecules.

The nature of adsorption at the surface is largely dependent on the nature of polymer molecule and of the porous matrix surface. Eirich et al.[21] have noted that only one portion of the functional groups of a polymer molecule is in contact with solid surface and the rest of the polymer segments are in the bulk solution, facilitating the entanglement of other flowing polymer molecules. The salt concentration also helps in physical adsorption by reducing highly repulsive forces of —COO^- groups in partially hydrolyzed polyacrylamide and may also change the characteristics of the virgin rock. One can then fairly assume that adsorption is largely due to the net residual electronic charge of the polymer molecule as well as the rock in the dynamic flow conditions.

TABLE II

Flow Parameters in (−100 + 200) Mesh Unconsolidated Silica Sand Pack[a]

Type of polymer	Conc of polymer solutions (ppm)	Viscosity (μ) of polymer solution (cp)	Resistance factor (R)	Residual resistance factor (R_r)	Permeability (k) (darcy)	% of perm reduction	Pore diam (d_h) (μm)	Pore diam reduction (%)	Molecular diam (d_p) of polymers (μm)
Polyacrylamide	250	0.7746	1.27		7.69	12.5	18.79	6.42	
$M = 5 \times 10^6$	350	0.8799	1.47	1.13	7.60	13.5	18.68	6.97	0.260
$\alpha = 0\%$	500	0.9683	1.65		7.45	15.2	18.49	7.92	
Separan MG-200	250	0.8399	1.65		6.42	26.9	17.17	14.49	
$M = 9 \times 10^6$	350	0.9173	2.01	1.20	5.79	34.1	16.30	18.82	0.3152
$\alpha = 5\%$	500	1.0473	2.53		5.25	40.3	15.52	22.71	
Pusher 700	250	1.1059	6.42	3.85	2.19	75.1	10.03	50.05	0.3776
$M = 5 \times 10^6$ $\alpha = 31\%$	350	1.2942	8.79		1.87	78.7	9.26	53.88	
Pusher 500	250	0.9591	2.35		5.16	41.3	15.39	23.36	
$M = 3.5 \times 10^6$	350	1.0899	3.25	1.63	4.26	51.5	13.98	30.38	0.2744
$\alpha = 37\%$	500	1.3351	4.24		3.99	54.6	13.53	32.62	
Polyacrylic acid	250	0.7049	1.41		6.32	28.1	17.03	15.19	
$M = 0.23 \times 10^6$	350	0.7083	1.40	1.29	6.41	27.1	17.15	14.59	0.046
$\alpha = 100\%$	500	0.7118	1.38		6.55	25.5	17.33	13.69	

[a] Porosity (ϕ) = 43%; brine permeability (k_b) = 8.39 darcy; pore diameter (d_h) = 20.08 μm.

TABLE III
Flow Parameters in (−100 + 200) Mesh Sand Pack Pretreated with Crude Oil[a,b]

Type of polymer	Concentration of polymer solutions (ppm)	Viscosity (μ) of polymer solutions (cp)	Resistance factor (R)	Residual resistance factor (R_r)	Permeability (k) (darcy)	Perm reduction (%)	Pore diam (d_h) (μm)	Pore diam reduction (%)	Molecular diam (d_p) of polymers (μm)
Polyacrylamide $M = 5 \times 10^6$ $\alpha = 0\%$	250	0.7745	1.19	1.12	8.72	6.03	19.78	3.04	0.260
	350	0.8799	1.36	1.24	8.63	7.00	19.67	3.58	
	500	0.9683	1.58	1.10	8.20	11.60	19.18	5.98	
Separan MG-200 $M = 10 \times 10^6$ $\alpha = 5\%$	250	0.8399	1.38	1.12	8.16	12.07	19.13	6.23	0.3152
	350	0.9173	1.51	1.14	8.12	12.50	19.08	6.48	
	500	1.0473	1.78	1.19	7.51	19.07	18.35	10.05	
Pusher 700 $M = 5 \times 10^6$ $\alpha = 31\%$	250	1.1059	1.92	1.16	7.72	16.8	18.61	8.77	0.3776
	350	1.2942	2.38	1.14	7.29	21.4	18.08	11.37	
	500	1.6235	3.24	1.11	6.70	27.8	17.34	15.00	
Pusher 500 $M = 3.5 \times 10^6$ $\alpha = 37\%$	250	0.9519	1.36	1.06	8.58	7.5	19.62	3.82	0.2744
	350	1.0899	1.80	1.06	8.12	12.5	19.08	6.48	
	500	1.3351	2.35	1.13	7.61	18.0	18.48	9.41	
Polyacrylic acid $M = 0.23 \times 10^6$ $\alpha = 100\%$	250	0.7049	1.13	1.06	8.21	11.5	19.19	5.93	0.046
	350	0.7083	1.07	1.06	8.69	6.4	19.74	3.24	
	500	0.7118	1.04	1.05	8.92	3.9	20.00	1.96	

