Wetting Behavior of Aqueous Solutions of Polyacrylamide over Polyethylene Substrate

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Contact angles of polyacrylamide aqueous solutions over polyethylene substrate were measured. A wide range of polyacrylamide concentrations from 0 to 1000 g m^{-3} were covered. Because of the polyelectrolyte feature of polyacrylamide solution, different electrolyte materials were added to the polymer aqueous solutions. NaCl, $CaCl_2$, and $AlCl_3$ in the concentration range of 0−1.0 mol L^{-1} were added to the polyacrylamide aqueous solutions. The effects of these electrolyte materials on the contact angle and wetting behavior of the polyacrylamide aqueous solutions were investigated.

Introduction

The wetting process is one of the most widely applied technologies in our daily life. In general, the wetting phenomenon involves the three phases of fluid, fluid, and solid in contact. Wetting is the displacement of one fluid by another from the solid surface. This displacement process is an important technique in coating technologies where a desired coating liquid displaces air from a solid substrate. Also, the wetting phenomenon plays an important role in enhanced oil recovery where an aqueous solution of polyacrylamide is used to extract some of the trapped oil from the solid surface in oil formation.

Polyacrylamide has numerous applications in our modern industries as a suspending agent, a thickening agent, and a turbulent reduction agent, for example. One of the important applications of polyacrylamide is in extracting some of the remaining oil in the oil reservoir during enhanced oil recovery. The microscopic displacement of the trapped oil by polyacrylamide polymer flood is affected by the pore network structure, the fluid−solid properties (i.e., wettability, ion exchange, adsorption), the oil−polymer solution properties (i.e., density difference, viscosity ratio, interfacial tension, phase behavior), and the applied pressure gradient.[1]

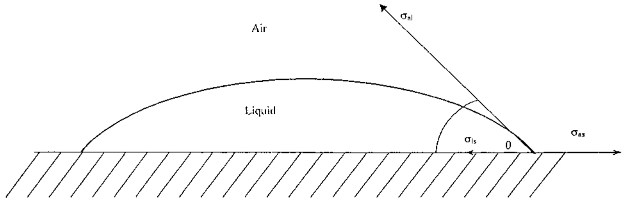

Figure 1. Definition sketch.

When a droplet of liquid is placed on a solid surface (Figure 1), it forms a contact angle at the liquid−air interface in contact with solid surface. This droplet might spread to cover the solid surface, or it might remain as a stable drop on the solid substrate. In spreading behavior, a liquid in contact with a solid surface spreads spontaneously to increase the solid−liquid and liquid−gas interfacial areas and decrease the solid−gas interfacial area. The spreading coefficient S_{ls} is defined by

$$S_{ls} = -\Delta G_w/A \tag{1}$$

$$S_{ls} = \sigma_{sa} - (\sigma_{ls} + \sigma_{al}) \tag{2}$$

where S_{ls} is the spreading coefficient, ΔG_w is the change in surface free energy, A is the surface area, σ_{sa} is the surface tension at the solid−air interface, σ_{ls} is the surface tension at the liquid−solid interface, and σ_{al} is the surface tension at the air−liquid interface. For spreading to occur spontaneously, the surface free energy per unit area ($-\Delta G_w/A$) must decrease during the spreading process. The liquid spreads spontaneously over the solid surface when S_{ls} is positive or zero. When S_{ls} is negative, the liquid remains as a drop with a definite angle of contact. Therefore, the spreading coefficient S_{ls} is a measure of the driving force behind the spreading process. Because of the difficulty of measuring the values of σ_{sa} and σ_{ls} directly, Young's equation should be used to modify the above equation.[2] Equation 2 becomes

$$S_{ls} = \sigma_{al}(\cos\theta - 1) \tag{3}$$

where θ is the contact angle at the liquid−air interface with the solid surface.

The purpose of this work is to investigate the contact angle between liquid−air−solid interfaces and the wetting behavior of different concentrations of polyacrylamide aqueous solutions over polyethylene substrate. The ionic strength of the polyacrylamide solution was adjusted by the addition of NaCl, $CaCl_2$, and $AlCl_3$.

