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(54) **Surfactant composition and process for the production of oil using such a composition**

(57) Surfactant composition for use in the production of oil, comprising an alcohol alkoxy acetate and an alkyl aryl sulphonate in the form of salts, in such quantities that the composition contains 10 to 100 pbw of the alkyl aryl sulphonate per 100 pbw of alcohol alkoxy acetate, optionally an alcohol being present in a quantity of up to 100 pbw per 100 pbw of alcohol alkoxy acetate.

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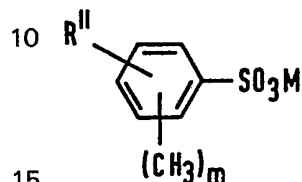
SPECIFICATION

Surfactant composition and process for the production of oil using such a composition

- 5 The invention relates to a surfactant composition for use in the production of oil and to a process for the production of oil from an underground oil-containing formation by injecting such a surfactant composition into said formation. 5
- The efficient recovery of oil from an underground oil-containing formation is of great importance. The production of oil from such a formation is commenced by reducing the pressure prevailing in the formation. However it has long been recognized that substantial amounts of oil remain in the formation after the pressure has decreased. To enhance the oil production it has been proposed to inject water, steam or gases like nitrogen, carbon dioxide, C₁-C₃ hydrocarbons, oxygen or air, into the formation. 10
- A very promising method for enhanced oil production comprises the injection of an aqueous surfactant-containing solution. It is assumed that the surfactant lowers the interfacial tension between oil and water. The lowering of the interfacial tension is often related to the formation of a three-phase system in the formation: an oil phase, a microemulsion phase and an aqueous (brine) phase containing substantially no surfactant. The micro-emulsion phase is a thermodynamically stable phase containing both oil and surfactant. The interfacial tension between oil and the microemulsion is considerably lower than the interfacial tension between oil and water or brine without surfactant. 15
- Due to this lower interfacial tension the oil can be driven out of the pores in the formation where the oil was left after the pressure decreases. 20
- The interfacial tension between the microemulsion phase and the aqueous (brine) phase is not very high, too, so that after having forced the oil out of the pores, the microemulsion in its turn is removed from the pores by the water. In this way the surfactant-containing microemulsion is used throughout the whole formation. 25
- The formation of a three-phase system is highly dependent on the salinity of the brine present in the formation, using a given surfactant or surfactant blend. By means of brine samples it is possible to determine the salinity and to adjust the surfactant-containing solution such that in model experiments three phases are attained at the salinity found. However, upon passing a surfactant-containing solution through the formation the salinity may change, e.g. it is possible that salts from the formation dissolve in the injected solution, or that ion exchange occurs between cations in the solution and cations in the formation. It then may happen that the microemulsion is no longer stable and disappears, so that oil production is considerably reduced. 30
- From the above it is evident that it is advantageous to apply a surfactant composition capable of creating a three-phase system in a salinity range as wide as possible. 35
- The invention provides a surfactant composition capable of forming a three-phase system over a wide salinity range. 40
- The invention, therefore, relates to a surfactant composition for use in the production of oil from an oil-containing underground formation, comprising an alcohol alkoxy acetate and an alkyl aryl sulphonate in the form of their salts in such quantities that the composition contains between 1 and 100 pbw of the alcohol alkoxy acetate. 45
- The alcohol alkoxy acetate boosts the compatibility of the surfactant composition with saline water, whereas the alkyl aryl sulphonate favours the oil-solubility. 45
- The relative quantities of both surfactants mentioned above can be varied between the limits given, as required by the salinity of the brine in the formation. Preferably, the composition contains between 10 and 100 pbw of the alkyl aryl sulphonate per 100 pbw of the alcohol alkoxy acetate, thereby increasing the salinity range in which three phases occur. 50
- The surfactants in the composition are used and stored in the form of their salts, preferably their alkali metal, in particular sodium, salts. However use of the surfactant in the form of other salts, like the ammonium, alkylammonium or alkanolammonium salt, is also possible. 50
- Preferably, the alcohol moiety in the alcohol alkoxy acetate comprises 6 to 20 carbon atoms. The "alcohol moiety" does not only comprise aliphatic alcohols, but also alkylated phenols. 55
- Suitable alkoxy groups are ethoxy and 1,2-propoxy, the ethoxy group being preferred. When the alcohol alkoxy acetate comprises ethoxy groups, the alcohol ethoxy acetate advantageously contains 1 to 30 ethoxy groups. So, according to the above preferred embodiments by "alcohol alkoxy acetate" compounds are understood which have the following general formula: 55
- 60 $RO(CH_2C(R')HO)_nCH_2COOM,$ 60
- in which R is an alkyl group having 6-20 carbon atoms, R' is a hydrogen or methyl group, M is a cation, e.g. sodium or ammonium, and n is a number in the range from 1 to 30. 65
- The alcohol ethoxy acetate is generally prepared via reaction of an alcohol ethoxylate with chloro acetic acid or by catalytic oxidation of an alcohol ethoxylate with oxygen in the presence 65

