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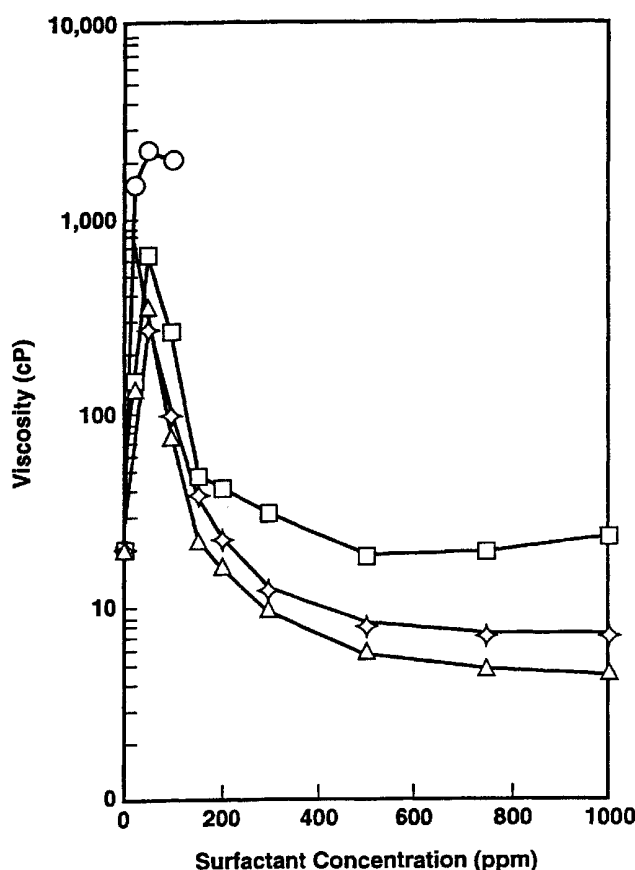
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(54) Title: **BRINE VISCOSIFICATION FOR ENHANCED OIL RECOVERY**



(57) Abstract: The present invention is related to an aqueous composition of at least one hydrophobically associating polymer and at least one surfactant, the mixture's viscosity being substantially constant or augmented over temperatures ranging from about 20 °C to about 60 °C. In another embodiment, the invention is related to a method for recovering oil from a subterranean reservoir by injecting into the reservoir a mixture of at least 100 to 25,000 ppm of a hydrophobically associating polymer per million parts by weight of water, about 25 to about 7,500 parts by weight per million parts by weight of water of one or more surfactants; and from about 0.5 wt.% to about 10 wt.%, based on the weight of water, of salts selected from the group consisting of alkali and alkaline earth metal halides and mixtures thereof.

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BRINE VISCOSIFICATION FOR ENHANCED OIL RECOVERY

FIELD OF THE INVENTION

The present invention relates to improvements in brine viscousification, especially for use in enhanced crude oil recovery.

BACKGROUND AT THE INVENTION

It has been apparent for many years that only a portion of the original oil in a reservoir can be produced by primary recovery methods, i. e. methods that rely on the energy in the formation. Secondary recovery methods such as waterflooding result in further crude oil production, but as much as half the original oil may remain in the reservoir after application of primary and secondary methods. Enhanced oil recovery methods ("EOR") have been proposed to substantially increase production beyond the yields obtained using primary and secondary recovery. According to some EOR methods, the depleted petroleum reservoir is flooded with brine through an injection well, the oil being recovered from a producing well in the same reservoir. Such methods sometimes use a surfactant, a polymer, or both in combination with the brine in order to improve oil recovery.

The production, handling, and flow of multi-component aqueous hydrocarbon mixtures, such as those encountered in EOR, present a number of technical difficulties resulting from component immiscibility and viscosity differences. One such difficulty is viscous fingering, which occurs when one component of a two component liquid is more easily transported through a porous medium as a result of that component's lower viscosity. Viscous fingering detrimentally affects EOR production from a partially depleted

petroleum reservoir because, it is believed, the lower viscosity brine component by-passes the remaining oil and preferentially passes through regions of high permeability in the reservoir.

Viscous fingering may become more pronounced in high temperature regions of the reservoir because, as is well known, brine solutions have decreasing viscosity with temperature.

There is therefore a need for improved EOR compositions and methods that make use of one or more surfactants in brine that provide a wide range of viscosities thereby permitting closer matching of the viscosity of the surfactant-brine solution to the crude oil and better mobility control. There is also a need for improved EOR compositions having a viscosity that is constant or increases with increasing temperature.

SUMMARY OF THE INVENTION

In one embodiment, the invention is a composition for use in enhanced oil recovery and capable of viscosifying a brine, comprising:

(a) from about 100 to about 25,000 parts by weight of a hydrophobically associating polymer per million parts by weight of the brine, the polymer being selected from the group consisting of copolymers of mono and dialkyl-acrylamides of 4 to about 18 carbon atoms with acrylamide, partially hydrolyzed derivatives thereof, and terpolymers of mono or dialkyl acrylamides of 4 to about 18 carbon atoms with acrylamide and an ethylenically unsaturated sulfonic acid salt of an alkali metal or ammonia;

(b) from about 25 to about 7,500 parts by weight per million parts by weight of the brine of at least one surfactant.

In another embodiment the invention is a method for recovering oil from a subterranean formation, comprising:

(a) forming a brine of water and salt, the salt being present in an amount ranging from about 0.5 to about 10 wt.% based on the weight of water;

(b) adding to the brine from about 100 to about 25,000 parts by weight of a hydrophobically associating polymer per million parts by weight of the brine, the polymer being selected from the group consisting of copolymers of mono and dialkyl-acrylamides of 4 to about 18 carbon atoms with acrylamide, partially hydrolyzed derivatives thereof, and terpolymers of mono or dialkyl acrylamides of 4 to about 18 carbon atoms with acrylamide and an ethylenically unsaturated sulfonic acid salt of an alkali metal or ammonia;

(c) adding to the brine and polymer from about 25 to about 7,500 parts by weight per million parts by weight of the brine of at least one surfactant in order to form a brine solution; and then

(d) injecting the brine solution into the subterranean formation.