Experimental Section

Materials. Polyacrylamide (PAA, from BDH Ltd., Poole, England) with a molecular weight of 5×10^6 was employed to prepare aqueous solutions of different concentrations. The addition of small quantities of PAA to distilled water significantly increases the solution's viscosity.[3,4] This important characteristic of PAA enhances the mobility behavior of oil in porous media.[5] The polymer solution was prepared by adding a known mass of PAA to double distilled water and gently mixing to prepare an aqueous

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solution of a specific concentration. The polymer aqueous solutions were used immediately after the complete dissolution of PAA into distilled water. This study covered the wide range of polymer concentrations of 0−1000 g m^{-3}.

The amide groups of the polyacrylamide molecules (NH_2) are hydrolyzed to form carboxyl groups (COO^-) and ammonia. The degree of hydrolysis can be defined as the number of carboxyl groups replacing amide groups divided by the total number of macromolecule groups. The number of negative charges on the polymer chain increases as a result of the polymer hydrolysis.

One of the important properties of PAA aqueous solutions is the polyelectrolyte effect. Therefore, sodium chloride, calcium chloride, and aluminum chloride were added to control and adjust the ionic strength of the polyacrylamide solutions. Solutions with a wide range of concentrations of these different electrolytes (0, 0.2, 0.4, ..., 1.0 mol L^{-1}) were added to the PAA aqueous solutions to study their effect on the contact angle and wetting behavior on a polyethylene substrate.

Experimental System. A Plexiglas environmental chamber of dimensions 10 × 15 × 17 cm was designed to accommodate both the solid substrate and the liquid droplet. The environmental chamber was saturated with PAA solution vapor to avoid any volume changes due to droplet evaporation.

Most solid surfaces are not completely clean or consistent, and they support different wetting behaviors. Such behaviors could result from oxidation, coating, and adsorption. Wettability behavior is very sensitive to these effects. Therefore a polishing technique was applied to the polyethylene (PE) substrate after each experimental run to ensure that a new and fresh substrate surface would be in contact with the PAA polymer solution. A polished PE sheet of dimensions 3 × 4 × 0.6 cm (from Cadillac Plastic Division, Edmonton, Alberta, Canada) was used as the solid substrate. The polyethylene substrate was used because of its hydrophobicity behavior, low surface energy, and low wetting behavior. A 50-μL PAA aqueous solution droplet was placed on the PE sheet from a special hole in the environmental chamber using a microsyringe.

The still macrophotography technique was used to record the contact angle of the PAA aqueous solution droplet. This system consisted of a Nikon F3 camera with a 50-mm F11.8 lens in the reverse position, a PB-6 bellows focusing attachment, and a PB-6E extension bellows. Illumination was supplied by an arc lamp source. It consisted of a power supply, a lamp housing with a condensing lens, and a 200-W mercury lamp. This illumination system provided approximately 149 mW in a 35-mm highly collimated beam. The macrophotographic system was aligned with the illumination system on opposite sides of the Plexiglas environmental chamber. Measurements of contact angles were recorded at room temperature (22 °C).

Results and Discussion

Contact angles were recorded using images obtained with the still macrophotography system, and the produced images were placed into a slide projector to produce a magnified images that were about 24 times the original size of the object. The measurements of the contact angle were carried out using a digitizer−microcomputer system. The analysis of the recorded image of the PAA contact angle on the PE substrate was repeated five times, and the average value was taken. The wetting behavior of the PAA solutions over the PE substrate was obtained using eq 3. The details of these procedures are reported elsewhere.[6]

Table 1. Contact Angle Measurements for 100 g m^{-3} PAA solution

t (min)	θ_L	θ_R
15	88.1	90.1
30	87.4	88.1
45	87.1	88.4
60	87.4	88.1
90	84.0	83.7
120	83.3	84.0
150	83.7	84.1
210	83.3	83.7

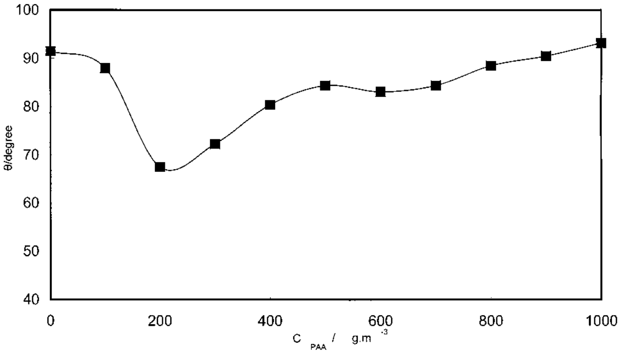

Figure 2. Contact angle as a function of PAA concentration.

