# Flows of Dilute Hydrolyzed Polyacrylamide Solutions in Porous Media under Various Solvent Conditions

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## Synopsis

Experimental results on pressure losses of flows of dilute polymer solutions through porous media are summarized. The polymer products employed in this study consisted of partially hydrolyzed polyacrylamides (HPAM) with different degrees of hydrolysis. The effect of the hydrolysis on the pressure drop is investigated in a porous media test section designed to minimize polymer degradation. The investigations were carried out for various solvent conditions, and it is shown that the maximum increase in pressure drop is mainly dependent on the molecular weight of the polymers. The onset of the polymer action is measured for various fluid and solvent properties. Particular attention is given to measurements near $\theta$-conditions. The results stress the importance of the solvent properties on the actions of the polymers and on the resultant pressure drop for porous media flows. The addition of salt ions to solutions of partially hydrolyzed polyacrylamides yields onset behavior previously observed for nonionic polymers. The differences measured between various solvent properties can be explained by the actual hydrodynamic molecule dimensions for a given molecular weight and polymer concentration. To quantify the influences of the solvent properties on the polymers, measurements were carried out in aqueous solutions for various pH values and therefore at various degrees of dissociation. The importance of separating polymer effects caused by their linear dimension in the solution from those that are introduced by an increase in solvent viscosity is shown. Measurements were performed to quantify the effects of solvent viscosity on the polymer action and to separate these effects from those due to changes in molecule dimensions. The implications of the present results are stressed in connection with applications of polymer solutions in tertiary oil recovery, and the positive features of the molecule actions on flow in such applications are described.

## INTRODUCTION

When high-molecular-weight polymers are added to a liquid flow through a porous medium, a pressure drop increase with flow rate is observed beyond a characteristic onset value. This phenomenon is well known and has been described in many experimental investigations.[1-7] For these studies, detailed experimental results have become available that provide quantitative information on the resistance increase with respect to the corresponding flow resistance of Newtonian fluids. In addition, various phenomenological models have been proposed to explain the physical causes of the increased pressure losses by linearly extended molecules acting on the properties of the flow.[4-6] These treatments allow the actions of the molecules on the flow field to be understood but do not consider the complex interaction between the strain and the molecules to yield their extension. Furthermore, the models are too simple to permit physicochemical interactions between the solvent and the molecules to be explained. The present article shows that such interactions occur and quantifies their effects on the resultant pressure losses of flows through porous media. This interaction is most severe for ionic polymers that change their linear hydrodynamic di-

mensions as the physicochemical properties of the used solvent are changed. To quantify this, results of an experimental study are reported that were obtained for partially hydrolyzed polyacrylamides manufactured by Chemische Fabrik Stockhausen & Cie. All products had the same molecular weight but different degrees of hydrolysis.

The experimental section briefly describes the experimental equipment and the porous medium test section used in the measurements. The description is relatively short since details have already been provided in a previous paper[7] where the same test section was employed to study the effects of nonionic polymers on the pressure loss of flows through porous media. Whereas in the previous study, several sphere sizes were used to make up the porous matrix, only a single size was employed in the present experiments. The microscopically measured size distribution of the spheres used in the present experiments is also given. Information on the preparation of the porous matrix and some special features of the complete equipment are given.

The experimental section also summarizes the experimental procedure developed to prepare the dilute polymer solutions of hydrolyzed polyacrylamides. In order to ensure reproducibility of the data, the same preparation procedure was used for all the solutions. Particular care was taken to ensure that all material was dissolved in the final solution, and molecule degradation was minimized by providing only a minimum mechanical enhancement during the preparation of the solution.

The actual measurements are described in the results section. Results of a previous study of nonionic polymer solutions are presented, where it is shown that nonionic polymers exhibit the well-known onset behavior of drag increase with flow rate, whereas ionic polymers show this typical onset only for special solvent properties.

The results of the present study suggest the application of polymers in many industrial processes, especially in tertiary oil recovery. A demonstration experiment is described which shows that polymer solutions with low viscosity can prevent the break through of water (water fingering) due to the pressure drop increase beyond the onset flow rate. The experiments quantify that the pressure drop increase is not strongly affected by the addition of salt ions to the solution whereas the observed pressure loss increase for Reynolds numbers smaller than the onset Reynolds number diminishes to negligible values with salt addition.

## CHARACTERIZATION OF THE EMPLOYED PARTIALLY HYDROLYZED POLYACRYLAMIDES AND SOLVENT SYSTEMS

The four polyacrylamide samples employed in the present study were specially prepared by Chemische Fabrik Stockhausen & Cie and were characterized by numbers A968, A970, A971, and A972. The samples showed an increasing degree of hydrolysis with increasing number. According to the available information, sample A968 had been prepared by free radical polymerization of a water solution of the monomers with potassium persulfate as initiator. Due to the reaction heat set free during the polymerization process, hydrolysis had already taken place to a small extent. It is for this reason that the final product A968 already contained 3.4 mol % hydrolyzed base molecules and showed slight polyelectrolyte properties.

The product A968 served as a starting material for the other three samples, i.e., A970, A971, and A972, which were also produced by Chemische Fabrik Stockhausen & Cie, by an alkaline hydrolysis reaction. In this way, four samples of the same molecular weight but with different degrees of hydrolysis (DH) were available:

$$----\left[CH_2-CH-\right]_x\left[CH_2-CH-\right]_y--- \qquad DH = \frac{y}{x+y}$$
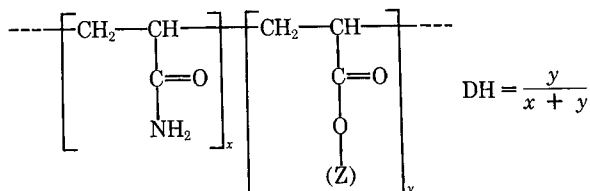
The partially hydrolyzed polyacrylamides A968–A972 were delivered to the authors in the form of powders and had to be dissolved before being employed to study their effects in porous media flow. Together with the products, a table was provided that summarized the properties of the polymers obtained by Stockhausen & Cie using different analytical techniques. Table I provides this information and the following points are worth mentioning: (a) The degree of hydrolysis varies from 3.4 to 47.5%. The values have been confirmed by the authors using potentiometric titration of the H-form of the samples. (b) All samples contain water; the amount increases with increasing degree of hydrolysis. (c) The carboxylate groups ($-COO^-$) are predominantly in the form of sodium salt (Z = Na). The amounts of ammonium salt (Z = $NH_4$) and the H-form (Z = H) are small. (d) The last column gives the amount of base molecules or monomer units in mmol/g. This information is essential for the preparation of the different HPAM solutions to get solutions with the same polymer concentration, i.e., solutions with the same number of molecules per unit volume.

The molecular weight of the A968 product was determined by Chemische Fabrik Stockhausen & Cie employing a 10% sodium chloride/water solution at 20°C in a capillary viscometer.[8] The value given to the authors was

$$M = 6.7 \times 10^6 \pm 10\% \text{ g/mol}$$

This property was again remeasured by the authors taking into account the

TABLE I
Chemical Characterization of the Employed Partially Hydrolyzed Polymer Products[a]

| Product | Water Content | Degree of Hydrolysis D.H. | | Poly (acrylamide) Content | | Poly (sodium acrylate) Content | | Poly (ammonium acrylate) Content | | Poly (acrylic acid) Content | | Base Molecules |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | % | mol % | weight % | mmol/g | weight % | mmol/g | weight % | mmol/g | weight % | mmol/g | weight % | mmol/g |
| A 968 | 11.59 | 3.4 | 3.53 | 11.94 | 84.87 | 0.02 | 0.19 | 0.27 | 2.40 | 0.13 | 0.94 | 12.36 |
| A 970 | 15.10 | 11.4 | 11.98 | 10.20 | 72.50 | 0.94 | 8.84 | 0.28 | 2.49 | 0.09 | 0.65 | 11.51 |
| A 971 | 15.52 | 30.5 | 30.63 | 7.58 | 53.88 | 3.03 | 28.50 | 0.02 | 0.18 | 0.27 | 1.95 | 10.90 |
| A 972 | 17.98 | 47.5 | 44.43 | 5.25 | 37.32 | 4.63 | 43.55 | 0.01 | 0.09 | 0.11 | 0.79 | 10.00 |

