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OXIDIZED PETROLEUM FRACTIONS AS CO-SURFACTANTS AND AS FEEDSTOCKS FOR THE MANUFACTURE OF SULFONATES FOR THE TERTIARY RECOVERY OF OIL

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ABSTRACT

Pure paraffinic hydrocarbons and petroleum fractions (which may be aromatic-free) on vapor phase oxidation give an oxidized product useful as a co-surfactant and as a feedstock for the synthesis of sulfonates. The oxidations may be carried out in a simple tubular reactor using oxygen or air as the oxidant and nitrogen or steam as the reactor diluent and reaction-heat absorber. The reaction is non-catalytic and occurs readily at atmospheric pressure at temperatures ranging from 300 to 400°C.

The major products of the oxidations are cyclic ethers mixed with varying proportions of olefins and carbonyls. Mild conditions (low temperatures and the use of diluents) favor the formation of the cyclic ethers and other oxygenated compounds over olefins. The cyclic ethers are largely composed of 5- and 4-membered rings containing carbon and a single oxygen atom. Such products are useful as co-surfactants and as starting material for the manufacture of sulfonates.

The oxidized products which are rich in cyclic ethers react readily with sulfur trioxide or oleum to give sulfonates as the principal products. Such sulfonates are effective surfactants in tertiary oil recovery.

Low concentration slugs formulated from the above surfactants have performed well in core tests. Highest oil recoveries have been achieved by matching the η_{min} of the slug with the EACN of the oil in place. Such matched properties always give slugs having low interfacial tensions with the oil to be recovered. The sulfonates in low concentration slugs without co-surfactants or viscosity control in the slug have produced oil in core tests at high efficiency levels.

INTRODUCTION

Sulfonates produced from aromatics present in petroleum fractions of the desired boiling range serve as a major source of the surfactants presently used in the tertiary recovery of oil. Instead of depending on a source of aromatic-containing fractions as a feedstock, paraffinic and naphthenic hydrocarbons may be used by employing a two-step procedure involving vapor phase oxidation followed by sulfonation of the oxidized product. The sulfonates made by such a route appear to be alkyl sulfonates containing either unsaturation or a hydroxyl group. Tests indicate that these sulfonates have strong potential in enhanced oil recovery processes. In addition, the oxidation products themselves are effective co-surfactants in low or high concentration slugs prepared with petroleum sulfonates. The objective of this study is to investigate the usefulness of oxidized products as co-surfactants, as feedstocks for the synthesis of surfactants and to evaluate the potential of these sulfonates for the recovery of oil.

OXIDATIONS

A series of mineral oil fractions was chosen to illustrate the range of boiling points and molecular structures available to produce sulfonates for surfactants. A paraffinic white oil averaging 26 carbon atoms per molecule (b.p. 390-460°C) and a naphthenic white oil with an average of 27 carbon atoms per molecule (b.p. 360-530°C) were chosen as examples of carbon-carbon paraffinic chains and 5- and 6-membered saturated ring structures. Two hydrocarbon fractions from a PA crude oil including a C_{17} to C_{21} (b.p. 315-341°C) and a C_{17} to C_{43} (b.p. 315-480°C) represent the top fractions from an atmospheric and a vacuum fractionation, respectively. These fractions contain aromatic components in the range of 10 to 15 percent.

The oxidations were made in a vertical tubular reactor 1.3 meters in length and 5.1 cm in diameter as shown in Figure 1. Ten separate oxygen (or air) inlets were spaced at 10.2 cm intervals along the reactor length. Provision was made to mix the desired proportions of hydrocarbon feedstock and steam at the bottom inlets to the reactor. Additional steam could be added as desired along the length of the reactor at the points indicated. The steam used in this reactor serves two main purposes. That fed into the bottom of the reactor with the hydrocarbon feed allows vaporization of high boiling feed stocks by reducing the partial pressure

References and illustrations at end of paper.

287

of the hydrocarbon in the reactor. The steam also serves as a heat sink to control temperature rise due to the exothermic oxidation reaction. This latter function tends to limit the reaction to a single event per hydrocarbon molecule and thereby reduces the amount of chain breaking and CO_2 and H_2O formed.

Operation of the reactor is simple and feedstocks and oxygen (or air) flow rates ranging as high as 4 liters per hour and 400 grams per hour respectively are possible.