In another embodiment the invention is a product by process, the process comprising:

(a) forming a brine of water and salt, the salt being present in an amount ranging from about 0.5 to about 10 wt.% based on the weight of water;

(b) adding to the brine from about 1000 to about 25,000 parts by weight of a hydrophobically associating polymer per million parts by weight of the brine, the polymer being selected from the group consisting of copolymers of mono and dialkyl-acrylamides of 4 to about 18 carbon atoms with acrylamide, partially hydrolyzed derivatives thereof, and terpolymers of mono or dialkyl acrylamides of 4 to about 18 carbon atoms with acrylamide and an ethylenically unsaturated sulfonic acid salt of an alkali metal or ammonia; and

(c) adding to the brine and polymer from about 25 to about 7,500 parts by weight per million parts by weight of the brine of at least one surfactant.

In another embodiment the invention is an aqueous mixture of at least one hydrophobically associating polymer and at least one surfactant, the mixture's viscosity being substantially constant or augmented over temperatures ranging from about 20°C to about 60°C.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows the influence of the degree of ethoxylation on the viscosity of linear polydisperse ethoxylate surfactants as a function of surfactant concentration.

Figure 2 shows the influence of the degree of ethoxylation on the viscosity of branched polydisperse ethoxylate surfactants as a function of surfactant concentration.

Figure 3 shows the effect of surfactant concentration on hydrophobically associating polymer solution.

Figure 4 shows the effect of surfactant concentration on polymer solutions wherein the polymer does not contain a hydrophobic group.

Figure 5 shows the influence of surfactant concentration in solutions that do not contain polymer.

Figure 6 shows the dependence of viscosity as a function of temperature for aqueous mixtures of hydrophobically associating polymer containing 1,000 ppm of non-ionic surfactant.

DESCRIPTION OF THE INVENTION

The invention is based on the discovery that a brine's viscosity can be continuously varied over the range of about 20 to about 2,500 centipoise by combining at least one hydrophobically associating polymer and at least one surfactant. More specifically, for brines containing from about 100 to about 25,000 parts by weight of a hydrophobically associating polymer per million parts by weight of the brine, it has been discovered that varying surfactant concentration in the brine over a range of about 25 to about 7,500 parts per million parts by weight of brine results in brine viscosities ranging from about 20 to about 2,500 centipoise.

The invention is also based on the discovery that the maximum viscosity for such a brine-surfactant-hydrophobically associating polymer mixture occurs at a surfactant concentration slightly below the surfactant's critical micelle concentration for anionic, non-ionic, and cationic surfactants. Moreover, it has been discovered that aqueous mixtures of an appropriate

amount of at least one hydrophobically associating polymer and an appropriate amount of at least one surfactant have a substantially constant or even increasing viscosity over typical reservoir temperature ranges.

The hydrophobically associating polymers suitable in the practice of the present invention include copolymers of mono or dialkyl acrylamides with acrylamide, their partially hydrolyzed derivatives, and terpolymers of mono and dialkyl acrylamides, acrylamides, and one of an ethylenically unsaturated sulfonic acid salt of an alkali metal or ammonia, and/or N-vinyl pyrrolidone. The alkyl groups of the mono and dialkylacrylamides will typically be in the range of about 4 to 18 carbons and preferably will be in the range from about 6 to 12. The mol% of the alkyl group in the polymer will typically be in the range of about 0.1 to 4.0 and preferably will be in the range from about 0.2 to 1.5.

A particularly preferred hydrophobically associating polymer used in the practice of the present invention is a copolymer of acrylamide and n-octylacrylamide which has been partially hydrolyzed to form a polymer containing from about 10 mol% to about 30 mol% carboxylic acid groups.

In the compositions of the present invention the hydrophobically associating polymer will be present in an amount ranging from about 1,000 to about 25,000 parts by weight per million parts of water.

The surfactants suitable in the practice of the present invention include anionic and non-ionic surfactants such as alkali metal salts of alkyl sulfates having from about 6 to 22 carbon atoms in the alkyl group, alkali metal salts of alkylethoxy sulfates having from about 6 to 22 carbon atoms in the alkyl group and having about 3 to 50 ethoxy groups, alkyl ethoxylates having from about 6 to 22 carbon atoms in the alkyl group and having from about 3 to 50

ethoxy groups, branched alkyl sulfonate with the number of carbon atoms in the alkyl group ranging from about 6 to about 22, and polyoxyethylene(n) alkyl ether with n ranging from about 2 to about 22 and the number of carbon atoms in the alkyl group ranging from about 6 to about 22. In the above surfactants the preferred alkali metal is sodium. Cationic surfactants such as alkyltrimethylammonium bromide with about 6 to about 22 carbon atoms in the alkyl group are also useful in the invention.

The surfactants are present in the composition of the present invention in an amount ranging from about 25 parts by weight to about 7,500 parts by weight per million parts by weight of water.

The brines of the invention include a water and a salt selected from the group consisting of alkali and alkaline earth metal halides and mixtures thereof. The preferred salt is an alkali metal halide, especially chloride. Preferably, the salt is present in an amount ranging from about 0.5 to about 10 wt.% based on the weight of water. The preferred salinity will depend, among other criteria, on the salinity of the subterranean formation.

In the practice of the present invention, a mixture is formed in the reservoir of crude oil and a sufficient amount of an aqueous treatment solution. The mixture is capable of flowing through the subterranean formation unit in response to a pressure differential, the effects of viscous fingering being substantially mitigated.

Preferably, the crude oil's viscosity is estimated or determined and a brine solution (i.e., the aqueous treatment solution) of at least one polymer and at least one surfactant is formed, the brine solution having a substantially equal or greater viscosity than the crude oil's. The viscosity determination may be

performed at ambient temperatures, or preferably at elevated temperatures more representative of reservoir temperatures. Such a mixture is capable of efficiently displacing the crude oil. More preferably, the brine solution will have a viscosity that is substantially constant or increases at increased reservoir temperatures.

While not wishing to be bound by any theory, it is believed that hydrophobically associating polymers interact with aqueous surfactant solutions at or near the critical micelle concentration ("CMC") in a way that causes the polymer associations to be considerably strengthened. This strengthening is believed to result from the presence of pre-micellar aggregates of surfactants in the solution. Accordingly, it is preferable to first determine the viscosity of the petroleum in the reservoir and to evaluate the reservoir permeability in order to select a polymer-surfactant brine composition having a viscosity substantially equal to or greater than the viscosity of the petroleum.