of sodium hydroxide and a palladium-containing catalyst.

Suitable alkyl aryl sulphonates are those in which the aryl moiety comprises benzene, toluene or xylene. Preferred alkyl aryl sulphonates are C₆-C₂₀-alkyl xylene sulphonates. Even more preferred are latter sulphonates when derived from o-xylene. The length of the alkyl chain can be varied in accordance with the requirements set by the formation. The alkyl aryl sulphonates are conveniently prepared by alkylation of benzene, toluene or xylene with an olefin, followed by sulphonation and neutralization. So, according to the above preferred embodiments by "alkyl aryl sulphonate" compounds are understood, having the following general formula:



where m is 0, 1 or 2, R'' is a C₆-C₂₀ alkyl group and M is a cation, e.g. sodium or ammonium.

Advantageously, the surfactant composition comprises, apart from water, an alcohol as cosolvent. The quantity of the alcohol usually ranges up to 100 pbw per 100 pbw of the alcohol alkoxy acetate. Amongst others, the purpose of the alcohol is to reduce the viscosity of the microemulsion. The alcohol also increases the rate at which the equilibrium between the phases is reached. The nature of the alcohol is suitably such that it substantially does not interfere with the phase behaviour of the surfactant composition, when this composition is contacted with oil and brine. Not only linear alcohols are suited. Branched alcohols, too, show a good performance. The use of glycol derivatives like mono alkyl ethers of mono-, di- or triethylene glycol or of mono-, di-, or tripropylene glycol is also possible. Preferably the alcohol comprises 2 to 9 carbon atoms. In particular s-butanol and the butyl ether of ethylene glycol are preferred.

The surfactant composition is preferably stored and transported in the form of a concentrate. Near the oil field where it is used the composition is diluted with water to produce an aqueous surfactant-containing solution which solution is injected. During the dilution the salinity of the solution can be adjusted to the requirements of the formation. The term "surfactant composition" in the application does not only refer to a diluted aqueous solution but also to a concentrate. When the surfactant composition is stored or transported in a concentrated form, the alcohol alkoxy acetate and alkyl aryl sulphonate are typically present therein in a quantity of 60 %w, calculated on the total composition. The balance of the composition is then water and optionally the alcohol.

A concentrate of the surfactant composition is suitably prepared by mixing an aqueous solution containing at least 10 %w of sodium hydroxide with a C₂-C₉ alcohol and by neutralizing an alkyl aryl sulphonic acid with the mixture obtained and subsequently by adding an alcohol alkoxy acetate to the composition formed.

A preferred process for the preparation of such a surfactant composition comprises mixing an aqueous solution containing at least 10 %w of a neutralizing agent with a C₂-C₉ alcohol and by adding to this mixture an alcohol alkoxy acetic acid and subsequently an alkyl aryl sulphonic acid. As already indicated above, suitable C₂-C₉ alcohols are s-butanol and butyl ether of ethylene glycol. The neutralizing agent may conveniently be an ammonium or, preferably, an alkali metal hydroxide. Sodium hydroxide has been found to be very satisfactory.