Table 2. Surface Tension Measurements and Spreading Coefficients for PAA Solutions

PAA conc (g m^{-3})	$\sigma_{20\,°C}$	$\sigma_{30\,°C}$	$S_{20\,°C}$	$S_{30\,°C}$
0.0	72.45	71.75	−74.35	−73.63
80	71.70	71.65	−69.20	−69.1
160	71.68	71.63	−52.40	−52.36
200	71.65	71.10	−44.23	−43.89
280	71.80	71.60	−49.97	−49.83
360	71.95	71.75	−57.73	−57.57
400	72.13	72.00	−60.10	−59.99
600	72.48	72.10	−63.77	−63.44
800	72.53	72.40	−70.63	−70.50
1000	72.70	72.63	−76.76	−76.68

Contact Angle. Initially, the contact angle measurements were carried out to measure the left and right sides of 100 g m^{-3} PAA droplets on the PE substrate as a function of resting time. This set of measurements was important in establishing the elapsed time required to record the PAA solution droplet on PE. Table 1 shows the values of the left- (θ_L) and right- (θ_R) side contact angles for the 100 g m^{-3} PAA solution. This experimental run lasted for 3.5 h, and it shows that there is no significant difference between the left- and right-side values after 45 min. Therefore, the contact angle was recorded after 50 min in the rest of the required experiments.

Figure 2 shows the behavior of the contact angle at the air−polymer solution−solid three-phase contact line for 50-μL droplets with different PAA concentrations at room temperature (22 °C) on the polyethylene substrate. This plot shows an initial gradual reduction in the contact angle measurements from the contact angle value of pure distilled water to that of a 200 g m^{-3} PAA solution. Then, a gradual increase is reported from 200 to 1000 g m^{-3} PAA concentration. This behavior can be explained more clearly by measuring the surface tension values of these concentrations. As is already well-established, surface tension measurements reflect the behavior of the contact angles. Table 2 reports the surface tension and spreading coefficient measurements for the entire range of PAA concentrations at 20 and 30 °C. Measurements of the surface tension were accomplished using a Fisher surface tensi-

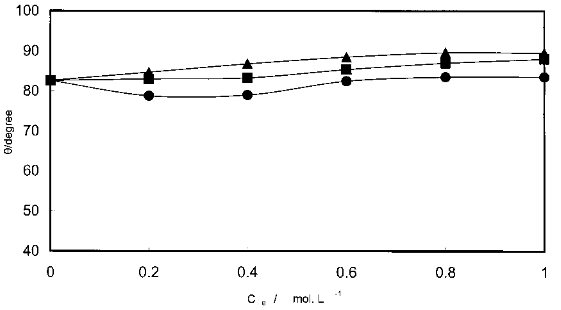

Figure 3. Effect of electrolyte concentration on contact angle of 600 g m^{-3} PAA solution.

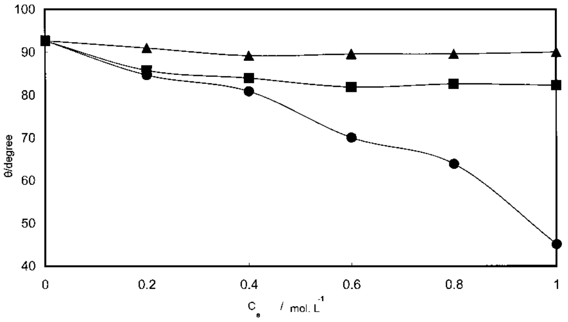

Figure 4. Effect of NaCl, CaCl$_2$, and AlCl$_3$ on contact angle of 1000 g m^{-3} PAA solution.