[a] Calculations:

$$\% \text{ of permeability reduction} = \frac{\text{brine permeability} - \text{polymer solution permeability}}{\text{brine permeability}} \times 100$$

$$\% \text{ of pore diam reduction} = \frac{\text{initial pore diam} - \text{final pore diam}}{\text{initial pore diam}} \times 100$$

[b] Porosity (ϕ) = 44%; brine permeability (k_b) = 9.28 darcy; pore diameter (d_h) = 20.4 μm.
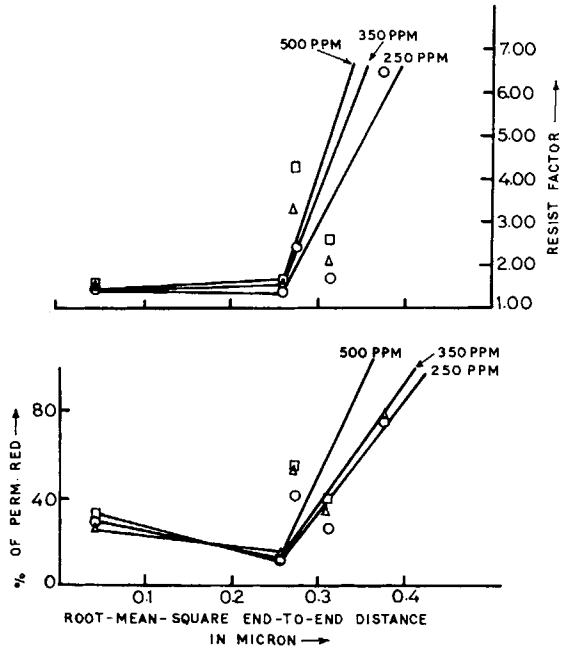
Fig. 5. Permeability reduction and resistance factor vs. polymer molecular diameter in (−100 + 200) mesh fresh sand pack.

It seems both factors play important roles in the retention of the polymer within porous media. Permeability reduction by mechanical entrappment may decrease with brine flush, and in some cases most of the loosely entrapped polymer molecules may be washed out by the several pore volumes of brine flush. Thus this factor is relatively less permanent in comparison to the adsorption of the polymer on the pore surface. The desorption of the polymers from the surface is comparatively more difficult as interaction forces hold it rigidly. It is very difficult to predict the nature of these forces, but it is fair to assume that it is similar to the case of dipole–dipole interaction between molecules. In this type of interaction, surface characteristics of the porous matrix also play an important role. In order to confirm this fact, clean sand pretreated with oil was used as one of the porous media to compare the flow parameters with fresh sand of same particle size dimension. It has been observed that the resistance factor and permeability reduction are much lower than in the fresh sand pack.

The resistance factor, reduction of permeability, and pore diameter for both packs at different polymer concentrations were plotted against the polymer molecular size of five polymers (Figs. 5–7). It is observed that, as the polymer concentrations are increased, the above flow parameters are also increased, but, in the fresh silica sand pack, the curves are steeper than in the pretreated sand pack. This shows the pronounced effect of the molecular size in a virgin porous surface. The concentration effect is also less marked in the fresh sand pack; this may suggest the importance of polymer surface interaction on the fresh sand surface. This assumption is mainly due to the fact that both the packs have almost identical pore size distribution, surface area, and physical properties except the change in electrostatic nature of the surface.
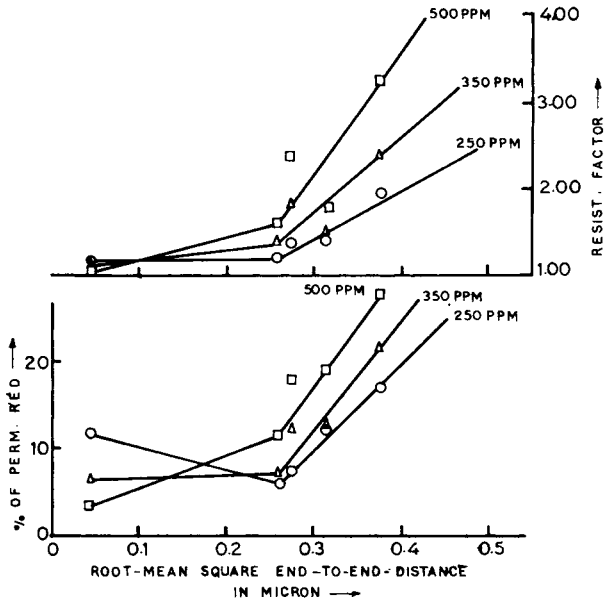
Fig. 6. Permeability reduction and resistance factor vs. polymer molecular diameter in (−100 + 200) mesh pretreated sand pack.