The compositions of the invention can be easily prepared, within the range of parameters outlined above, which will have the requisite viscosity. In general, the polymer is first dissolved in the brine, then the surfactant is added, and the components are mixed at room temperature.

In many cases, it is desirable to use the minimum amount of surfactant necessary to provide the greatest increase in brine viscosity. As shown in figures 1, 2, and 3 for a wide range of surfactants, the greatest brine viscosity is obtained at a molar surfactant concentration generally ranging from about 85% to about 100% of the CMC. Providing surfactant concentrations in this range is beneficial because, among other reasons, the brine's viscosity is a weak function of surfactant concentration near the maximum, and consequently the brine's viscosity will be relatively insensitive to small changes in surfactant

concentration, as shown in figures 1, 2, and 3. Where a mixture of surfactants is used, the desired surfactant concentration should preferably be in the range of about 85% to about 100% of a linear combination of the individual CMCs.

In cases where brines having augmented viscosity at elevated temperature are desired, surfactants such as decaethylene glycol oleyl ether, polyethylene glycol octadecyl ether, polyethylene glycol hexadecyl ether, and mixtures thereof may be used. In cases where brines having a substantially constant viscosity at elevated temperature are desired, an "increasing-viscosity" surfactant such as decaethylene glycol oleyl ether, polyethylene glycol octadecyl ether, polyethylene glycol hexadecyl ether, and mixtures thereof may be combined with a "decreasing-viscosity" surfactant such as diethylene glycol oleyl ether, polyethylene glycol dodecyl ether, polyethylene glycol steryl ether, and mixtures thereof. The properties of surfactant mixtures, such as viscosity, may be predicted from linear combinations of component surfactant properties according to methods known in the art.

Example 1

Figure 1 shows a system in which the concentration of polymer is 2,000 ppm in 2% NaCl. The polymer is a hydrolyzed acrylamide-octylacrylamide copolymer where the degree of hydrolysis is 18% and the mole fraction of octylacrylamide in the copolymer is 1.25%. The behavior of the viscosity at a shear rate of 1 s^{-1} is shown as surfactant concentration is varied. The behavior for four different surfactants is shown. The surfactants all have a linear dodecyl moiety as the hydrophobe, and are polydisperse in the number of ethoxylate groups. In the figure, circular points represent a linear C_{12} surfactant and an average of 3 ethoxylate groups. Square points represent a linear C_{12} surfactant having an average of 5 ethoxylate groups. Diamond points represent a

linear C_{12} surfactant having an average of 6 ethoxylate groups, and triangular points represent a linear C_{12} surfactant having an average of seven ethoxylate groups. The figure's ordinate shows the viscosity in centipoise and the abscissa shows surfactant concentration in ppm. As can be seen in the figure, the viscosity of each of the solutions is dramatically increased at a surfactant concentration of about 100 ppm. This is in the CMC range for each of the surfactants. The increase is more than a factor of 15 for all of them and is as much as a factor of 100 for one of them. The combination of surfactant and polymer is clearly much more effective than either polymer or surfactant alone.

Example 2

Figure 2 shows the results of measurements using the same polymer and salt in the same concentration as used in Example 1. However, the results in Figure 2 were obtained using a variety of other nonionic surfactants which are similar in structure to those of Example 1 except that the alkyl hydrophobe of the surfactant is branched. Again, even at very low surfactant concentrations, the viscosity is very substantially increased. The surfactant concentration range where viscosification is maximum is in the CMC range for each of the surfactants.

In Figure 2, square points represent a branched C_{12} surfactant having an average of 6 ethoxylate groups, hour-glass points represent a branched C_{12} surfactant having an average of 7 ethoxylate groups, circular points represent a branched C_{12} surfactant with an average of 5 ethoxylate groups, and triangular points represent a branched C_{12} surfactant having an average of 4 ethoxylate groups. The ordinate shows the viscosity and the abscissa shows concentration as in Figure 1.

Examples of some polymer-surfactant fluids compositions useful in the present invention are given in Table 1. As can be seen, fluid viscosities ranging from 17 to about 2,500 centepoise are achievable by the compositions' salt.

TABLE I

POLYMER	SALT WT.% NaCl	SURFACTANT	SURFACTANT CONC. (ppm)	FLUID VISCOSITY @ 1.28s ⁻¹ (cP)
P1	2.0	ℓ -C ₈ H ₁₇ (OCH ₂ CH ₂) $\frac{m}{5}$ —OH	400	17
P2	3.3	ℓ -C ₈ H ₃₅ (OCH ₂ CH ₂) $\frac{p}{10}$ —OH	50	66
P3	3.3	ℓ -C ₁₂ H ₂₅ (SO ₄ ⁻ Na ⁺)	2,500	154
P1	2.0	Br-C ₁₂ H ₂₅ (OCH ₂ CH ₂) $\frac{p}{7}$ —OH	100	224
P3	3.3	ℓ -C ₁₂ H ₂₅ (SO ₄ ⁻ Na ⁺)	5,000	241
P1	2.0	ℓ -C ₁₂ H ₂₅ (OCH ₂ CH ₂) $\frac{p}{5}$ —OH	100	348
P1	2.0	Br-C ₁₂ H ₂₅ (OCH ₂ CH ₂) $\frac{p}{5}$ —OH	50	485

POLYMER	SALT WT.% NaCl	SURFACTANT	SURFACTANT CONC. (ppm)	FLUID VISCOSITY @ 1.28s ⁻¹ (cP)
P1	2.0	ℓ -C ₁₃ H ₂₇ (OCH ₂ CH ₂) ₅ ^m —OH	750	561
P1	2.0	Br-C ₁₂ H ₂₅ (OCH ₂ CH ₂) ₅ ^m —OH	500	845
P1	2.0	ℓ -C ₁₂ H ₂₅ (OCH ₂ CH ₂) ₆ ^p —OH	25	927
P1	2.0	ℓ -C ₁₂ H ₂₅ (OCH ₂ CH ₂) ₅ ^p —OH	200	1028
P1	2.0	Br-C ₁₂ H ₂₅ (OCH ₂ CH ₂) ₄ ^p —OH	200	1450
P1	2.0	ℓ -C ₁₂ H ₂₅ (OCH ₂ CH ₂) ₃ ⁻ SO ⁺ Na ⁺ ₄	25	1534

