Interfacial Properties of Polyacrylamide Solutions

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ABSTRACT: Surface tension of the polyacrylamide solution was measured as a function of the polyacrylamide concentration $(0-1000 \text{ gm/m}^3)$ and temperature $(10-60^{\circ}\text{C})$. The static contact angles of the polyacrylamide solutions in the range of $0-1000 \text{ gm/m}^3$ were reported on the polyvinyl chloride and *Teflon* substrates. Surface tension, static contact angle, and spreading behavior of the polyacrylamide solutions in the presence of different concentrations of NaCl, CaCl₂, and AlCl₃ are discussed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 219–227, 1999

Key words: polyacrylamide; contact angle; surface tension; wetting behavior

INTRODUCTION

Tertiary oil recovery is an important challenge to modern technology. A new oil well first produces spontaneously and then, by a pumping system, until the oil rate of production becomes uneconomical. Additional oil may be produced by injecting water into the formation and pumping out a mixture of oil-water at other locations. Eventually, this becomes uneconomical; however, 40-50% of the original oil still remains in the formation. Tertiary oil recovery is a process to extract this residual oil. This residual oil is distributed in unconnected ways through the capillary system of the formation. Reducing the pressure drop across the oil/water interface seems to be important and might be achieved by reducing the oil/water interfacial tension. Therefore, water could displace oil at the oil/solid interface.

Such natural and synthetic polymers as xanthan gum, polysaccharides, polyacrylamides, polyethylene oxide, and others play important roles in modern technological products as thickening agents. Some examples of such technologies are food production, pulp and paper, coating products, and so forth. One important application of such polymers is in the enhanced oil recovery processes, either to recover the oil remaining in the oil reservoir or to push surfactant solutions in the tertiary oil recovery stage.

One widely applied technology of great interest to everyday life is the wetting process. Wetting, in general, is the displacement of one fluid by another from the solid surface. Wetting always involves three phases fluid/fluid/solid in contact. This displacement process is an important technique in the coating technology and in enhanced oil recovery where aqueous solution of polyacrylamide is used to displace oil from the solid surface in the oil formation.

Introduction of chemicals in the enhanced oil recovery stage to mobilize the trapped residual oil, which remains in the formation after the economical production stages, would be affected by the physicochemical environment of oil reservoirs. The chemical flooding is meant to include the surfactant floods, alkaline water floods, and polymer floods. The microscopic displacement mechanism¹ is greatly influenced by geometry of the pore network, fluid/fluid properties (i.e., interfacial tension, density difference, bulk viscosity ratio, and phase behavior), fluid/solid properties (such as wettability, ion exchange, and adsorption), and applied pressure gradient and gravity.

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The importance of interfacial properties of different crude oils has been discussed by several researchers.^{2–6} Radke et al.^{2,3} measured the interfacial properties of acidic crude oils, and Taylor et al.⁴ examined surfactant-oil alkaline flooding systems. Cambridge and his co-workers⁵ reported that a synthetic acidic oil–alkali system displays behavior differing from that of natural crude oils. Neale et al.⁶ investigated the effect of oil viscosity on the interfacial tension of crude oil–alkali systems.

When a liquid droplet is placed on a solid surface (Fig. 1), it may spread to cover the solid surface or it may remain as a stable drop on the solid surface. For the spreading to occur spontaneously, the surface free energy of the system must be decreased during the spreading process. The total decrease in surface free energy per unit area A attributable to spreading

$$-\Delta G_w / A = \sigma_{\rm sa} - (\sigma_{\rm ls} + \sigma_{\rm al}) \tag{1}$$

If the quantity above is positive, the system decreases in surface free energy during the wetting process, and the process occurs spontaneously. However, if $(-\Delta G_w/A)$ is negative, the liquid will not spread spontaneously over the solid substrate. Therefore, this quantity is a measure of the driving force behind the spreading process, which is usually called the spreading coefficient $S_{\rm ls}$. Because surface tension of solid/air and liquid/solid interfaces cannot be measured directly, the spreading coefficient equation should be modified using Young's equation (1805). Then eq. (1) becomes

$$S_{ls} = \sigma_{al}(\cos\theta - 1) \tag{2}$$

The objective of this study is to investigate the surface tension, the contact angle between liquid/ air/solid interfaces, and the wetting behavior of the polyacrylamide solutions using different concentrations of polyacrylamide solutions over the temperature range of $10-60^{\circ}$ C. The ionic strength of the polyacrylamide solution was controlled by the addition of different concentration of NaCl, CaCl₂, and AlCl₃.