[a] Information Supplied by CHEMISCHE WERKE STOCKHAUSEN & CIE, KREFELD, Germany.
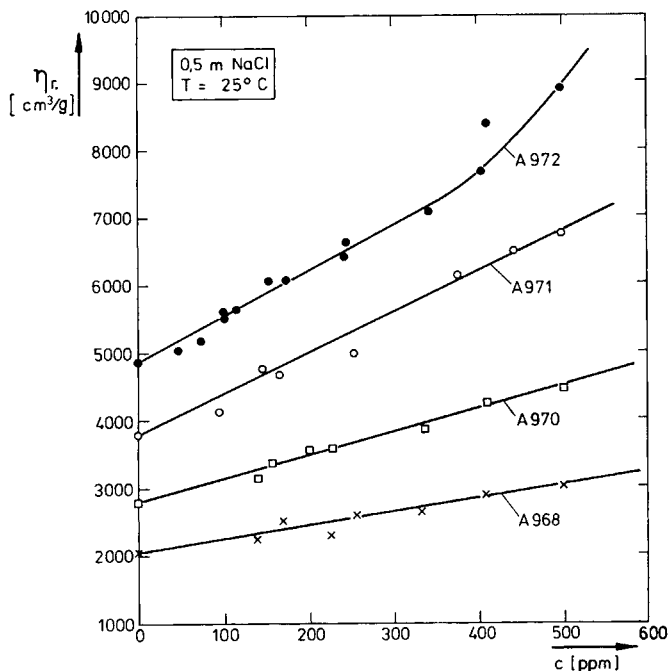
Fig. 1. Results of viscosity measurements for the employed polymer products with a low-shear Zimm–Crothers viscometer. $0.5m$ NaCl; $T = 25°$C.

following findings: (1) According to Shawki and Hamielec,[9] the effect of shear rate on the molecular weight determination of polyacrylamides must be taken into account if the molecular weight exceeds $10^6$ g/mol. (2) The parameters $K_\eta$ and $a_\eta$ in the relationship for the intrinsic viscosity

$$[\eta] = K_\eta \cdot M^{a_\eta} \qquad (1)$$

depend on the degree of hydrolysis of polyacrylamides. Data were taken for these quantities from a study of Klein and Conrad[10] for a $0.5m$ aqueous NaCl solution.

Considering point 1, the intrinsic viscosity measurements in the present study were carried out with a low-shear Zimm–Crothers viscometer.[11] The results of these measurements are shown in Figure 1, and the corresponding molecular weights are given in Table II. This table shows all products have about the same molecular weight, with only the A971 showing a value that deviates somewhat from the other values. Table II also shows that the molecular weight determined by the authors is higher than the value given above. This again stresses the need to determine the intrinsic viscosity by means of low-shear viscometers.

It has been demonstrated in a previous study[7] that the effects of ionic polymers on flow through porous media strongly depend on the nature and concentration of counterions present in the solution. The preliminary result given in Ref. 7 indicated that the observed polymer effects for ionic polymers, e.g., onset of drag increase at particular strain rates, are similar to the effects measured for nonionic polymers if the pH value and ionic strength of the solution are adjusted to certain values which depend on the polymer properties. This finding initiated the

TABLE II
Molecular Weights Determined by Using a Low-Shear Zimm–
Crothers Viscometer

| Product | D. H. | $[\eta]$ | [x] $K_\eta$ | [x] $a_\eta$ | $M = ([\eta]/K_\eta)^{1/a_\eta}$ |
|---------|-------|----------|-----------|-----------|----------------------------------|
| | mol % | $cm^3/g$ | x) according to Klein et al. [10] | | g / mol |
| A 968 | 3.4 | 2050 | $7.00 \times 10^{-3}$ | 0.782 | $9.79 \times 10^6$ |
| A 970 | 11.4 | 2800 | $6.45 \times 10^{-3}$ | 0.806 | $9.88 \times 10^6$ |
| A 971 | 30.5 | 3800 | $6.66 \times 10^{-3}$ | 0.830 | $8.71 \times 10^6$ |
| A 972 | 47.5 | 4850 | $8.10 \times 10^{-3}$ | 0.827 | $9.68 \times 10^6$ |

a According to Klein et al.[10]

present study in which pressure drop measurements in the porous media flow were carried out under well-controlled solvent conditions and for known polymer properties.

All measurements in aqueous solutions were performed at pH values of 3.03, 4.0, and 8.8. For this purpose, three buffer systems were selected which are given in Table III together with their ionic strengths, $I_b$. The ionic strength of the solvent, $I_{sa}$, was adjusted by salt addition and calculated according to

$$I_{sa} = \frac{1}{2} \sum_{i=1}^{w} m_i z_i^2 \qquad (2)$$

where $m_i$ is the molarity of the ionic species of salt, $i$; $z_i$ is the electrochemical valence of the ionic species for the salt, $i$; and $w$ is the number of ionic species of the salt.

The ionic strength of the solution was determined by the summation of the ionic strengths of the buffer and the salt:

$$I = I_b + I_{sa} \qquad (3)$$

In those cases where the ionic strength of the buffer is small, the ionic strength of the solution is entirely defined by salt addition, i.e., $I \approx I_{sa}$. Since at high salt concentration the pH value of the solution can change appreciably, the final pH value is given if, in connection with the results, it exceeds 0.1 pH units of the buffer values.

Further information on the polymer–solvent system was obtained via titration measurements carried out for the products A970 to A972 by systematically varying the ionic strengths of their solutions. From the resultant diagrams of pH values vs. the degree of dissociation $\alpha$ shown in Figure 2, the number of

TABLE III
Buffer Systems Employed in the Experiments

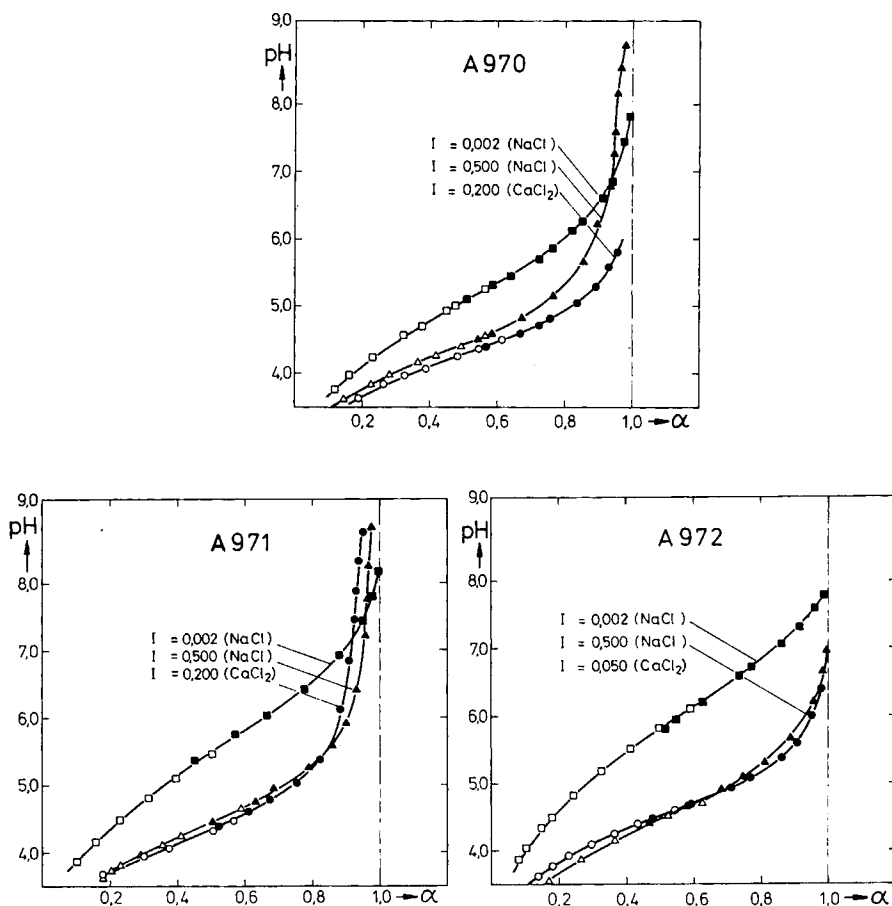| Buffer pH | Ionic Strength $I_b$ mol / dm$^3$ | Composition of Buffers | |
|-----------|-----------------------------------|------------------------|---|
| 8.80 | 0.0045 | 0.050 m Triethanol amine<br>0.055 m Hydrochloric acid | Ref.[12] |
| 4.00 | 0.050 | 0.280 m Acetic acid<br>0.050 m Sodium hydroxide | Ref.[13] |
| 4.00 | 0.100 | 0.450 m Acetic acid<br>0.100 m Sodium hydroxide | Ref.[13] |
| 3.03 | 0.005 | 0.280 m Acetic acid<br>0.005 m Sodium hydroxide | Ref.[13] |

Fig. 2.  H$^+$ titration curves of the HPAM polymers A970, A971, and A972.

charges carried in the average by each molecule can be calculated using information on the degree of hydrolysis of the various polymer products.

The degree of dissociation $\alpha$ is defined as

$$\alpha = \frac{[\text{---COO}^-]}{[\text{---COOH}] + [\text{---COO}^-]} \tag{4}$$

which means $\alpha$ represents the relative amount of carboxylate groups (---COO$^-$) with respect to the total number of ---COO--- groups along the polymer chain. This information allows the charge density $q = (\alpha \times DH)$ of the various polymer products in different aqueous buffer solutions to be calculated.