POLYMER	SALT WT.% NaCl	SURFACTANT	SURFACTANT CONC. (ppm)	FLUID VISCOSITY @ 1.28s ⁻¹ (cP)
P1	2.0	ℓ -C ₁₂ H ₂₅ (OCH ₂ CH ₂) $\frac{p}{5}$ —OH	100	348
P1	2.0	Br-C ₁₂ H ₂₅ (OCH ₂ CH ₂) $\frac{p}{5}$ —OH	300	2128

POLYMERS

- P1 = Copolymer of n-octylacrylamide and acrylamide; 1.25 mole % n-octyl content; 18% hydrolysis; 2000 ppm concentration
- P2 = Copolymer of n-octylacrylamide and acrylamide; 0.75 mole % n-octyl content; 18% hydrolysis; 1500 ppm concentration
- P3 = Terpolymer of n-octylacrylamide, acrylamide and 2-acrylamido-2-methylpropane sulfonate, 0.75 mole % n-octyl content; 2000 ppm concentration

SURFACTANTS

- ℓ = Linear hydrocarbon chain
- Br = Branched hydrocarbon chain
- m = Monodisperse ethoxy group
- p = Polydisperse ethoxy group

Example 3

Figures 3 and 4 show a comparison of the behavior of two polymers, one of which does not contain a hydrophobic group (PAM 310X2), prepared by free radical polymerization under identical conditions. Neither of the polymers is hydrolyzed and both are dissolved in water at a concentration of 5000 ppm at 55°C. Again, very substantial increases in viscosity are seen for the hydrophobically associating polymer (Figure 3), but not for the homopolyacrylamide (Figure 4). As shown in Figure 3, all three surfactants, cetyltrimethylammonium bromide (CTAB), sodium dodecylsulfate (SDS) and a branched hexadecyl sulfonate, sodium salt ($C_{16}SO_3$), exhibit a viscosity maximum. The CMC of each of the surfactants are indicated on the curves, and it may be seen that the viscosity maximum occurs a little below the CMC of the surfactant.

Figure 5 shows the specific viscosity of these surfactants without polymer over the same concentration range. No viscosity maximum is present. In Figures 3, 4, and 5 diamonds represent the $C_{16}SO_3$ data, circles represent the CTAB data, rectangles represent the SDS data, and the diamonds represent the data from a linear C_{12} surfactant having an average of 8 ethoxylate groups.

Example 4

Figure 6 shows the behavior of 1000 ppm aqueous solutions of 25% hydrolyzed alkyl polyacrylamide, when mixed with 1000 ppm of various nonionic surfactants. The copolymer had 0.75 mole % of octylacrylamide copolymerized with acrylamide, then hydrolyzed with base to a degree of hydrolysis of 25%. This figure shows that with three of the five surfactants, the viscosity actually increased with temperature when the temperature was above

about 40°C. Solutions represented by solid diamonds contain decaethylene glycol oleyl ether surfactant, solutions represented by filled solid rectangles contain polyethylene glycol hexadecyl ether surfactants, solutions represented by open rectangles contain polyethylene glycol steryl ether surfactant, solutions represented by open triangles contain polyethylene glycol dodecyl ether surfactant, and solutions represented by solid triangles contain diethylene glycol oleyl ether surfactant.

CLAIMS:

1. A composition for use in enhanced oil recovery comprising:
 - (a) brine,
 - (b) from about 100 to about 25,000 parts by weight of at least one hydrophobically associating polymer per million parts by weight of the brine, the polymer being selected from the group of copolymers of mono and dialkyl-acrylamides of 4 to about 18 carbon atoms with acrylamide, and partially hydrolyzed derivatives thereof; and
 - (c) from about 25 to about 7,500 parts by weight of a nonionic surfactant or mixtures thereof per million parts by weight of the brine wherein the surfactant or mixtures thereof is selected from polyoxyethylene (n) alkyl ethers with n ranging from about 2 to about 22 and the number of carbons in the alkyl group ranging from about 6 to about 22 and wherein the composition has a viscosity that increases with increasing temperature.
2. A method for recovering oil from a subterranean formation, comprising:
 - (a) forming a brine of water and salt, the salt being present in an amount ranging from about 0.5 to about 10 wt.% based on the weight of water;
 - (b) adding to the brine from about 100 to about 25,000 parts by weight of at least one hydrophobically associating polymer per million parts by weight of the brine, the polymer being selected from the group of copolymers of

mono and dialkyl-acrylamides of 4 to about 18 carbon atoms with acrylamide, partially hydrolyzed derivatives thereof, and terpolymers of mono or dialkyl acrylamides of 4 to about 18 carbon atoms with acrylamide and an ethylenically unsaturated sulfonic acid salt of an alkali metal or ammonia;

(c) adding to the brine and polymer from about 25 to about 7,500 parts by weight per million parts by weight of the brine of at least one surfactant in order to form a brine solution; and then

(d) injecting the brine solution into the subterranean formation.

3. The method of claim 2 wherein the surfactant is selected from the group of anionic, cationic, and nonionic surfactants, and mixtures thereof.

4. The method of claim 3 wherein the surfactant is one of cetyltrimethylammonium bromide, branched alkyl sulfonate, decaethylene glycol oleyl ether, diethylene glycol oleyl ether, polyethylene glycol dodecyl ether, polyethylene glycol hexadecyl ether, and polyethylene glycol stearyl ether.

5. The method of claim 4 wherein the surfactant is present at a concentration ranging from about 85% to about 100% of the CMC based on the surfactant concentration, provided that when more than one surfactant is used, the total surfactant concentration ranges from about 85% to about 100% of a linear combination of the surfactant CMCs based on the total surfactant concentration.