EXPERIMENTAL

The experimental system used in this work was designed to measure the surface tension, contact angle of liquid droplet at solid/liquid/air interface, and wetting behavior using eq. (2) with various concentrations of polyacrylamide solutions.

Surface tension values were measured using Fisher Surface Tensiomat based on the du Nouy method. The du Nouy method employs a platinum-iridium ring of precise dimensions. The circumference of the ring is 6 cm, and the wire diameter is 0.0356 cm. Before each measurement, the platinum-iridium ring first is cleaned by dipping it in benzene then spraying it with acetone to remove the benzene and allowing the acetone to evaporate.

Measurements of the contact angle of liquid droplets at the solid/liquid/air interface were made using a still-macrophotography system. This consisted of a Nikon F3-mm camera with 50-mm F11.8 lens in reverse position, a PB-6 bellows focusing attachment, and a PB-6E extension bellows. Illumination was provided by a powerful 150-watt Philips lamp from the opposite side of the environmental chamber. An environmental chamber was made of *Plexiglas* with $10 \times 15 \times 17$ cm dimension to accommodate the solid substrates. The environmental chamber was saturated with solution vapor to retard droplet evaporation.

A polished polyvinyl chloride (PVC) and Teflon (TEF) with $3 \times 4 \times 0.6$ cm dimension (Cadillac Plastic Division Edmonton, Alberta, Canada) were used as the solid substrates. A 50 μ l liquid droplet was placed on each solid substrate from a certain hole in the environmental chamber using a microsyringe.

The polymer solution was prepared by dissolving polyacrylamide (PAA, BDH, Ltd., Poole, England, molecular weight 5 \times 10⁶, production #29788) in double-distilled water. The addition of small quantities can substantially increase the solution's viscosity. This well-known property increases the mobility control of fluids in porous media.⁷ The polymer powder is first dispersed and dissolved in double-distilled water and gently mixed. Under normal conditions, the amide groups (NH₂) of the polyacrylamide molecules are hydrolyzed to produce carboxyl groups (COO⁻) and ammonia. The degree of hydrolysis defined as the number of carboxyl groups substituted to the amide groups over the total number of the macromolecule groups is about 2%. Once the polymer is hydrolyzed, the number of the negative charges on the polymer chain increases. The polymer concentration range of 0–1000 gm/m³ was covered.

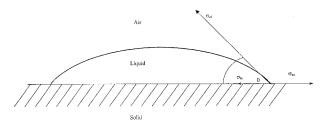


Figure 1 Definition sketch.

Tanford⁸ reported that the polyacrylamide solutions are polyelectrolytes. Therefore, sodium chloride, calcium chloride, and aluminum chloride were used to increase the ionic strength of the polyacrylamide solutions. NaCl, CaCl₂, and AlCl₃ (0, 0.2, 0.4, ..., 1 g mole/l) were used to study the effect of various concentrations of different electrolytes on surface tension, contact angle, and wetting behavior of polyacrylamide solutions.

RESULTS AND DISCUSSION

Effect of Temperature

Surface tension was measured using Fisher Surface Tensiomat based on the du Nouy method for all polyacrylamide solutions in the range of 0 to 1000 gm/m³ at temperatures of 10, 20, \ldots , 60°C. Figure 2 shows the behavior of the surface tension of the polyacrylamide solutions versus their concentration at different temperatures. Surface tension is a characteristic property of each solution, which reflects the attraction between the molecules of the solution at the surface. Figure 2 shows that the surface tension of all solutions decreases significantly as the temperature increases from 10 to 60°C. Higher temperature increases the kinetic energy of each molecule in the solution, which decreases the attraction forces between the molecules at the solution surface and, consequently, causes significant reduction of the surface tension values.

Figure 2, also, shows a maximum reduction of the surface tension at each temperature. The surface tension of double distilled water, at 10° C, reduced from 72.5 mN/m by the addition of polyacrylamide until the concentration of 200 gm/m³ because of the interaction of the attraction forces between polyacrylamide and water molecules. At a concentration higher than 200 gm/m³, the attraction forces between polyacrylamide molecules were predominant and, consequently, increased the value of the surface tension to higher values than 72.5 mN/m at 1000 gm/m³.