omat based on the du Nouy method. Surface tension measurements were repeated several times for each concentration, and average values are reported. For more information about these measurements, see Ghannam.[7] Table 2 shows an initial reduction of the surface tension and gradual improvement of the spreading coefficient from the value of pure distilled water to the value of 200 g m^{-3} PAA. The measurements of surface tension experience a gradual increase for the range of 200−1000 g m^{-3} concentrations. However, the spreading coefficient shows a gradual reduction for the range of 200−1000 g m^{-3}. The surface tension of the double distilled water decreases from its initial value upon the addition of PAA molecules. The attractive forces between water molecules are reduced by the PAA molecules up to a concentration of 200 g m^{-3} PAA. At higher concentrations, the attractive forces between PAA molecules become greater than the attractive forces between water molecules, which leads to higher surface tension measurements.

Effect of Different Electrolytes. Tanford[8] and Morawetz[9] reported that polyacrylamide solutions are polyelectrolytes. Therefore, the addition of a simple electrolyte substance such as NaCl, CaCl$_2$, and AlCl$_3$ to a PAA aqueous solution affects the apparent size of the macromolecules in the polymer solution. This effect will adjust the macroscopic rheological and interfacial properties of the solution.

High salinity plays important roles in polymer flooding. One of these roles is to enhance the adhesion between the electrical double layers of rock surfaces and bacteria, thus limiting bacterial activity through an oil reservoir. Bacteria have significant ability to attack crude oil in an oil reservoir, which eventually decrease the *n*-paraffin content.[10] This conclusion has been confirmed by Evans et al.[11] and Baily et al.[12] Consequently, studying the effect of NaCl, CaCl$_2$, and AlCl$_3$ on the contact angle and spreading coefficient of polyacrylamide solutions on a polyethylene substrate is of great importance.

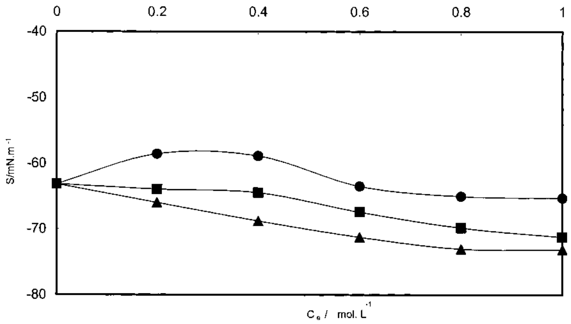

Figure 5. Effect of electrolyte materials on spreading behavior of 600 g m^{-3} PAA solution.

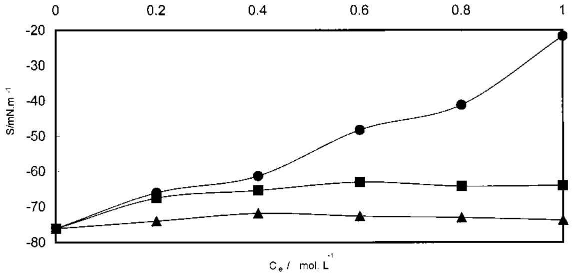

Figure 6. Effect of NaCl, CaCl$_2$, and AlCl$_3$ on spreading behavior of 1000 g m^{-3} PAA solution.

Figures 3 and 4 show the effects of adding different electrolytes on the contact angle of PAA on a PE substrate. The concentrations of the electrolytes vary from 0 to 1 mol L^{-1} of PAA solution. Figure 3 shows that the electrolyte materials slightly adjust the contact angle behavior on the PE substrate. The addition of NaCl to a 600 g m^{-3} PAA solution slightly lowers the contact angle, whereas the addition of the other two electrolytes does not reduce the contact angle. However, in the higher-concentration PAA solution of 1000 g m^{-3}, the effect of adding different electrolytes on the contact angle measurements is more significant. Because of the negative charges of the carboxylic groups, the hydrodynamic radius of the PAA macromolecules is large in double distilled water.[5] As the concentration of NaCl in the polymer solution increases, the repulsive forces on the carboxyl groups decrease. This leads to a decrease in the hydrodynamic radius of the macromolecules. Figure 4 shows a significant effect for NaCl on the contact angle of the 1000 g m^{-3} PAA solution. NaCl reduces the apparent size of the polyacrylamide macromolecule and, therefore, lower the contact angle significantly. CaCl$_2$ and AlCl$_3$ slightly decrease the contact angle values of the 1000 g m^{-3} solution.