6. The method of claim 5 wherein the surfactant is a mixture of a first and at least second surfactant.

7. The method of claim 6 further comprising measuring the viscosity of the oil.

8. The method of claim 6 further comprising combining the first and the second surfactant in an appropriate ratio to provide the brine solution with a substantially constant or increasing viscosity over a temperature ranging from about 20 °C to about 60 °C.

9. An aqueous composition of at least one hydrophobically associating polymer and at least one surfactant, the mixture's viscosity being substantially constant or augmented over temperatures ranging from about 20 °C to about 60 °C.

10. The composition of claim 1 wherein the surfactant is selected from decaethylene glycol oleyl ether, polyethylene glycol octadecyl ether, polyethylene glycol hexadecyl ether and mixtures thereof.

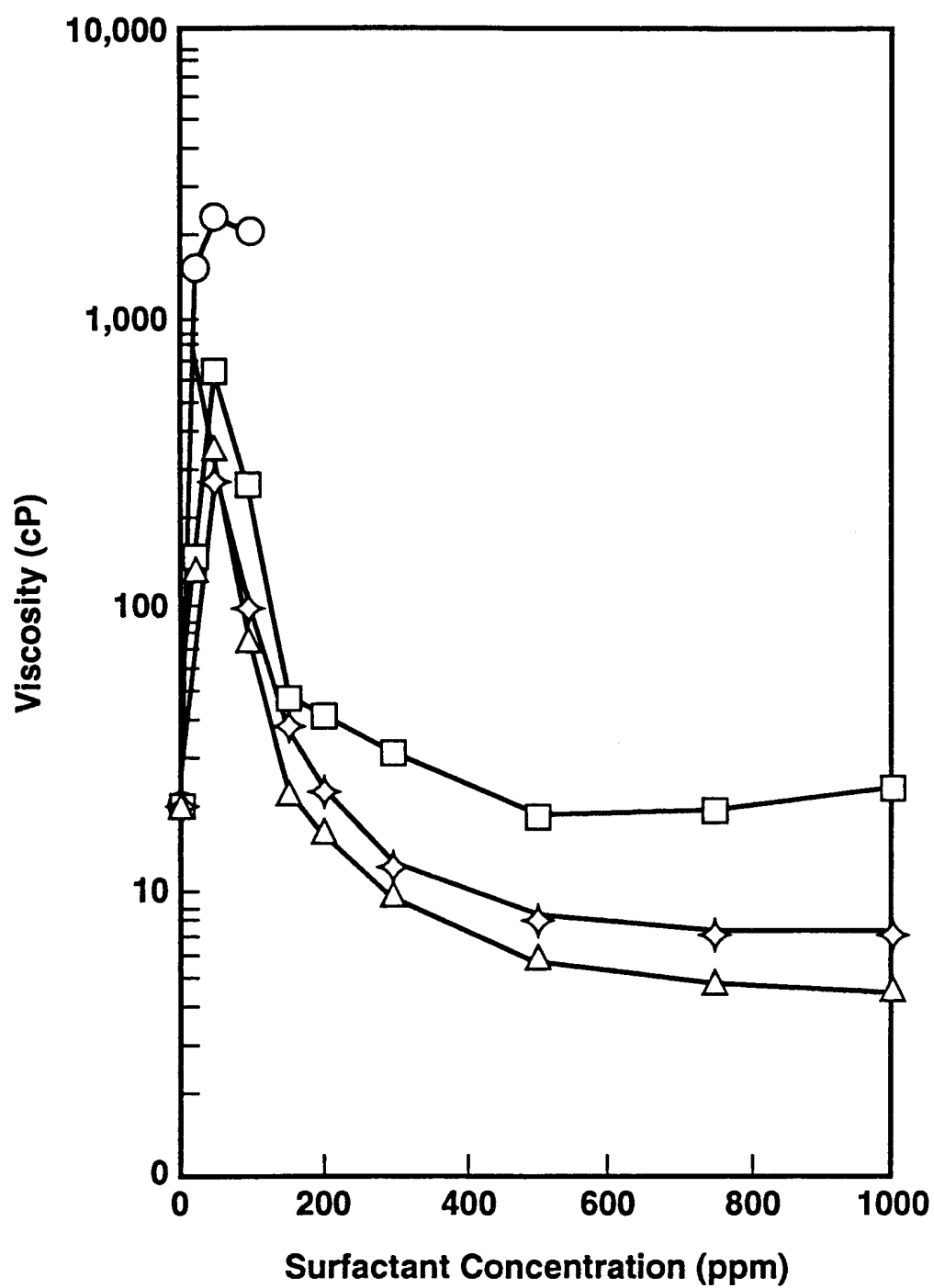
11. In the method of thickening a water solution by adding to the solution a surfactant and from about 100 to about 25,000 parts by weight of a hydrophobically associating polymer per million parts by weight of the water, the polymer being selected from the group consisting of copolymers of mono and dialkylacrylamides of 4 to about 18 carbon atoms with acrylamide, and their partially hydrolyzed derivatives, the improvement wherein the surfactant is selected from nonionic surfactants and mixture thereof that are capable of providing the solution with a viscosity that increases with increasing temperature from about 20°C to about 60°C and is added in an amount of from about 25 to about 7,500 points by weight per million parts by weight of the water.

12. The improvement of claim 11 wherein the surfactant or mixtures thereof is selected from polyoxyethylene (n) alkyl ethers with n ranging from about 2 to about 22 and the number of carbons in the alkyl group ranging from about 6 to about 2.

13. The improvement of claim 11 wherein the surfactant is selected from decaethylene glycol oleyl ether, polyethylene glycol octadecyl ether, polyethylene glycol hexadecyl ether and mixtures thereof.