Figure 2 shows a significant effect for temperature on the surface tension of the polyacrylamide solutions except at the range of 20-30 °C. The surface tension of all solutions of polyacrylamide decreases as the temperature increases and becomes zero at the critical temperature. The variation of the surface tension with temperature could be represented by the Ramsay-Shields equation⁹

$$\sigma(M/\rho)^{2/3} = k(T_c - T - 6) \tag{3}$$

 $(M/\rho)^{2/3}$ is a quantity proportional to the molar surface of the solution.

$$\sigma = k(T_c - T - 6)/(M/\rho)^{2/3}$$
(4)

$$\sigma = -KT + K(T_c - 6) \tag{5}$$

According to eq. (5), a plot of the solution surface tension versus temperature should be a straight line with slope equal to -K. Regression analysis was carried out for all the experimental data to calculate the values of K, $K(T_c - 6)$, and T_c as indicated in Table I.

Contact Angle Measurement

A still-macrophotography system was used to record the contact angle measurements of all polyacrylamide solutions on each solid substrate (PVC and Teflon). A digitizer-microcomputer sys-

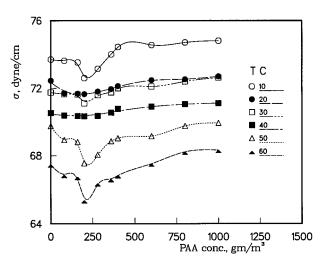


Figure 2 Effect of temperature on the PAA surface tension.

PAA Conc.	K	$K(T_c - 6)$	T_c (K)	r
0	0.116	74.987	654.8	0.97
80	0.124	74.860	610.4	0.95
160	0.125	74.832	604.3	0.95
200	0.141	74.687	537.3	0.91
280	0.133	74.858	570.9	0.95
360	0.135	75.358	562.7	0.96
400	0.139	75.717	552.7	0.95
600	0.132	75.747	578.6	0.98
800	0.120	75.647	635.6	0.97
1000	0.121	75.802	634.3	0.97

 Table I
 Regression Analysis of Eq. (5)

tem was used to measure the contact angles. A slide projector was used to magnify and provide the image to the digitizer. This system of recording and analyzing the contact angle was used to provide the highest possible reproduction ratio. The reproduction ratio achieved was around 24 times the real size.

The contact angle values for left and right sides of 100 gm/m³ of PAA droplets on each solid substrate of PVC and TEF versus time of resting were reported. This study was very helpful to obtain the elapsed time required to record the liquid droplet for each solid substrate. It shows there is no significant difference between left and right values of each droplet on each solid substrate after 45 minutes. Therefore, the contact angle was recorded for all solutions on each solid substrate 50 minutes after application of each droplet.

Figure 3 shows the flow behavior in terms of viscosity for 0.25% by weight of PAA and 0–10 gm NaCl/Liter of PAA solution as an example. PAA solutions experience shear-thinning behavior up to a critical shear rate. At this critical shear rate, the viscosity of the tested solution shows a shear-thickening behavior. Figure 3 shows that the viscosity of PAA solution decreases with NaCl concentration. By adding NaCl, the sodium ion concentration increases to reduce the repulsive forces between the carboxylic groups of the PAA macromolecules. Therefore, the hydrodynamic radius of the PAA network decreases and, consequently, reduces the viscosity of PAA solution significantly.

Figure 4 displays the values of the contact angle at the three-phase contact line of 50 μ L of each polyacrylamide solution on low-energy solid substrates of PVC and TEF. Low-energy solid surfaces are substrates for which surface free-energy

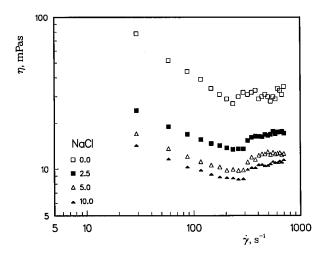


Figure 3 Viscosity curves of 0.25% PAA as a function of NaCl concentration.

is small for any adsorbate. PVC solid substrate shows lower contact angle for all polyacrylamide solutions as compared to Teflon substrates. Osipow¹⁰ mentioned that, as the chlorine content in the polymer increases, the contact angle for given liquid decreases. The role of the chlorine in the polymer is to decrease the adhesion of the polyacrylamide solution on the solid substrate and, consequently, improve the wetting behavior of the polymer; therefore, it lowered the value of the contact angle of the polyacrylamide solution on the solid substrate.