As can be seen from the H$^+$ titration curves in Figure 2, the adjustment of the pH value to 8.8 results in a degree of dissociation of $\alpha \cong 1.0$, i.e., fully dissociated molecules.   This state is reached at pH 8.8 independently of the ionic strengths of the solutions, whereas at low pH values of 3 to 4, a low degree of dissociation results, $\alpha \approx 0.2$.   These two limits were present in the experiments carried out with buffer systems listed in Table III.

For the more hydrolyzed samples, A970, A971, and A972, it is possible to change the physicochemical state of the dissolved polymers in aqueous solution by varying the kind of salt, by adjusting the salt concentration, and by changing

the pH value.   In the case of A968, these changes are rather limited because of the low degree of hydrolysis.   Large solvent-property changes can then only be realized by employing organic solvents and/or mixed solvents.   For example, Klein and Conrad[10] claim that ethylene glycol at 25°C is almost a $\theta$ solvent with $a_\eta = 0.54$ and can be used to study polymer properties in this solvent state.

Furthermore, the author's study shows that a volume mixture of methanol: water = 1:2 at $T = 25°C$ also gives a $\theta$ condition for polyacrylamide with low degree of hydrolysis.   These two systems have been used in the case of polymer A968 in addition to aqueous solutions.   To increase the speed of the solubility, a mixture of 1 volume water to 29 volumes ethylene glycol was used.   In some of the experiments it was desirable to eliminate the slight polyelectrolyte effect of A968 by a small amount of $MgCl_2$ ($I_{sa} = 0.05$) added to the mixed solvents.

## EXPERIMENTAL

### Equipment and Tests

The present experiments were carried out in an experimental unit shown schematically in Figure 3.   This experimental equipment was employed in a previous study and has been described in detail.[7]   The parts of the flow test section consisted of glass and Perspex or glass and metal, depending on whether aqueous or organic solvents were used in the flow experiments, respectively.   As Figure 3 shows, to drive the flow through the porous-media test section, compressed air was supplied through a well-controlled pressure regulator to the liquid container which held the different test fluids.   From the liquid container, the liquid was fed through a spiral glass tube, which acted as heat exchanger and was positioned in a temperature-controlled water bath.   This ensured the temperature to be constant at 25°C over all the experiments.

As indicated in Figure 4, the geometric dimensions of the test section, i.e., the housing of the porous bed, were kept relatively small utilizing experiences obtained during previous studies of porous media flows.[7]   In this way, reproducibility of the data was assured and mechanical degradation of the polymer action
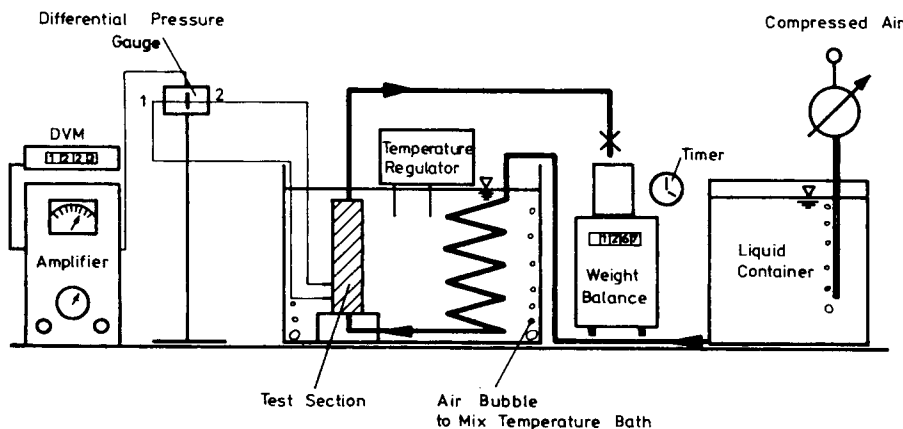


Fig. 3. Experimental equipment and test section for study of polymer flows through porous media.
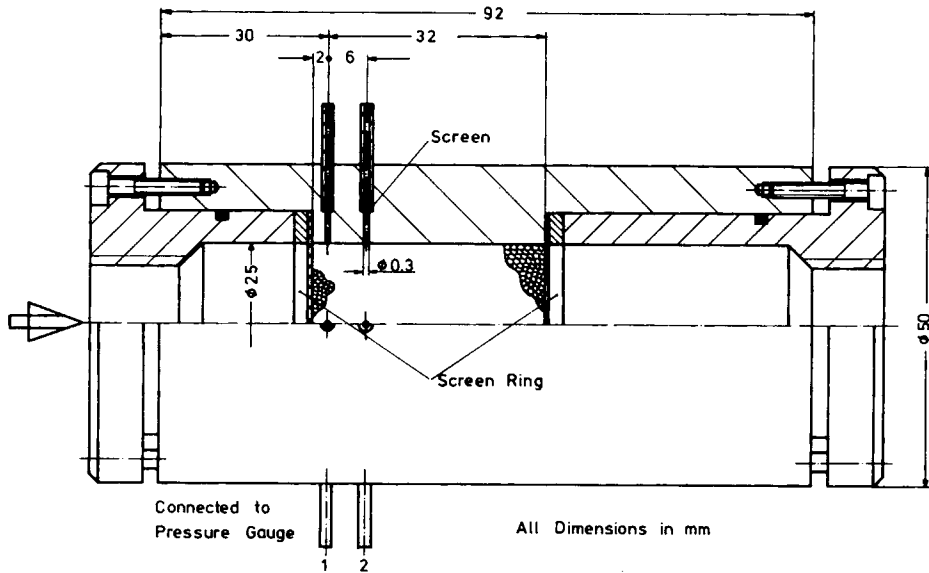
Fig. 4. Details of the actual test section; location of pressure tappings.

was minimized. The main dimensions of the test section are given in Figure 4 together with details of the locations of the pressure tappings. The pressure difference between the tappings was measured by a differential pressure gauge. An amplified output was recorded by a digital voltmeter providing a reading proportional to the actual pressure drop. The corresponding flow rates were determined by measuring the weight and time for a certain fluid volume to pass the test section.

Figure 5 illustrates the size distribution of the glass spheres employed to prepare the porous matrix. The indicated narrow size distribution was obtained by applying subsequent sieving to a mixture of quartz spheres with a wider size distribution.
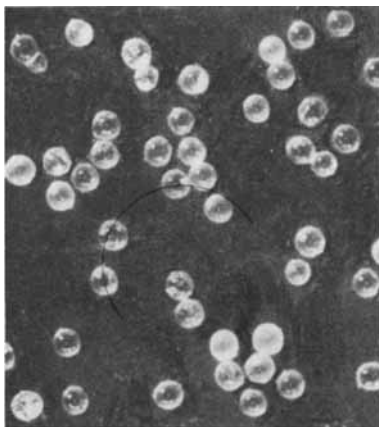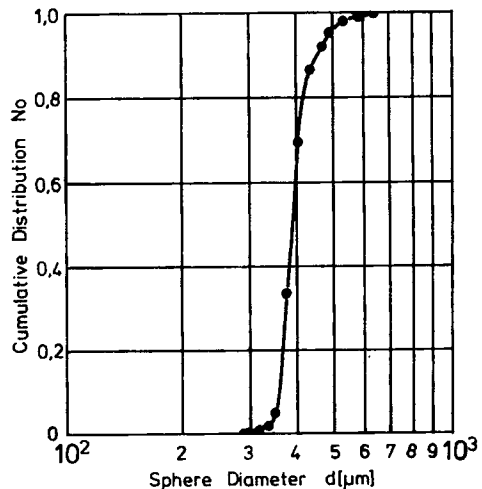


d = 392 μm

Fig. 5. Photograph of the glass spheres used in the experiments and particle size distribution.

As previous investigations of nonionic polymer flows through porous media have shown,[7] the influence of sphere diameter is correctly accounted for via a mean strain rate defined by the ratio of average flow rate and sphere diameter. Some preliminary measurements also indicated similar results for ionic polymers. It was, therefore, sufficient for the present experiments to only use a single diameter, and $d = 392 \ \mu m$ was chosen.

### Preparation of the Polymer Solutions

All aqueous solutions were prepared with deionized water produced by KKS Deionizing Equipment (Aquafine Type K70, Mannheim). This equipment is permanently installed in the Institute of Hydromechanics of the University of Karlsruhe and delivers deionized water with an ionic strength close to zero. Hence, the ionic strength of the final solution was entirely controlled by the buffer compositions and by the salt addition.