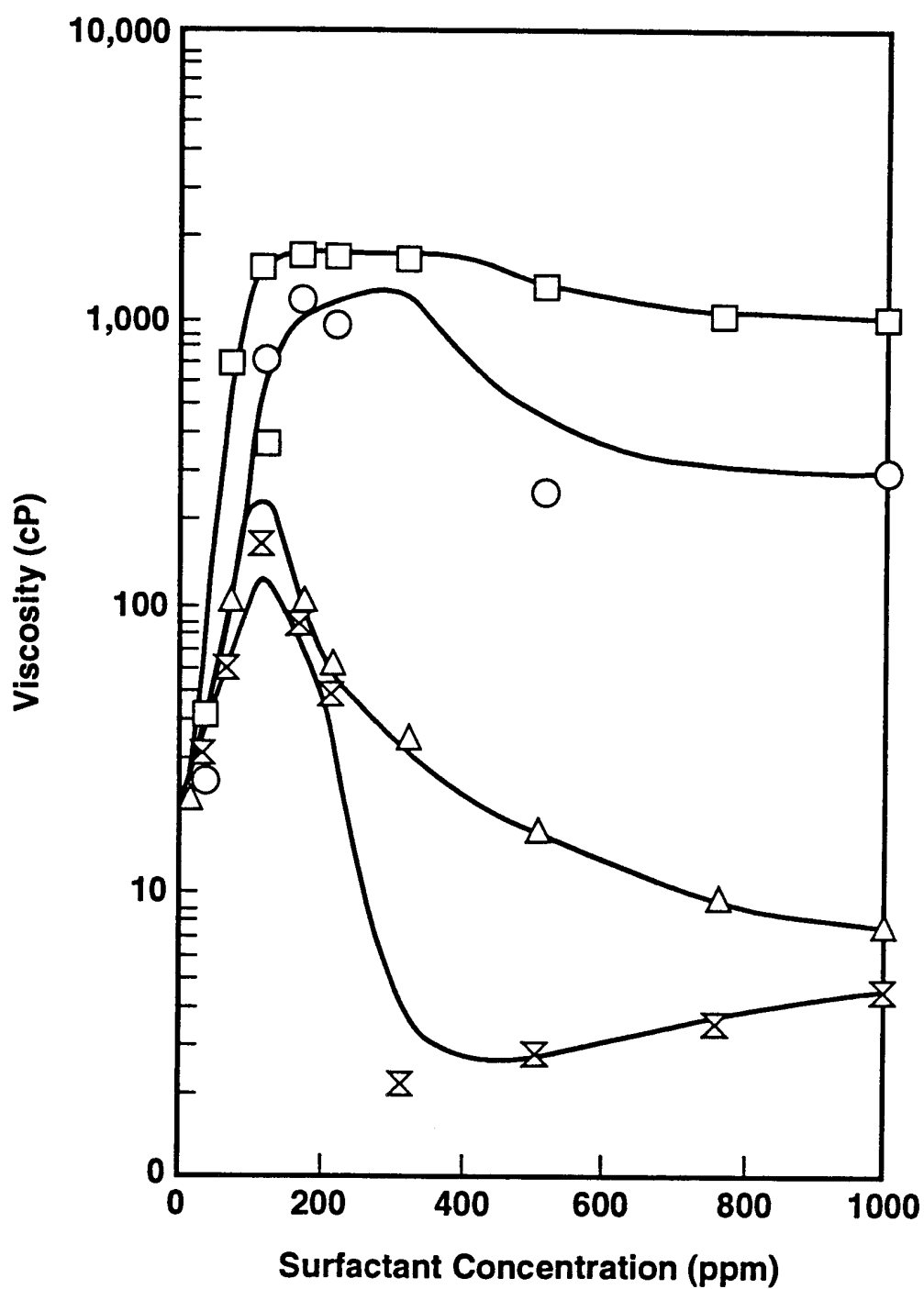
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FIGURE 1



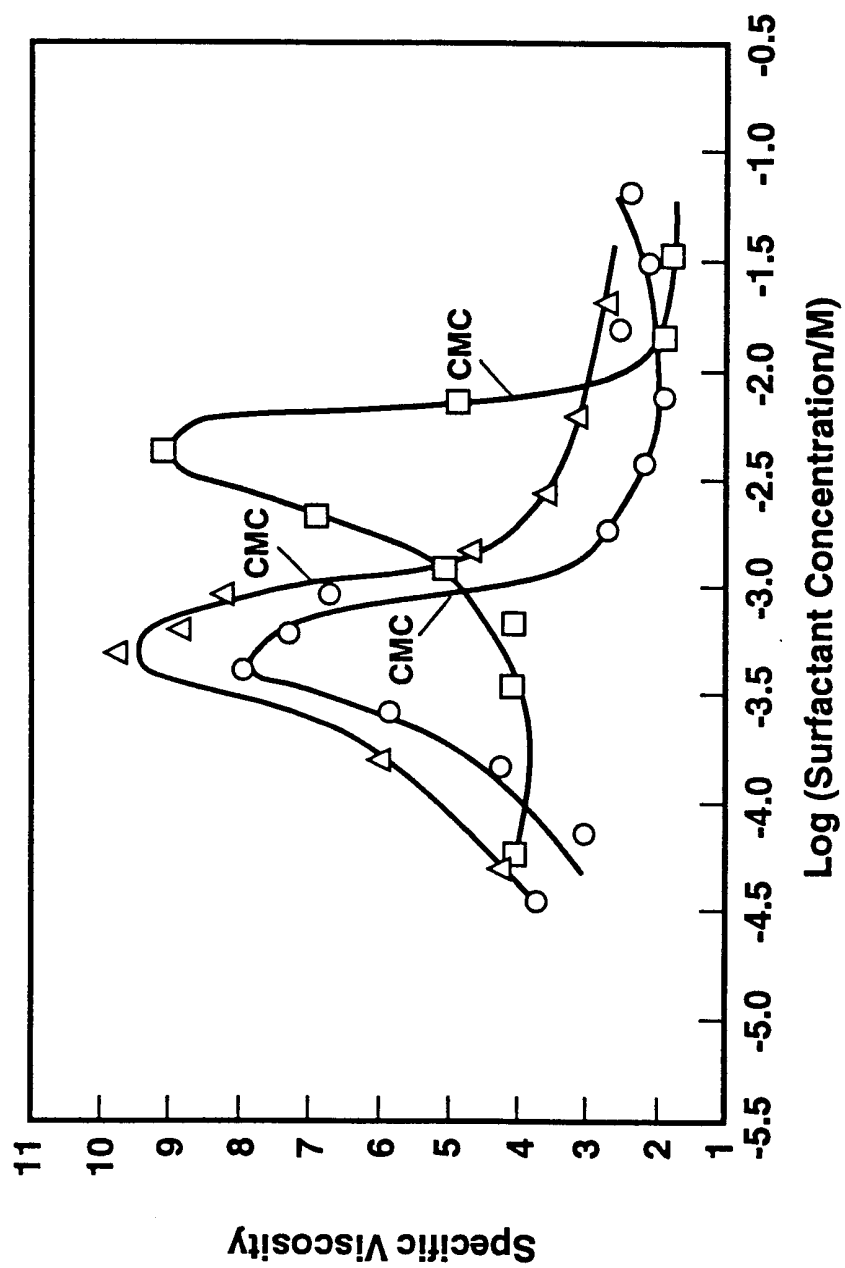
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FIGURE 2