The invention also relates to a process for the production of oil from an oil-containing underground formation by injecting a surfactant composition as defined above into said formation. The composition may suitably be used in well stimulation or in flooding processes.

The invention will now further be elucidated with reference to the following Examples.

EXAMPLE I

In a number of experiments properties were determined of a system comprising a Far Eastern crude oil, a synthetic brine (indicated as synthetic reservoir water, SRW) and one or more surfactants. For each experiment a series of tests were run. In each test 1 meq surfactant was placed in a test-tube. To the surfactant(s) 0.1 g of s-butanol was added and the tube was filled with water and oil such that the volume ratio water to oil was 3:1. The total volume was 18 ml. In each tube water having a different salinity was applied.

The synthetic reservoir water was made up of a NaCl and CaCl₂ solution, the Na/Ca molar ratio being 231. The salinity is expressed in percentage SRW, 100% SRW corresponding with 10.0 g/l NaCl and 0.082 g/l CaCl₂.

The testtube thus filled was gently moved, placed into a thermostat and kept there until no changes in the volumes of the phases were observed. By means of this procedure (sometimes referred to as salinity scan) it is possible to determine at which salinity a three-phase-system starts to occur, is present and stops to occur. The width of the salinity range in which a three-

phase-system occurs is often called the salinity window (SW) and is generally expressed in % SRW. The tests were run at two different temperatures, corresponding with potential formation temperatures.

The following surfactants were used in the experiments: Surfactant I was a sodium alcohol ethoxy acetate in which the alcohol moiety comprised for 42 mol.% a linear C₁₂ chain and for 58 mol.% a linear C₁₃ chain, whereas the average number of ethoxy groups per molecule was 4.5. 5

Surfactant II was similar to Surfactant I but had an average number of 6 ethoxy groups per molecule.

Surfactant III was a sodium alcohol ethoxy acetate with an average of 9 ethoxy groups per molecule. The alcohol moiety comprised linear chains with 12 (20 mol.%), 13 (30 mol.%), 14 (30 mol.%) and 15 (20 mol.%) carbon atoms. 10

Surfactant IV was a sodium alkyl aryl sulphonate which was derived from o-xylene and which consisted for 40 %w of C₈-C₁₀ alkyl xylene sulphonate, for 35 %w of C₁₁-C₁₂ alkyl xylene sulphonate and for 25 %w of C₁₃-C₁₄ alkyl xylene sulphonate. The average molecular weight was 370. The alkyl aryl sulphonate is commercially available under the registered trade mark "Enordet LXS/370". 15

The results of the experiments are summarized in Table I.

TABLE I

Exp. No.	Surfactant blend	Temperature °C	Salinity starts to occur	Surfactant stops to occur	SW
			% SRW	% SRW	% SRW
1	100 pbw I +	67	150	215	65
2	233 pbw IV	90	165	245	80
3	100 pbw I +	67	375	475	100
4	79 pbw IV	90	350	450	100
5	100 pbw I	67	turbid unspecific phases formed		-
6		90	no three phases formed		-
7	100 pbw II +	67	210	285	75
8	203 pbw IV	90	228	303	75
9	100 pbw II +	67	575	750	175
10	69 pbw IV	90	475	675	200
11	100 pbw II	67	turbid unspecific phases formed		-
12		90	no three phases formed		-
13	100 pbw III +	67	300	425	125
14	186 pbw IV	94	275	450	175

TABLE I (cont'd)

Exp. No.	Surfactant blend	Temperature °C	Salinity at which the three phase-system starts to occur	SW stops to occur	% SRW	% SRW	% SRW
15	100 pbw III +	67	900	1050	150		
16	61 pbw IV	94	< 700	900	> 200		
17	100 pbw III +	67	1600	1770	170		
18	18 pbw IV	90	1150	1450	300		
19	100 pbw III	67	turbid unspecific phases formed		-		
20		90	no three phases formed		-		

Of the experiments only experiments 3, 4, 9, 10, 15, 16, 17 and 18 are carried out with compositions according to the invention. In these experiments a relatively wide salinity window is observed. It is shown that using only alcohol ethoxy acetate the surfactant does not form a stable three-phase-system (cf. experiments 5, 6, 11, 12, 19 and 20). Using more than 100 pbw of alkyl aryl sulphonate per 100 pbw of alcohol ethoxy acetate the salinity window is becoming narrower (cf. experiments 1, 2, 7, 8, 13 and 14).