When the flow parameters were plotted against the degree of hydrolysis of partially hydrolyzed polyacrylamides, it can be noticed that, at one particular degree of hydrolysis, the maximum values of the flow parameters are observed at all concentrations (shown in Fig. 8). The particular phenomenon can be ex-
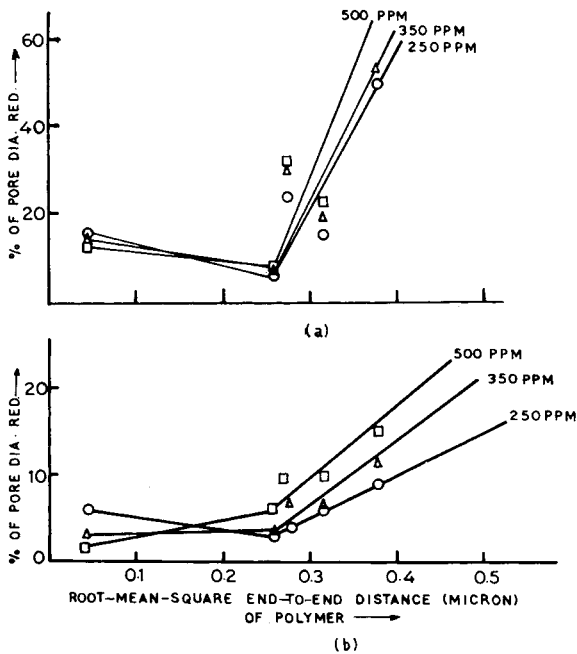
Fig. 7. (a) Pore diameter red. vs. polymer molecular diameter in (−100 + 200) mesh fresh sand pack. (b) Pore diameter red. vs. polymer molecular diameter in pretreated (−100 + 200) mesh sand pack. (□) 500 PPM; (△) 350 PPM; (○) 250 PPM.
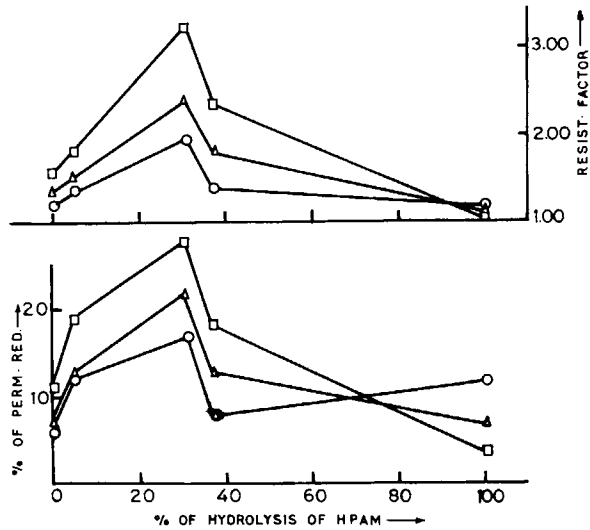
Fig. 8. Permeability reduction and resistance factor vs. % of hydrolysis of polyacrylamides in (−100 + 200) mesh pretreated sand pack.

plained if we assume that, under certain molecular conditions, the polymer molecule can be deformed easily in dynamic conditions, thus permitting greater interaction with the surface of the porous materials of the media. In partially hydrolyzed polyacrylamides, this condition may depend on the ratio of carboxyl–amide groups in the polymer chain. In case of the polymer as in polyacrylamide and Separan MG-200, where there is low degree of carboxyl groups in the polymer chain which may not permit decoiling of the chain, the polymer may remain as a spherical ball, facilitating in passing through the pore channels of the porous media.[22] On the other hand, if there are only carboxyl groups as in polyacrylic acid, then, due to strong electrostatic repulsion, the molecule may acquire an almost rigid rodlike structure which will not permit the interaction with the solid surface. Therefore, one can expect in both cases a poor reduction in permeability due to lack of interaction with the surface of the porous materials. The critical ratio of carboxyl to amide groups in Pusher 700 confirms the assumption that a certain molecular geometry is needed in the polymer chain to attain a desired flexibility to promote the adsorption at the surface by interaction. The experimental data on these polymers confirms the above assumption. The large reduction of pore diameter with Pusher 700 is not only due to polymer–surface interaction, but can be attributed to several factors like mechanical entrapment, inaccessible pore volume to the polymer molecule,[23] and entanglement with flowing polymer molecules,[24] etc. The desired flexibility of polymer molecule as in case of Pusher 500 and Pusher 700 may also increase the viscosity, which may also help in increasing the flow resistance in tortuous path of the media.

NOMENCLATURE

A cross-sectional area (cm^2)
d_h hydraulic diameter or pore diameter
d_p molecular diameter of polymer

k	permeability (darcy)
K_z	Kozeny constant
L	length (cm)
M	molecular weight
ΔP	pressure drop (atm)
q	volumetric flow rate (cc/s)
R	resistance factor
$\sqrt{\bar{r}^2}$	root mean square end-to-end distance
r_h	hydraulic radius
μ	coefficient of viscosity (cp)
$[\mu]$	intrinsic viscosity (dL/gm)
ϕ	porosity
α	degree of hydrolysis (%)

Subscripts

b	brine solution
p	polymer solution

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