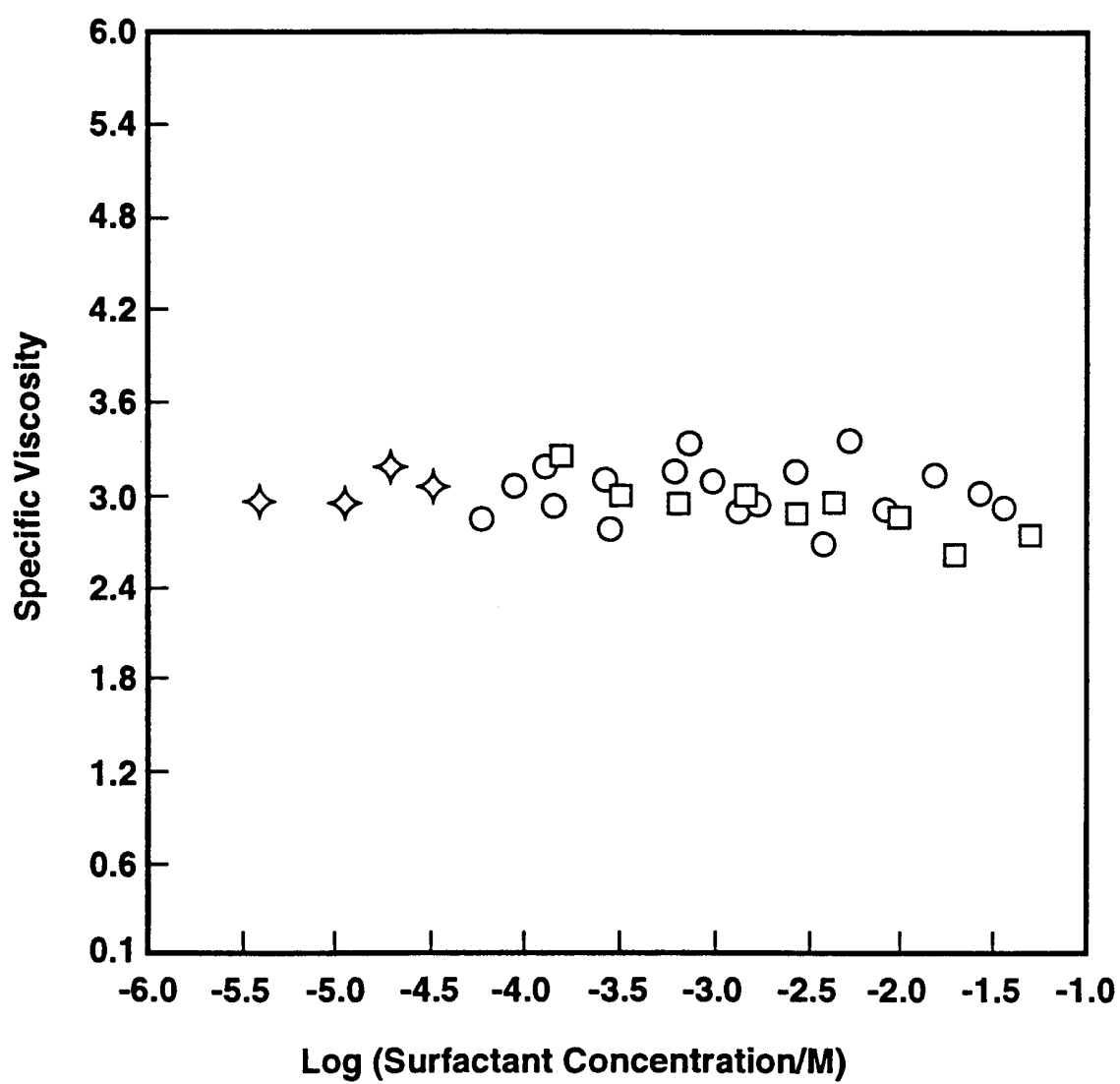
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FIGURE 3