Observations agree with the assumption that spreading of aqueous solutions of polyacrylamide on low-energy solid substrates depends upon the surface tension of the solution and σ_c of the sub-

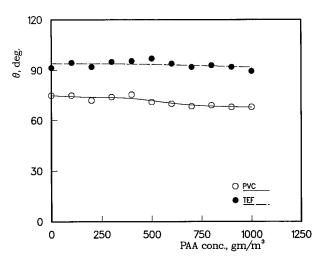


Figure 4 Contact angle versus PAA concentration.

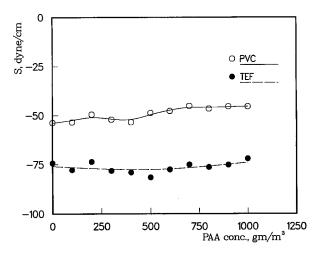


Figure 5 Spreading coefficient behavior for PAA solutions.

strate. σ_c is defined as the critical surface tension of the solution below which liquids will spread on the polymer substrate. The critical surface tension of the Teflon is¹⁰ 16.5–19.5 mN/m. None of the polyacrylamide solutions has a surface tension value low enough to spread on Teflon. Therefore, the values of the contact angle for Teflon are higher than the PVC substrate. This conclusion can be seen more clearly in Figure 5, where the spreading coefficient S of all polyacrylamide solutions are plotted against polyacrylamide concentration. This figure shows that the PVC offers higher spreading coefficient, and, consequently, higher wetting characteristic than the Teflon substrate.

Effect of Electrolyte

Bacteria have been suspected of being able to attack crude oil in the reservoir. Davis¹¹ showed that crude oil could be attacked by soil bacteria, causing a decrease of n-paraffin content. It was suggested that the major mechanism of alteration is the microbes carried by the recharge water that brings dissolved oxygen and other nutrients required for bacteria activity. This work has been confirmed and extended by Evans et al.¹² and Bailey et al.¹³

High saline concentration has the opposite effect on bacterial growth, and it compresses the electrical double layers of rock surfaces. Therefore, it enhances the adhesion between the electrical double layers of rock surfaces and bacteria, and then limiting bacteria transport through an oil reservoir. Morawetz¹⁴ and Tanford⁸ mentioned that the polyacrylamide solutions are polyelectrolytes; that is, substances containing a large number of electrostatic charges. The addition of a simple electrolyte to the solution decreases the apparent size of macromolecules in the solution, thereby modifying the macroscopic rheological and interfacial properties of the solution. In this work, we reported the results of an extensive investigation of the effect of sodium chloride, calcium chloride, and aluminum chloride on the surface tension, the contact angle, and the spreading coefficient of the polyacrylamide solutions.

Figure 6 shows the effect of adding sodium chloride salts on the surface tension of the polyacrylamide solution at room temperature. Sodium chloride is studied from 0.0 to 1 gmole/Liter in 0.2 increments. Surface tension measurements were taken five times for each sample, and the average values were reported. Experimental results show a slight increase for the surface tension with sodium chloride salts for all the examined polyacrylamide solutions. The hydrodynamic radius of the polyacrylamide macromolecules is large in double deionized water because of the negative charges of the carboxylic groups.¹⁵ As the concentration of the NaCl increases in the polymer solutions, the repulsive forces within the polymer network decrease because of charge screening effects. This causes the hydrodynamic radius of the chain to decrease and the degree of polymer chain entanglement to diminish. This behavior reduces the apparent size of the polyacrylamide macromolecule that increase the surface tension values.

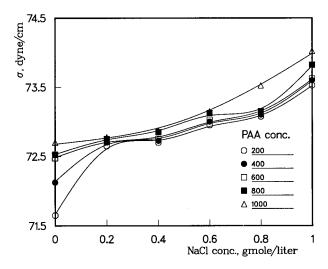


Figure 6 Effect of NaCl on the surface tension of PAA solutions.

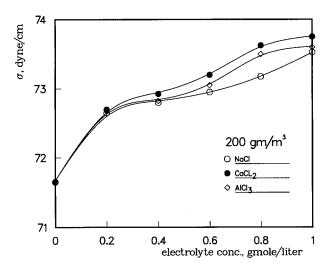


Figure 7 Surface tension of 200 gm/m³ PAA solution versus NaCl, CaCl₂, and AlCl₃ concentrations.