As already mentioned, four different hydrolyzed polyacrylamide samples were available to be investigated in porous media flow under various solvent conditions. To get comparable results, a constant polymer concentration of 50 ppm was chosen for all polymer–solvent systems. A quantity of 5 dm$^3$ dilute polymer solution was found to be sufficient to carry out a single data series. For aqueous solutions with different pH values and ionic strengths, the buffer solutions were prepared by mixing deionized water, the buffer compositions,[12,13] and the necessary amounts of salts. The required amount of polymer powder was calculated, using information from Table I, to ensure that the different hydrolyzed polyacrylamide products had the same number of base molecules per unit volume (0.699 mmol/dm$^3$ = 50 ppm A968). To prepare the solutions, the powder was dispersed in a small quantity of isopropanol and mixed with the buffer solution by gently stirring the solution for about 2 h. The resultant polymer solution was left to dissolve for at least 15 h and was then filtered through a 100-$\mu m$ sieve prior to performing the final experiments.

The mixed solvents were only employed with PAM A968. They consisted of water/methanol or water/ethylene glycol mixtures. To prepare the solutions, the polymer powder was first dissolved in water as mentioned above and later mixed with the organic part. The water/methanol mixture required the same dissolving time of 15 h, whereas the water/ethylene glycol mixtures took a longer time to give a homogeneous solution.

Prior to each flow test, a small amount of the solvent or polymer solution was required to measure their fluid properties such as viscosity and density. These measurements were performed with a Cannon–Fenske viscometer and a conventional densitometer, respectively. Only clear and filtered polymer solutions were used in the experiments. Working with highly hydrolyzed PAM solutions, precipitation of the polymer is possible under certain solvent conditions and may lead to uncontrolled plugging of the porous matrix. Consequently, in all experiments in the porous media flow, the solvent conditions were chosen to avoid precipitation and the accompanying plugging. This is indicated in the resultant diagrams, where the symbol "↓" is used to indicate the conditions for which precipitation of the polymers occurred and no measurements could be taken.

## MEASUREMENTS AND SUMMARY OF RESULTS

### Investigations of Porous Media Flows with Nonhydrolyzed Polyacrylamides

The influence of polymer additives on flows through porous media is best studied by quantifying deviations of the characteristic flow properties from those of Newtonian fluids. For example, for the pressure loss per unit length, polymer-caused deviations occur, and this quantity can be used to characterize the polymer action.

Laminar flow of Newtonian fluids through porous media is usually described in terms of modified Ergun coordinates defined as follows:

$$f = \frac{\Delta p}{\Delta L} \cdot \frac{d}{\rho \cdot \bar{v}^2} \cdot \frac{n^3}{(1-n)} \qquad \text{friction factor} \qquad (5)$$

$$Re = \frac{\bar{v} \cdot d \cdot \rho}{\eta(1-n)} \qquad \text{Reynolds number} \qquad (6)$$

where $\Delta p/\Delta L$ represents the pressure drop per unit length of the porous bed, $\bar{v}$ the average superficial velocity (flow rate per unit area of the empty bed), $\eta$ the fluid viscosity, $\rho$ the fluid density, and $n$ the porosity of the porous matrix.

The above coordinates permit pressure losses of Newtonian fluid flows to be described by a constant resistance coefficient, given as

$$R = f \cdot Re \qquad \text{resistance coefficient} \qquad (7)$$

Measurements for various Newtonian liquids and for various bead diameters were carried out in the test section described in the experimental section to yield an average resistance coefficient of $R \cong 185$.

The actual data are shown in Figure 6, which indicate the $-1$ slope expressed by eq. (7) for this double-logarithmic presentation of friction factor vs. Reynolds number. If the data are replotted in terms of resistance coefficient vs. Reynolds number, a straight horizontal line exists for the laminar range (Fig. 7), $Re \lesssim 5$, beyond which the resistance coefficient starts to increase due to transitional laminar or turbulent flow in the entire matrix or part of it.

Figures 6 and 7 also contain the results of pressure loss measurements obtained for a dilute solution of a nonhydrolyzed polyacrylamide (PAM W25). Data are presented for various polymer concentrations ranging from 6.25 to 100 ppm. The results clearly show that addition of small amounts of polyacrylamide makes the resistance coefficient deviates from the value given for Newtonian fluids. Deviation occurs at a characteristic onset Reynolds number which corresponds to a mean onset strain rate, as shown in Ref. 7. Increasing the Reynolds number beyond the onset value causes the resistance coefficient to increase until a maximum value is reached. This maximum increases linearly with the polymer concentration, at least for the dilute polymer solutions in the concentration range given in Figures 6 and 7.

It is worth noting that there is no difference between the resistance coefficient measured for Newtonian liquids and for dilute solutions of nonionic polyacrylamides if the Reynolds number is below the onset value. It was shown[7] that this is characteristic of nonhydrolyzed polyacrylamide solutions. It was also
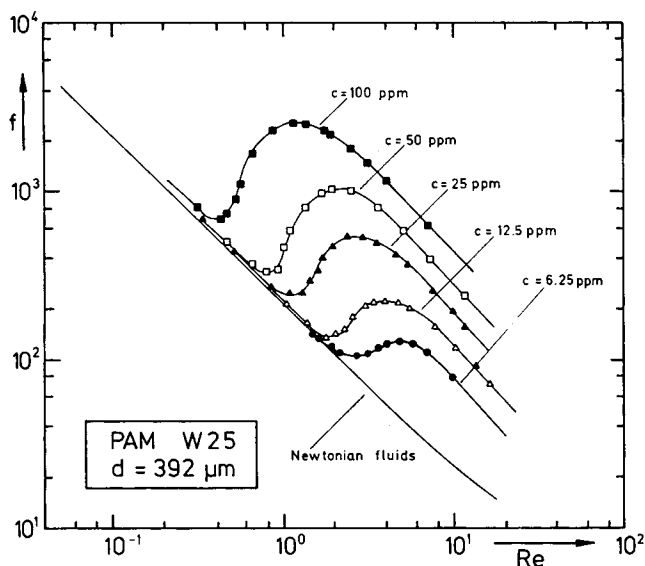
Fig. 6. Friction factor/Reynolds number relationships for nonionic PAM W25 solutions in deionized water. $d = 392\,\mu$m.

claimed that all nonionic polymers will show this behavior whereas ionic polymers will yield deviations from the resistance coefficient measured for small Reynolds numbers and Newtonian fluids. It has been the aim of the present study to quantify this for polyacrylamides of the same molecular weight but different degrees of hydrolysis. Experiments were planned to be carried out for well-controlled physicochemical properties of the solvent.

## Investigations with Partially Hydrolyzed Polyacrylamides

*Precipitation Phenomena of the Used HPAM Polymers Under Various Solvent Conditions*

During the preparation of solutions of hydrolyzed polyacrylamides with well-known physicochemical properties, precipitation of the polymers from the
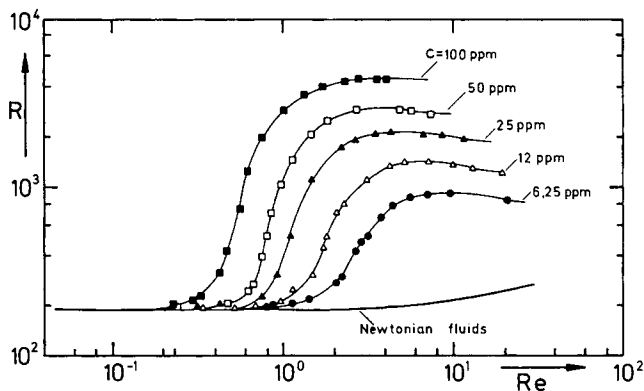


Fig. 7. Resistance coefficient/Reynolds number relationships for nonionic PAM W25 solutions in deionized water. $d = 392\,\mu$m.

solution was observed, a phenomenon well known from the determination of the $\theta$ conditions for a given solvent–polymer system. Since the authors wanted to avoid precipitation as an influence in their measurements, detailed experiments had to be carried out in order to find those solvent conditions under which molecules remain in solution. A detailed study of the complex precipitation phenomena observed for the employed hydrolyzed polyacrylamides is given in Ref. 14. In this section, only a summary of the results is provided in order to point out those facts important for porous media flows.

Figure 8 shows a typical result of a phase diagram for the investigated system A972–$CaCl_2$ that indicates the range in which unclouded polymer solutions can be prepared for pressure loss measurements in porous media flows. This range very much depends on the degree of hydrolysis of the polymers, on the type of salt added to the solution, on the pH value of the solution, and on the solution temperature. In order to reduce the number of influencing parameters, all precipitation measurements were carried out at 25°C; the same temperature was employed for the pressure loss measurements in the porous medium study.