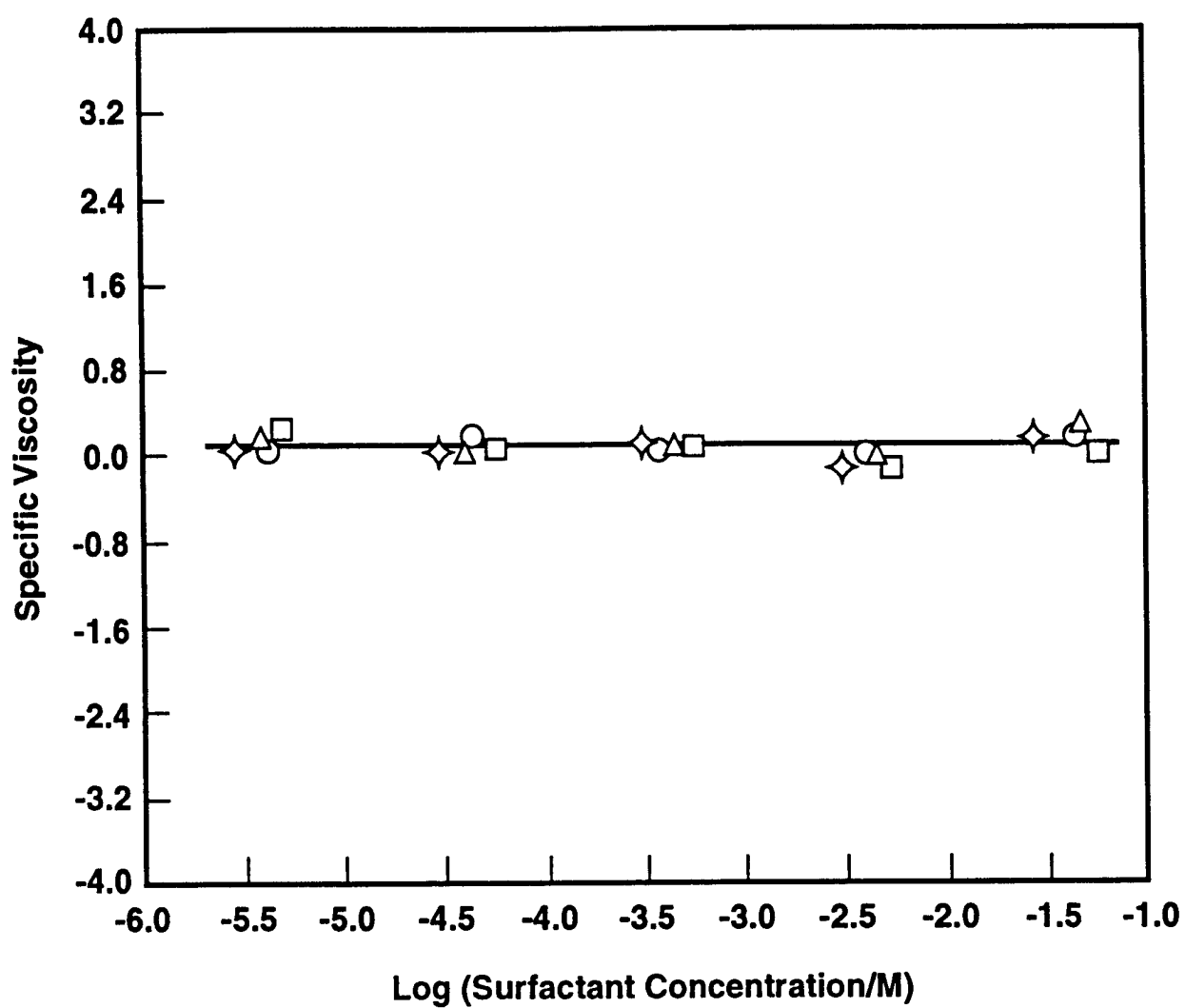
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FIGURE 4



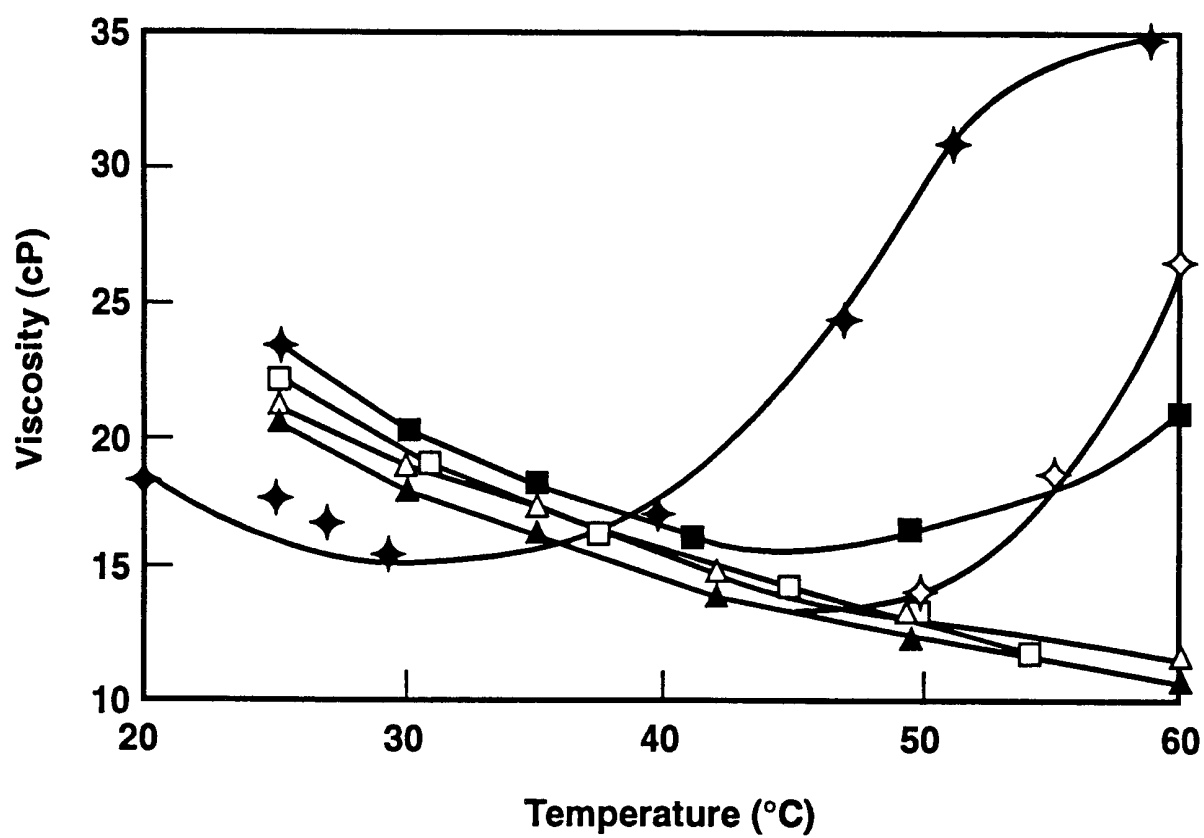
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FIGURE 5



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FIGURE 6



INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/14627

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 E21B43/25 E21B43/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 E21B C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 702 319 A (BOCK JAN ET AL) 27 October 1987 (1987-10-27)	2
Y	column 3, line 64 -column 4, line 29 column 5, line 23 -column 6, line 43 column 7, line 17 -column 8, line 44 column 10, line 13 - line 31; claim 6 ---	1,3,4, 9-13
Y	US 4 709 759 A (BOCK JAN ET AL) 1 December 1987 (1987-12-01) column 4, line 31 - line 63 column 6, line 20 -column 7, line 63; claim 6 --- -/--	1-4,9-13



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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