The modification of the polyacrylamide macromolecules is influenced by the valences of the electrolytes. NaCl, in the range from 0 to 1.0 mol L^{-1}, shows the strongest effect among all of the tested electrolytes. Figures 5 and 6 illustrate this conclusion more clearly by displaying the spreading coefficients of PAA solutions of 600 and 1000 g m^{-3} concentrations versus the electrolyte concentration. Figure 5 shows the behavior for the concentration of 600 g m^{-3} as a function of NaCl, CaCl$_2$, and AlCl$_3$ contents. NaCl slightly enhances the spreading coefficient; however, the other two materials do not exhibit this influence. Figure 6 better illustrates the spreading coefficient enhancement. CaCl$_2$ and AlCl$_3$ slightly improve the spreading coefficient, but NaCl clearly shows its ability to enhance the wetting behavior of the 1000 g m^{-3} PAA solution on the PE substrate. This is again a result of the effect of NaCl in reducing the hydrodynamic radius of the PAA and, therefore, in lowering the contact angle of PAA on the PE substrate.

Table 3. Spreading Coefficient Improvement for 1000 g m^{-3} PAA

electrolyte conc (mol L^{-1})	S_{NaCl}	S_{CaCl_2}	S_{AlCl_3}	WIP_{NaCl}	WIP_{CaCl_2}	WIP_{AlCl_3}
0.0	−76.13	−76.13	−76.13	0.0	0.0	0.0
0.2	−66.05	−67.56	−74.02	13.9	11.2	2.8
0.4	−61.35	−65.40	−71.83	20.0	14.1	5.6
0.6	−48.25	−63.04	−72.64	37.1	17.2	4.6
0.8	−41.18	−64.21	−73.06	46.3	15.7	4.0
1.0	−21.70	−63.98	−73.78	71.7	15.9	3.1

Figure 6 shows a significant spreading coefficient improvement for 1000 g m^{-3} PAA in the presence of NaCl in comparison with $CaCl_2$ and $AlCl_3$. Table 3 reports this behavior in addition to the new quantity WIP, which is the wetting improvement parameter. It can be defined as

$$WIP = (S_i - S_f) \times 100/S_i \qquad (4)$$

where WIP is the wetting improvement parameter, S_i is the spreading coefficient without electrolyte, and S_f is the spreading coefficient with electrolyte. Table 3 shows that NaCl enhances the wetting characteristic to the extent of 71.7% at 1.0 mol L^{-1}; however, $CaCl_2$ and $AlCl_3$ improve the wetting behavior to the extents of 17.2 and 5.6% at concentrations of 0.6 and 0.4 mol L^{-1}, respectively.

Conclusions

The contact angles of polyacrylamide aqueous solutions in the concentration range of 0−1000 g m^{-3} were measured on a polyethylene substrate. Contact angles for 100 g m^{-3} PAA showed insignificant differences between left and right images after 45 min of resting time. A minimum angle was reported for the 200 g m^{-3} PAA concentration as a result of a balance between the interfacial activities of the PAA macromolecules and the double distilled water molecules.

Different concentrations of NaCl, $CaCl_2$, and $AlCl_3$ in the range of 0−1.0 mol L^{-1} are added to the PAA aqueous solutions. Whereas $CaCl_2$ and $AlCl_3$ slightly change the wetting behavior of the PAA aqueous solutions on polyethylene substrate, NaCl significantly lowers the contact angle and enhances the wetting behavior of PAA solutions on polyethylene substrates, especially for the higher concentration of 1000 g m^{-3} PAA solution. The addition of 1 mol L^{-1} NaCl improves the spreading behavior of the 1000 g m^{-3} PAA aqueous solution over the polyethylene substrate by 71.7%, whereas $CaCl_2$ and $AlCl_3$ increase the spreading behavior by 17.2 and 5.6% at concentrations of 0.6 and 0.4 mol L^{-1}, respectively.

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