At this temperature, it is found that aqueous, salt-free solutions of hydrolyzed polyacrylamides could be prepared without difficulties. In addition, the experiments revealed that the addition of chlorides with monovalent counterions, e.g., the addition of NaCl, did not cause polymer precipitation from the solutions with pH 8.8, at least up to the highest NaCl concentration employed in this study which corresponded to an ionic strength of $I_{sa} = 2.0$. Opposite to these findings, chlorides with divalent counterions, e.g., $CaCl_2$ and $MgCl_2$, caused precipitation for the polyacrylamides with higher degrees of hydrolysis, e.g., samples A971 and A972. As Figure 8 shows for the A972 product, precipitation only occurred in a certain range of $CaCl_2$ salt concentration. No significant precipitation was observed for the A971 polymer, but an observable cloudiness occurred within
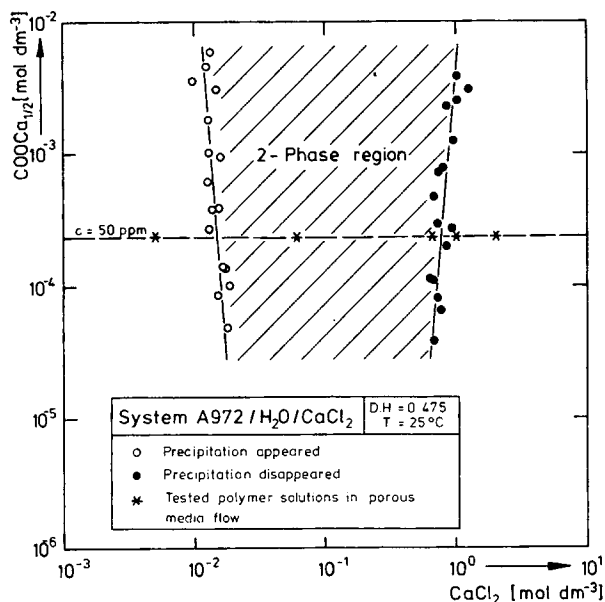


Fig. 8. Phase diagram for polymer A972 at 25°C, indicating concentration range over which precipitation occurs.

a specific range of salt concentration. Differences between the influences of $CaCl_2$ and $MgCl_2$ are attributed to the different interactions of the single counterions with the ionized polymer molecules. Extended considerations of the physicochemical aspects of the observed precipitation phenomena are given by Kaczmar.[14]

An experimental investigation carried out by Muller et al.[15] is worth mentioning who studied the effects of the dissociation $\alpha$ of the polymers in solution and the effects of salt addition (NaCl, $CaCl_2$, $MgCl_2$) on the dimensions of commercially available high-molecular-weight polyacrylamides with various degrees of hydrolysis. Viscosity and light scattering measurements were performed at a temperature of 25°C. Regarding precipitation, the results of Muller et al.[15] are in excellent agreement with the results of the present study, although quite different commercially available hydrolyzed polyacrylamide polymers were used in both studies.

Muller et al. showed by light scattering measurements the existence of a minimum of the molecule dimensions just prior to the observed precipitation of molecules from the solution. The general agreement of the authors' finding with some of the data by Muller et al. justifies conclusions regarding the polymer dimensions drawn in this section and in the discussion section where results of pressure loss measurements for dilute polymer flows relative to Newtonian flows are explained partially by variations of molecular dimensions. Quite a number of the observed differences in measured resistance coefficients can be explained with the variation of the molecular dimensions under various solvent conditions, e.g., smaller maximum resistance increases are measured for the $\theta$ conditions and higher-onset strain rates.

## Measurements with HPAM Polymers in Aqueous Solutions

Results of pressure drop measurements in Ref. 7 indicate that the influences of ionic polymer products on flows through porous media are strongly dependent on the physicochemical properties of the solution. Preliminary measurements revealed differences between pressure losses with and without polymer additives that already occurred at low flow rates, e.g., at low Reynolds numbers, and were strongly dependent on the ionic content of the solvent. More detailed studies show that the pressure losses of dilute ionic polymer solutions are strongly dependent on the molecular weight of the polymers, the polymer concentration, the degree of hydrolysis, the pH value, and the ionic strength of the solution and the counterions present in the solvent. Measurements were carried out to quantify these influences for the hydrolyzed polyacrylamide samples characterized in the previous sections. As mentioned, all samples had the same molecular weight so that molecular weight influences were not part of the present investigation. All measurements were also carried out at a single concentration of 50 ppm and at a temperature of 25°C in order to reduce the number of significant parameters. All remaining influencing factors were experimentally studied, and results of pressure loss measurements are given in Figures 9 to 15.

Figure 9(a) shows resistance coefficient measurements obtained for solutions with a pH value of 8.8 and an ionic strength of the buffer solution estimated from Ref. 12 to be $I_b = 0.0045$. Data for all four polymer products are given on the

figure which indicates that only the polymer sample A968 with the low degree of hydrolysis shows the typical deviation from the resistance–coefficient curve for Newtonian fluids observed for nonionic polymers. For this material, the typical onset of resistance increase is found together with a maximum resistance increase dependent on the molecular weight and on the polymer concentration. In this special case, the charge density $q$ is so small that the ionic strength of the buffer solution is high enough to neutralize the free charges of the A968 molecules. All other samples with higher degree of hydrolysis show increased resistance coefficients already at lower Reynolds numbers, and the typical onset of resistance increase with Reynolds number is not apparent. It is this increased resistance coefficient at low Reynolds number that clearly indicates that not all molecule charges are shielded by the counterions of the buffer solution, and strong interactions between molecules are to be expected.

Figure 9(b) demonstrates that the addition of a small amount of divalent salt $CaCl_2$, providing an ionic strength of the solution of $I_{sa} = 0.0156$, decreases the resistance increase for lower Reynolds numbers and also yields the characteristic onset for all polymer samples. A further increase in ionic strength increases this effect as shown in Figure 10(a). If $MgCl_2$ is added as a divalent salt, a single line for all polyacrylamide samples is obtained, as shown in Figure 10(b). However, no measurements could be obtained for the A972 solutions due to polymer precipitation from the solution at these higher salt concentrations.

A comparison of Figures 9 and 10 shows that the type of salt added to increase the ionic strength of the solution has an influence on the resistance coefficient variation with Reynolds number. This was studied in more detail, and Figures 11 and 12 show variations of resistance coefficients with Reynolds number for
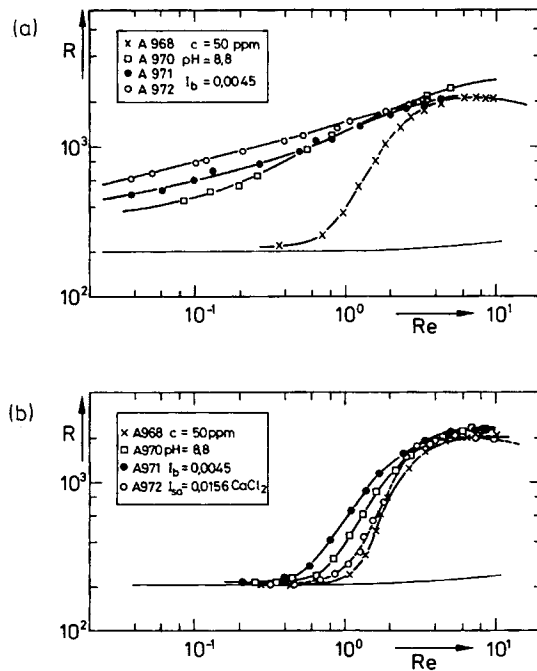


Fig. 9. Resistance coefficient/Reynolds number relationships for different HPAM solutions at pH 8.80: (a) $I_{sa} = 0$; (b) $I_{sa} = 0.0156$ $CaCl_2$.
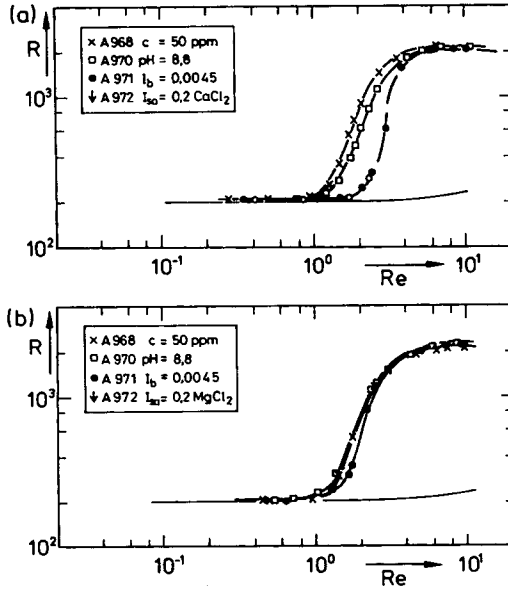
Fig. 10. Resistance coefficient/Reynolds number relationships for different HPAM solutions at pH 8.80: (a) $I_{sa}$ = 0.2 CaCl$_2$; (b) $I_{sa}$ = 0.2 MgCl$_2$.

polymer solutions of the same ionic strength set up with different salt additions.