The effect of different electrolytes of NaCl, CaCl₂, and AlCl₃ on the 200 gm/m³ of polyacrylamide solutions is shown in Figure 7. In general, all the tested electrolytes have a significant influence on the apparent size of the polyacrylamide macromolecules, which increase the value of the surface tension. The modification of the polyacrylamide macromolecules is influenced by the electrolytes valence. Therefore, the surface tension of the polyacrylamide solution increases slightly in the presence of $CaCl_2$ (valence is 2) as compared to NaCl (valence is 1). However, the addition of AlCl₃ slightly decreases the surface tension of the 200 gm/m³ PAA solution as compared to the effect of CaCl₂. The same behavior is recorded in the case of 600 gm/m³ of polyacrylamide solution shown in Figure 8. AlCl₃ (valence is 3) has an opposite effect on the modification of the apparent size of the polyacrylamide macromolecules, which reduces the values of the surface tension as compared to CaCl₂. Figure 9 shows a greater opposite effect for the AlCl₃ to reduce the surface tension of the polyacrylamide solution as compared to CaCl₂ in the case of 1000 gm/m³ of polyacrylamide solution. To summarize, the effect of different valences of electrolyte solution, NaCl and CaCl₂ have noticeably reduce the apparent size of the PAA macromolecules. This increases their concentration at the air/liquid interface, which increases the surface activity and, consequently, the surface tension. Aluminum chloride, on the other hand, has an opposite effect to reduce the surface tension value as compared to CaCl₂.

Figures 4 and 5 showed that the PVC substrate provides better wetting behavior than Teflon.

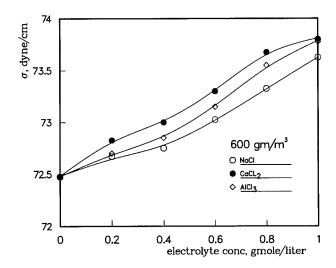


Figure 8 Surface tension of 600 gm/m³ PAA solution versus NaCl, CaCl₂, and AlCl₃ concentrations.

Therefore, we focus our next discussion on this particular substrate to study the effect of different electrolyte materials on the contact angle and the spreading coefficient. Figures 10-12 show the behavior of the contact angles on the PVC substrate as a function of NaCl, CaCl₂, and AlCl₃ for 200, 600, and 1000 gm/m³, respectively. In general, sodium chloride has a greater ability to modify the behavior of the polyacrylamide macromolecules to lower the contact angle values than calcium chloride and aluminum chloride. The lower contact angle we have, the higher wetting behavior will be. Therefore, sodium chloride improves the wetting characteristic and increases the mobility of the polyacrylamide solution on the PVC

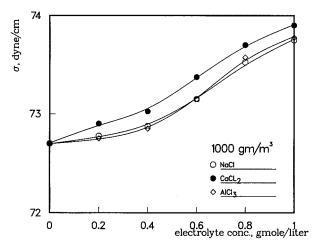


Figure 9 Surface tension of 1000 gm/m³ PAA solution versus NaCl, CaCl₂, and AlCl₃ concentrations.

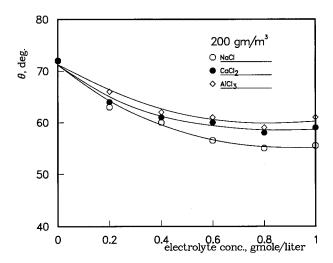


Figure 10 Effect of different electrolyte concentration on the contact angle of 200 gm/m^3 PAA solution.

substrate, which increases the displacement forces of the polyacrylamide solution in the pore network. This behavior can be seen more clearly in the Figures 13–15, which display the spreading coefficient versus electrolyte concentration of NaCl, CaCl₂, and AlCl₃ on PVC substrate for 200, 600, and 1000 gm/m³, respectively. Generally, NaCl achieved higher spreading coefficient than CaCl₂ and AlCl₃ on PVC substrate for all the examined PAA solutions. One important conclusion can be drawn from Figures 13–15: the higher concentration of polyacrylamide in the solution, the more pronounced the spreading coefficient achieved by NaCl as compared to the two other electrolytes of CaCl₂ and AlCl₃.

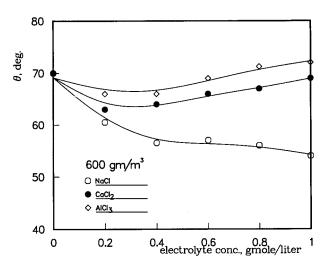


Figure 11 Effect of different electrolyte concentration on the contact angle of 600 gm/m^3 PAA solution.