EXAMPLE II

A concentrate of the surfactant composition was prepared by mixing 32 g of secondary butanol with a sufficient quantity of aqueous sodium hydroxide (concentration 46 %w). To this mixture was added with stirring 50 g of the alcohol ethoxy carboxylic acid (containing 85.3 %w pure acids). To the resultant blend was added with stirring 23 g of an alkyl aryl sulphonic acid (containing 94 %w pure acids). The resulting concentrate was a clear golden, mobile liquid.

A second concentrate was prepared in which the secondary butanol was replaced by the butyl ether of glycol. This concentrate was a clear, golden, mobile liquid.

Composition and viscosity of the two concentrates is given in Table II.

TABLE II

<u>Composition</u>	<u>1</u>	<u>2</u>
Alcohol ethoxy acetate, Na salt, pbw	100	100
Alkyl aryl sulphonate, Na salt, pbw	51	51
Secondary butanol, pbw	71	
Butyl ether of glycol, pbw		71
Surfactant blend, %w, based on total composition	57	57
Water (including minor amounts of incidental components), %w	16	16
Viscosity, cSt, 20 °C	88	132

CLAIMS

- Surfactant composition for use in the production of oil from an oil-containing underground formation, comprising an alcohol alkoxy acetate and an alkyl aryl sulphonate in the form of salts, in such quantities that the composition contains between 1 and 100 pbw of the alkyl aryl sulphonate per 100 pbw of alcohol alkoxy acetate.
- Surfactant composition according to claim 1, which contains between 10 and 100 pbw of the alkyl sulphonate per 100 pbw of the alcohol alkoxy acetate.
- Surfactant composition according to claim 1 or 2, in which the alcohol alkoxy acetate and the alkyl aryl sulphonate are in the form of sodium salts.
- Surfactant composition according to any one of claims 1-3, in which the alcohol moiety in the alcohol alkoxy acetate comprises 6 to 20 carbon atoms.
- Surfactant composition according to any one of claims 1-4, in which the alcohol alkoxy acetate is an alcohol ethoxy acetate.
- Surfactant composition according to claim 5, in which the alcohol ethoxy acetate contains 1 to 30 ethoxy groups.
- Surfactant composition according to any one of claims 1-6, in which the alkyl aryl sulphonate is a C₆-C₂₀ alkyl xylene sulphonate.
- Surfactant composition according to claim 7, in which the C₆-C₂₀ alkyl xylene sulphonate is derived from o-xylene.
- Surfactant composition according to any one of claims 1-8, which contains up to 100 pbw of an alcohol per 100 pbw of alcohol alkoxy acetate.
- Surfactant composition according to claim 9, in which the alcohol is present in an amount of from 5 to 80 pbw per 100 pbw of alcohol alkoxy acetate.
- Surfactant composition according to claim 8 or 9, in which the aliphatic alcohol comprises 2 to 9 carbon atoms.
- Surfactant composition according to claim 1, substantially as described hereinbefore with special reference to the Examples.
- Process for the preparation of a surfactant composition as claimed in claim 11, comprising mixing an aqueous solution containing at least 10 %w/w of a neutralizing agent with at least

one C₂-C₉ saturated alcohol, and adding to the resulting mixture an alcohol alkoxy acetic acid and subsequently an alkyl aryl sulphonic acid.

14. Process according to claim 13, in which the neutralizing agent is sodium hydroxide.

15. Process according to claim 1, substantially as described hereinbefore with special refer-
5 ence to Example II.

16. Surfactant composition, whenever prepared by a process according to any one of claims
13-15.

17. Process for the production of oil from an oil-containing underground formation by inject-
ing a surfactant composition according to any one of claims 1-12 and 16 into said formation.

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