The effects of the ionic strength for CaCl$_2$ as a salt additive are presented in
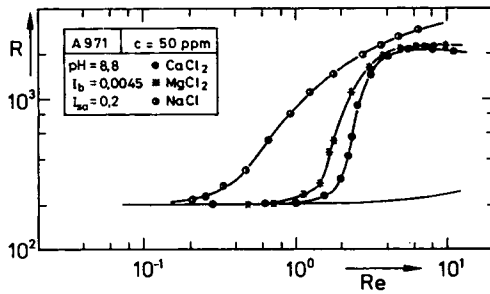


Fig. 11. Influence of different counterions on the resistance increase for a solution of A971 at constant pH and ionic strength.
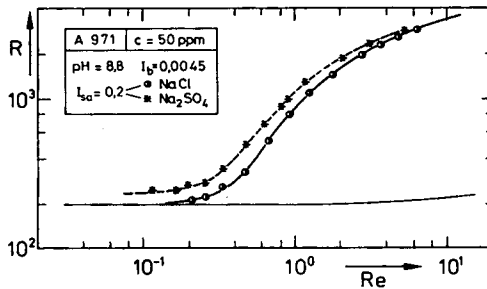


Fig. 12. Influence of different sodium salts on the resistance increase for a solution of A971 at constant pH and ionic strength.

Figures 13(a) and 13(b) for the two polyacrylamides with the highest degrees of hydrolysis. These curves show that a small change in the ionic strength already causes the difference in resistance coefficient with respect to Newtonian flow at low Reynolds numbers to decrease drastically. Further increases in the ionic strength cause the onset to be shifted to higher Reynolds numbers until precipitation of the polymer product from the solution occurs. Figure 13(b) indicates that the A972 sample could not be measured for ionic strengths $I_{sa}$ = 0.20 and 1.92 because the polymer precipitated from the solution. At higher salt concentrations yielding ionic strengths in excess of 3.00, measurements could be carried out. These showed a decrease in the onset Reynolds number with increasing ionic strength as shown in Figure 13(b). The same decrease in the onset Reynolds number can be observed for the A971 solutions at higher salt concentrations. These effects are mainly due to the increased solvent viscosities at higher salt concentrations.

Figure 14 indicates that the addition of salt NaCl does not yield the same effects on the resistance coefficient measurements as $CaCl_2$ and $MgCl_2$. In general, there is a difference in resistance coefficient between hydrolyzed polyacrylamide solutions with monovalent and divalent salt addition, although solutions of the same ionic strength are compared.

For the complete understanding of the above variations in resistance coefficient and onset Reynolds numbers with solvent properties, three main parameters have to be taken in account: (1) the solution viscosity changes with salt addition, (2) the neutralization of free charges of the molecules determined by the ionic
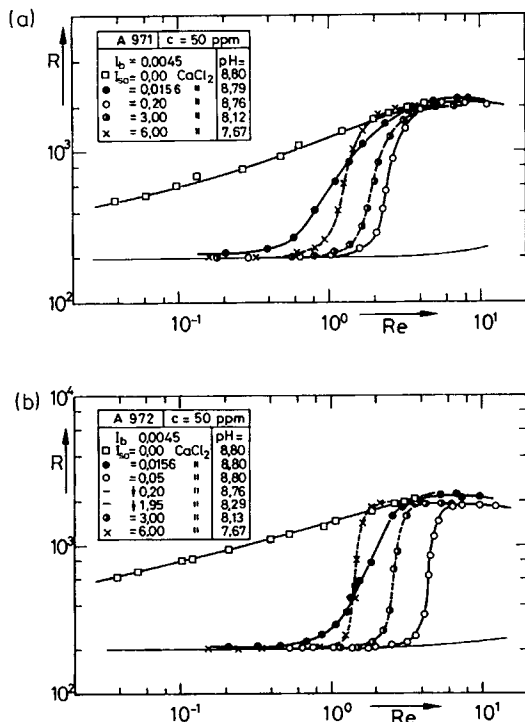


Fig. 13. Influence of the ionic strength ($CaCl_2$ addition) on the resistance increase for solutions of A971 and A972.
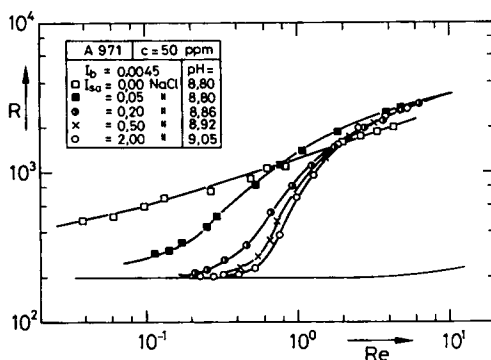
Fig. 14. Influence of the ionic strength (NaCl addition) on the resistance increase for solutions of A971 at pH 8.80.

strength of the solution, and (3) the quality of the solvent changed also by salt addition. From Figures 9, 11, 12, and 14 it can be seen that salts with monovalent counterions mainly are neutralizing the free charges of the dissolved molecules, whereas the salts with divalent counterions additionally are influencing the quality of the solvent; i.e., in certain salt concentration ranges, $\theta$ conditions are obtained for the higher hydrolyzed polyacrylamides. The latter fact is indicated in Figure 13 for the A972 sample. Since $\theta$ conditions are obtained close to the critical $CaCl_2$ concentration where precipitation occurs, the onset Reynolds number is highest under these conditions.

Additionally, some measurements of porous media flow with hydrolyzed polyacrylamide solutions were made at low pH values of 4.0 and 3.0. For these pH values, the titration curves in Figure 2 show the dissociation $\alpha$ to be small for all hydrolyzed polyacrylamide samples, and therefore the selected ionic strength of the buffer solutions should be high enough to neutralize the charges of the dissociated molecules. Indeed, the pressure loss measurements in porous media flow showed complete nonionic features with minor differences in the maximum resistance increases and the onset Reynolds numbers for the different hydrolyzed polymer samples. Figures 15(a) and 15(b) show resistance coefficient measurements for the polymer products A968–A972 at pH 4.0 and Figure 15(c), at pH 3.0. In particular, at pH 3.0 for the higher hydrolyzed samples A971 and A972, $\theta$ conditions were obtained indicated by the high onset Reynolds number in Figure 15(c).

*Pressure Drop Measurements Using HPAM Polymers in Mixed Solvents*

Results in the previous section clearly show the strong solvent–property dependence of the pressure loss of flows of dilute polymer solutions through porous media. Existing theoretical models[1-7] suggest this dependence to be caused by the effective hydrodynamic dimensions of the dissolved polymer molecules. These dimensions are dependent on the solvent properties; and, hence, variations in resistance coefficient vs. Reynolds number are to be expected as the solvent properties are changed. Quantitative results are presented in Figures 9 to 15 demonstrating that large variations of molecule dimensions by salt addition at high pH value, or solely by the buffer solution at low pH value, could be achieved for the polymer samples with degrees of hydrolysis in excess of 10%, e.g., for
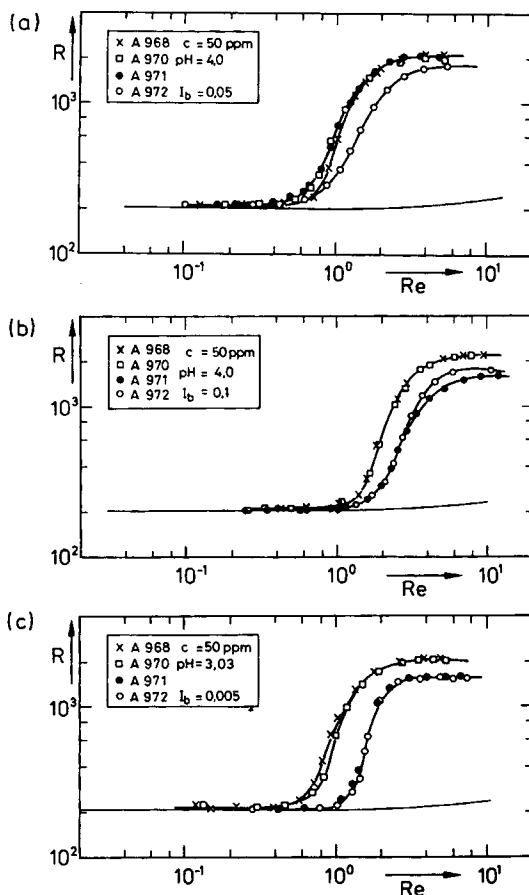
Fig. 15. Resistance coefficient/Reynolds number relationships for the different HPAM polymers at low pH values and various ionic strengths for the buffer.

samples A970 to A972.   The resistance increase measurements for aqueous solutions of the A968 product with the lowest degree of hydrolysis were affected only to a small extent, indicating low variations in molecule dimensions under variations of solvent conditions set up by addition of salt.   Large variations were observed through the employment of mixed solvents, e.g., when water/ethylene glycol or water/methanol mixtures were used as solvent of the polymers.   A summary of the obtained results is presented below.