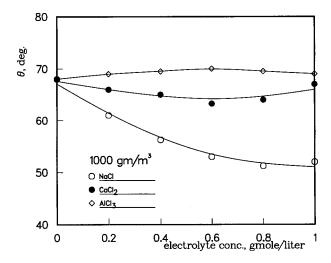


Figure 12 Effect of different electrolyte concentration on the contact angle of 1000 gm/m³ PAA solution.

CONCLUSIONS

The effect of the polyacrylamide concentration and temperature on the surface tension of the polyacrylamide solutions were studied in the range of 0–1000 gm/m³ of polyacrylamide and $10-60^{\circ}$ C. The macromolecules of polyacrylamide material have a significant influence on the surface tension behavior. Owing to the interaction forces between the polyacrylamide macromolecules and the double distilled water molecules, the surface tension lowered from 72.5 mN/m at 0.0 gm/m³ to a minimum value at 200 gm/m³ of PAA. However, the surface tension starts to in-

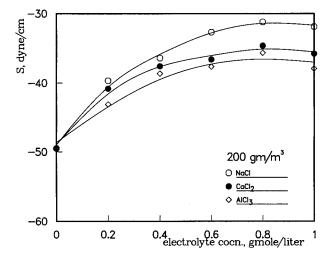


Figure 13 Spreading coefficient of 200 gm/m³ PAA solution versus concentration of NaCl, $CaCl_2$, and $AlCl_3$.

crease by adding more of the polyacrylamide substance because of the predominant effect of polyacrylamide macromolecules. This behavior is experienced for all temperature ranges. At higher temperature, the activity of the solution molecules is increased to reduce the attraction forces between them and, consequently, lower the surface tension value. The higher the temperature, the lower the surface tension recorded.

The contact angles of the polyacrylamide solution were reported on PVC and TEF substrates for all polyacrylamide concentrations. PVC substrate provides lower contact angles and higher spreading coefficients than Teflon because of the chlorine content in the PVC.

Because the polyacrylamide solution is polyelectrolyte, we studied the effect of NaCl, CaCl₂, and AlCl₃ on the surface tension and contact angle of the polyacrylamide solutions from 200 to 1000 gm/m³ at room temperature. All tested electrolyte materials modified the behavior of the polyacrylamide macromolecules and slightly increased the surface tension of the polyacrylamide solutions. Electrolyte valence plays an important role for controlling the surface tension value; the highest surface tension values were reported for CaCl₂ (valence is 2). However, AlCl₃ lowered the surface tension as compared to CaCl₂. The higher the polyacrylamide concentrations, the more reduction of the surface tension values were reported with $AlCl_3$ as compared to $CaCl_2$.

NaCl has a significantly lowers contact angles and improves the spreading coefficient for all polyacrylamide solutions as compared to CaCl₂

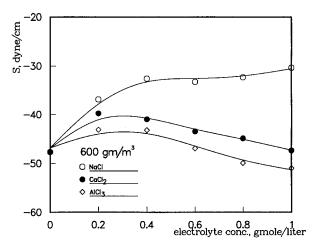


Figure 14 Spreading coefficient of 600 gm/m³ PAA solution versus concentration of NaCl, CaCl₂, and AlCl₃.

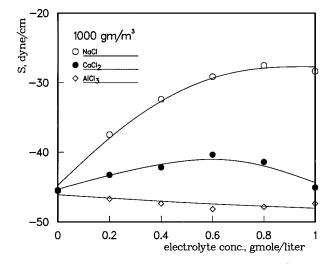


Figure 15 Spreading coefficient of 1000 gm/m³ PAA solution versus concentration of NaCl, $CaCl_2$, and $AlCl_3$.

and $AlCl_3$. The effect of NaCl on the spreading coefficient is more pronounced at a higher concentration of PAA solution.

NOMENCLATURE

- A surface area (m^2)
- ΔG_w change in surface free energy (mN/m)
- k constant of eq. (3)
- *M* solution molecular weight
- S spreading coefficient (mN/m)
- T temperature (K)
- T_c solution critical temperature (K)

Greek

- $\sigma_{\rm sa}$ surface tension at solid–air interface (mN/m)
- $\sigma_{\rm ls}$ surface tension at liquid–solid interface $(\rm mN/m)$
- $\sigma_{\rm al}$ surface tension at air-liquid interface (mN/m)
- θ static contact angle (°)
- ρ solution density (kg/m³)

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