Figure 16(a) shows results of resistance coefficient measurements for a 50-ppm solution of the HPAM A968 product in deionized water and in a mixture of deionized water and ethylene glycol made up of 2:1 volume parts.   For both solutions, the ionic strength was measured to be close to zero; and, hence, the A968 molecules were in their fully ionized state in the solutions.   This fact yielded the increased drag coefficient measured at low Reynolds numbers, e.g., for $Re < 10^{-1}$. For both mixtures a further increase in drag coefficient was measured with increasing Reynolds number until it leveled off, albeit at slightly different levels. The water/ethylene glycol solutions possessed a higher solvent viscosity, and this caused the increase in resistance coefficient to occur at a lower Reynolds number.
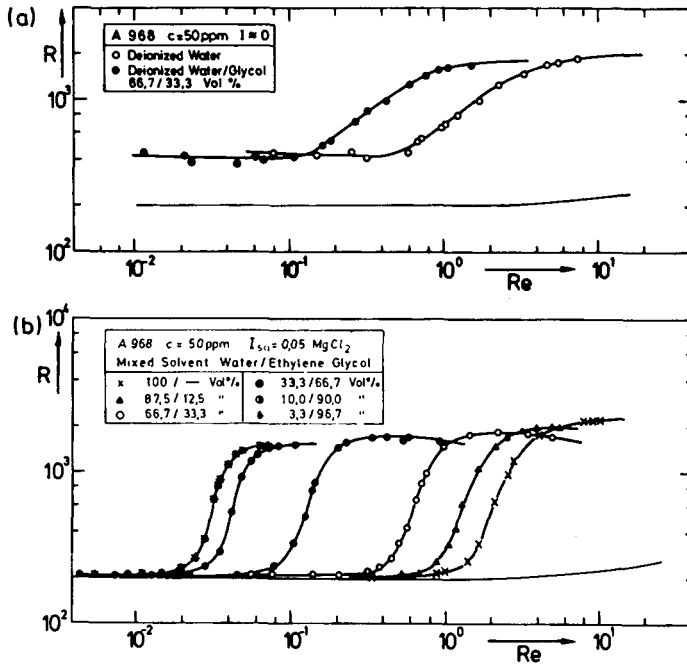
Fig. 16. Resistance coefficient/Reynolds number relationships for polymer A968 for different water/ethylene glycol mixtures.

Figure 16(b) shows that an increase of the ionic strength, by addition of $MgCl_2$ salt, to a value of $I_{sa} = 0.05$ was sufficient to reduce the resistance coefficient at lower Reynolds numbers to the value for Newtonian fluids. The change in fluid viscosity achieved for various water/ethylene glycol mixtures caused a reduction in onset Reynolds number. As the ethylene glycol part is increased the solvent becomes more and more a $\theta$ solvent as indicated by the increase in the slope of resistance coefficient/Reynolds number response curve shown in Figure 16(b). The shift of onset Reynolds number to lower values is caused by changes of the solvent properties. As already mentioned, the onset Reynolds number and the maximum value of resistance increase are complex functions of solvent viscosity, solvent quality, and degree of neutralization of free charges of the molecules.

Figure 17 shows results for water/methanol mixtures as polymer solvents. These mixtures show smaller variations in viscosity and therefore smaller dif-
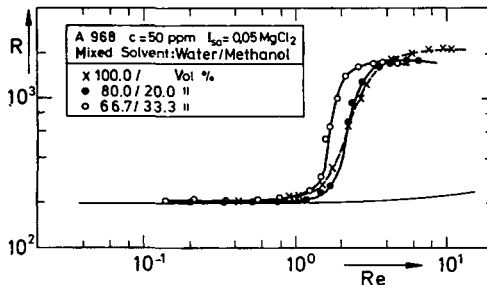


Fig. 17. Resistance coefficient/Reynolds number relationships for polymer A968 for different water/methanol mixtures.

ferences in onset Reynolds number. The reduction in maximum value of drag increase, which occurred when methanol was added, can readily be explained by the corresponding changes in solvent quality, i.e., a volume mixture of water to methanol made up of 1:2 volume parts represents nearly a $\theta$ solvent for polymer product A968.

## APPLICATION OF RESULTS TO PROBLEMS IN TERTIARY OIL RECOVERY

In tertiary oil recovery, various additives are employed to increase the viscosity of the driving liquid and in this way to yield similar mobilities for the crude oil and the flooding fluid. High-molecular-weight polyacrylamides have been suggested as additives and hydrolysis as a process to enhance the viscosity of dilute, aqueous solutions so that the viscosity is close to that of the crude oil. The present study shows, however, that the attempted increase in viscosity, i.e., the increase in pressure loss at low Reynolds numbers, diminishes to negligible values if small amounts of salt are added that increase the ionic strength of the solutions. Hydrolysis of polyacrylamides is therefore not considered a practical approach to increase the viscosity of the flooding fluid employed in tertiary oil recovery.

Irrespective of the degree of hydrolysis and also of the nature of the solvent, dilute solutions of high-molecular-weight HPAM products show an increased pressure loss for porous media flow if the Reynolds number is increased beyond a critical onset value. For water flow at 25°C, an average flooding velocity of 50 ft/day yields a Reynolds number of 0.03 for a porous rock formation with an effective grain diameter $d = 100 \mu$m and an effective porosity of $n = 0.37$. If a 50-ppm solution of polyacrylamide ($M \approx 10^7$ g/mol) is forced through such a porous matrix, an increased pressure loss is observed above an onset Reynolds number of 0.04. This clearly indicates that the polymer effects studied by the authors occur at flow rates utilized in tertiary oil recovery. The pressure loss increase due to polymer addition can be utilized therefore to prevent breakthrough of flooding water in some flow situations.

Figure 18(a) schematically shows the test rig used for demonstration experiments for problems which may occur in tertiary oil recovery. The test rig consists of cylindrical test sections of two different lengths with $L_2/L_1 = 10$ but with identical permeabilities. These were run with dilute solutions of high-molecular-weight polyacrylamides in water and ethylene glycol in the shorter test section and with North Sea crude oil as test fluid in the longer test section. The same pressure loss applied to the different test sections yielded differences in the flow rates for the crude oil in the longer cylinder and the pure water and/or ethylene glycol in the shorter. This is indicated in Figure 18(b), where the points A, B, and C give the flow rates measured for the water, the ethylene glycol, and the crude oil as test fluids. The diagram clearly shows that the flow rate in the longer test section is drastically smaller than in the shorter one due to the pressure loss applied over a larger length and also due to the higher viscosity of the oil.

Figure 18(b) also shows that the flow rate in the shorter test section is drastically reduced when polymers are added to the water and ethylene glycol flow. This decrease means a more economic usage of flooding water to drive the crude oil out of the longer test section.
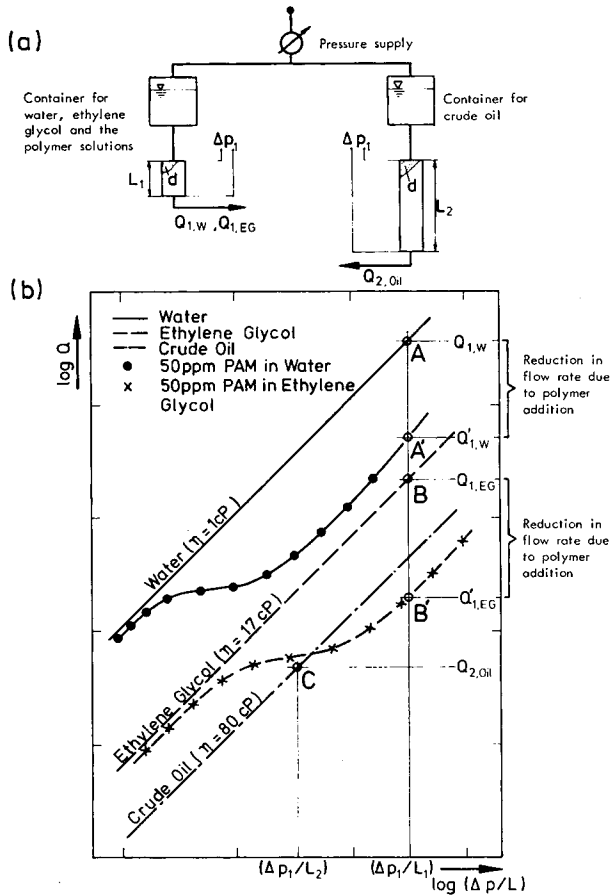
Fig. 18. Test rig (a) and verification experiments (b) for application of polyacrylamide polymers in tertiary oil recovery.

Figure 19(a) shows a similar test rig, but the different porous media are of the same length. For this test arrangement, the addition of polymer additives can yield lower flow rates of ethylene glycol than crude oil if the same pressure difference is applied. This only happens at large flow rates as indicated in Figure 19(b). At low flow rates, the additions of polymers does not affect the flow characteristics significantly. (The reader should keep in mind that this conclusion is only valid for the use of dilute polymer solutions.)

## DISCUSSION AND FINAL REMARKS

Pressure drop measurements for porous media flows have been presented for dilute solutions of partially hydrolyzed polyacrylamides of high molecular weight under well-controlled solvent conditions. In a previous study,[7] porous media flow of nonionic polymers was investigated, and it was shown in which way the molecular weight of the polymers, the polymer concentration, the properties of the porous matrix, etc., influence the pressure drop measured as a function of the Reynolds number. The present work is an extension of these investigations. To reduce the number of influencing parameters, experiments reported in this
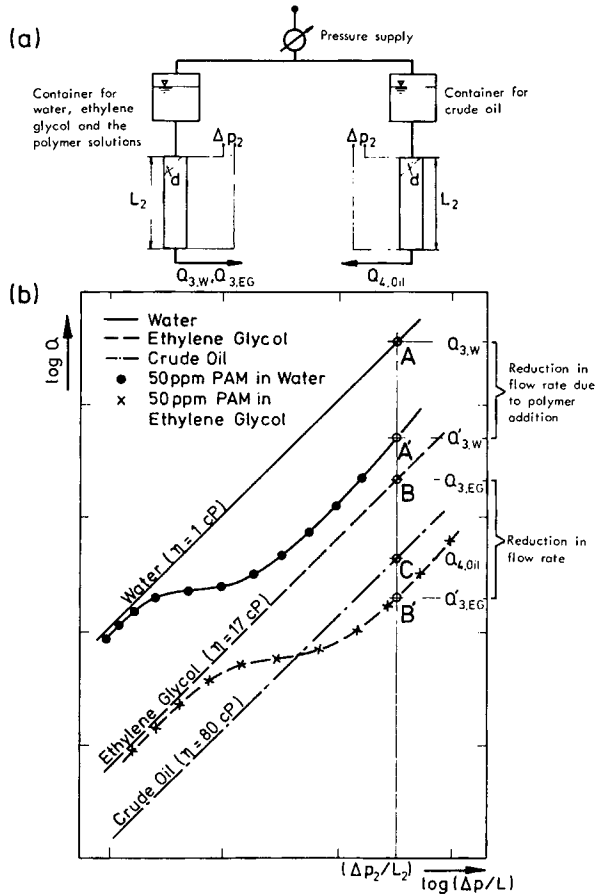
Fig. 19. Test rig (a) and verification experiments (b) for application of polyacrylamide polymers in tertiary oil recovery.

article were carried out at a constant temperature, for a single porous matrix, one particular polymer concentration, and one molecular weight, but for four different degrees of hydrolysis. Measurements were performed for aqueous solutions and mixed solvents. The properties of the aqueous solutions were altered in the experiments by variation of the pH value and by addition of NaCl, $Na_2SO_4$, $MgCl_2$, and $CaCl_2$ salts to yield solutions of known ionic strength.

The experiments showed that pressure drop measurements for porous media flows permit useful information to be deduced about the conformational properties of the hydrolyzed acrylamide polymers in various solvents. This information is obtained from changes in onset Reynolds number and from the measured resistance increase for Reynolds numbers higher than the onset value. These changes can readily be explained with existing knowledge on the physicochemical properties of high-molecular-weight polymer solutions in connection with various flow situations using simple molecule models available in the literature.[16]

Existing knowledge permits the following relationships to be deduced for onset value and maximum resistance increase, as shown by Durst and Haas[17]:

$$\left(\frac{\bar{v}}{d}\right)_0 = \frac{Re_0 \cdot \eta_p \cdot (1-n)}{d^2} \qquad \text{onset strain rate (experimental)} \qquad (8)$$

$$K_\eta \cdot M^{a_\eta+1} \cdot \eta_s \cdot \left(\frac{\bar{v}}{d}\right)_0 T^{-1} = \text{const.} \qquad \text{onset condition (theoretical)} \qquad (9)$$

$$R^* = \frac{R_{p,\max}(\eta_p/\eta_s) - R_s}{R_s} \qquad \begin{array}{l}\text{specific resistance coefficient} \\ \text{(experimental)}\end{array} \qquad (10)$$

$$R^* = \text{const.} \cdot K_\eta^{1/3} \cdot M^{(4+a_\eta)/3} \cdot C \qquad \begin{array}{l}\text{specific resistance coefficient} \\ \text{(theoretical)}\end{array} \qquad (11)$$

The above relationships for the onset value permit the following conclusions to be drawn:

(1) The strain rate at which the onset of increased pressure loss is measured decreases with increasing viscosity of the solution. If the viscosity of the solution is changed without altering the hydromechanic size of the molecules in the solution, i.e., without altering $K_\eta$ and $a_\eta$, the onset strain rate decreases inversely proportional to the viscosity.

The present results (see Fig. 16) can only roughly show this conclusion, because for the used water/ethylene glycol mixtures the Mark–Houwink constants are different and not known, and no exact theoretical computations can be performed for the onset shift in strain rate or Reynolds number.

(2) The strain rate is dependent on the effective size of the molecules in solution. The size depends on the solvent properties, e.g., on the physicochemical interactions between polymer molecules and solvent given by $K_\eta$ and $a_\eta$. Effects of these interactions have been quantified in the present study for one given molecular weight.

(3) The onset strain rate decreases with increasing molecular weight and decreasing temperature. These two parameters have not been studied in this work.

It should be mentioned that eq. (9) was exactly verified in the experiments by Durst and Haas,[17] using nonhydrolyzed polyacrylamide PAM W25 in $0.5m$ NaCl solution and pure ethylene glycol as solvents. In this case, the Mark–Houwink constants were known from the study by Klein and Conrad.[10]

The above relationships for the specific resistance coefficient indicate that (a) the specific resistance coefficient for flows of dilute polymer solutions through porous media is proportional to concentration; (b) the specific resistance coefficient also increases with molecular weight and is independent on the viscosity of the solvent; (c) the specific resistance coefficient depends on the physicochemical interactions between the polymer molecules and the solvent, given by $K_\eta$ and $a_\eta$. These interactions were again quantified in the present study.

For hydrolyzed polyacrylamide samples, the pH value of the solution determined the degree of dissociation $\alpha$ of the molecules and, hence, the charge density $q$ along the backbone of the dissolved molecules. An increased pressure loss at low Reynolds number is measured for flow of dilute polymer solutions through porous media if the ionic strength of the solution is too small to neutralize all the charges of the molecules. The present experiments showed that the addition of monovalent counterions (NaCl, Na$_2$SO$_4$) essentially causes shielding of the free charges of the dissociated molecules, whereas the addition of salts with divalent counterions (MgCl$_2$, CaCl$_2$) additionally influences the hydrodynamic dimensions of the molecules. For high degrees of hydrolysis and high salt concentrations, $\theta$ conditions are reached for some of the polymer–solvent systems investigated in this study. Under $\theta$ conditions, the onset Reynolds number for

aqueous polyacrylamide solutions reached a maximum, and the maximum resistance increase takes on a minimum value. This is in agreement with the observation by Muller et al.[15] who determined the molecule dimensions of polyacrylamides with light scattering measurements and showed the decrease in molecule dimensions as $\theta$ conditions were approached. Muller et al.[15] also studied the precipitation of molecules from the solution under salt addition and their influence on the effective size of the dissolved molecules. Their observation with light scattering techniques are in general agreement with the results of the present experiments.

# Nomenclature

| | |
|---|---|
| $a$ | Mark–Houwink exponent |
| $C$ | polymer weight concentration |
| $d$ | sphere diameter |
| $D$ | test section diameter |
| DH | degree of hydrolysis |
| $f$ | friction factor |
| $F$ | cross-sectional area of porous medium |
| $I$ | ionic strength |
| $K$ | Mark-Houwink-constant |
| $L$ | test section length |
| $\Delta L$ | length of porous bed for pressure drop calculation |
| $m$ | molarity |
| $M$ | polymer molecular weight |
| $n$ | porosity |
| $N_0$ | cumulative distribution |
| $p$ | pressure |
| $\Delta p$ | pressure drop |
| $q$ | charge density |
| $R$ | resistance coefficient |
| $Re$ | Reynolds number |
| $T$ | temperature |
| $\bar{v}$ | average superficial velocity |
| $w$ | number of ionic species |
| $z$ | electrochemical valence |

**Greek Symbols**

| | |
|---|---|
| $\alpha$ | degree of dissociation |
| $\eta$ | dynamic viscosity |
| $[\eta]$ | intrinsic viscosity |
| $\nu$ | kinematic viscosity |
| $\rho$ | density |

**Subscripts**

| | |
|---|---|
| $b$ | buffer |
| $o$ | onset |
| $p$ | polymer |
| $s$ | solvent |
| $sa$ | salt |
| $w$ | water |
| $\eta$ | viscosimetric |

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