Examples of a number of typical oxidations are summarized in Table 1. As the composition of the reactor feed shows, the first and last experiments listed used air as the oxidant; all other experiments used oxygen. Although the proportion of steam fed to the reactor was substantial on a mole basis, because of its low molecular weight the proportion of steam needed for good temperature control on a weight basis was much lower than that of the feedstock. In the first three experiments listed in the table, the proportion of oxygen fed to the reactor ranged from 0.87 to 2.6 moles per mole of feedstock. Although these proportions of oxygen were sufficient to burn only 2 to 6.6% of the hydrocarbon feedstock completely to CO_2 and H_2O, the actual feedstock conversions achieved ranged from 34 to 66%. The feed conversions were estimated from the solubilities of the oxidized products in 98% sulfuric acid. The proportions of oxygenated material present in the oxidized products was determined by measuring the amount adsorbed on Attapulgus clay by column chromatography. The difference between the sulfuric acid solubility and clay adsorption values gave an estimate of the proportion of olefins present.

As the data for the first three experiments in Table 1 show, the use of a low oxidation temperature (320°C), air as the oxidant, a low oxygen/ feedstock ratio, and a relatively high proportion of diluent (steam and nitrogen) gave a product containing a maximum proportion of oxygenated material. Gas chromatographic analyses also demonstrated that such liquid products contained a minimum of light ends. As the reaction temperature was increased or as the oxygen/ feedstock ratio was raised, a greater proportion of olefins appeared in the products and gas chromatographic analyses showed that such oxidation products contained 5 to 15% of light ends.

Oxidations of the C_{27} naphthenic fraction also demonstrated that such a feedstock can readily be oxidized at high conversions (67%) to give a product rich in oxygenated materials. The use of lower temperatures should yield a product containing an even greater proportion of oxygenated material.

Oxidations of the $C_{17}-C_{21}$ Pennsylvania gas oil gave similar oxidation products (oxys plus olefins) at relatively high conversions (42-44%). This feedstock tended to give a greater proportion of light ends (determined by gas chromatography) than the two former feedstocks.

The oxidations of the Pennsylvania heavy neutral were made at relatively high oxygen/feedstock mole ratios and hence at high conversion levels. Again, the use of air as oxidant favored the production of liquid oxygenated products at the expense of undesirable light ends.

For the case of most of the oxidations, substan-

tial yields (86 to 103 parts by weight of the feedstock) of liquid products were obtained. Although higher feedstock conversions could be achieved by utilizing higher oxygen/feedstock ratios, such conditions gave increased proportions of gaseous products and light ends at the expense of the desired liquid oxidation products.

The liquid oxidation products were used directly as a feedstock for the sulfonation reactions. For use as a co-surfactant, the liquid oxidation products were usually concentrated by means of a simple liquid-liquid extraction step using methyl alcohol as the solvent.

It is clear from the oxidation data presented that olefin production can be minimized and oxygen-containing product maximized at temperatures in the range of 300 to 320°C. The use of high levels of steam at this operating condition tends to minimize carbon-carbon chain breakage as well. It should be emphasized that the unreacted hydrocarbon from the oxidation test can be recycled to extinction after the desired oxidation product is removed by extraction or sulfonation.

SULFONATES

The liquid oxidized products were sulfonated either using a semibatch or continuous procedure. In the semibatch method, about 300-350 gram batches of the oxidized products contained in a glass bubbling tube were sulfonated by passing a mixture of sulfur trioxide and nitrogen into the reaction flask. The temperature rose to about 30-35°C during the progress of the run (8-12 hours). In the continuous method, the oxidized product (either neat or diluted with an equal volume of ethylene dichloride) was allowed to flow downward through a water-jacketed glass reactor tube (50 cm long x 1 cm diameter) together with a cocurrent stream of sulfur trioxide and nitrogen. The reactor was maintained at 43-44°C by means of the water jacket. The sulfonated products from either the batch or continuous procedures were dissolved in 40% isopropyl alcohol, neutralized with sodium hydroxide and extracted with hexane to remove the unreacted hydrocarbon feedstock. The sulfonate then was isolated according to the method described by Ashcraft and Saunders (1).

All of the oxygenated compounds and olefins present in the oxidized liquid product were capable of being sulfonated and the final unreacted feedstock recovered was in many cases a clear white oil in character. In most experiments, however, in an attempt to prevent polysulfonation, the sulfonations were not carried to completion. Besides, the unreacted feedstock could be recycled. The results of a number of typical sulfonations are summarized in Table 2.

In Experiments 21 and 22, the oxidized liquid products from the C_{26} paraffinic feedstock were sulfonated in the semibatch mode. The feedstocks for the two experiments contained 44 and 56% acid-soluble material, respectively. (The acid solubilities approximate the proportion of reactive intermediates present.) The sulfonations were carried out at conversions (of reactive liquid intermediates present) of about 75 and 66%, respectively. The products consisted of a sulfonate and an unreacted oil layer. The compositions of the two layers are as shown.

The equivalent weights of the sulfonates in the sulfonate product were lower than expected because of the presence of polysulfonated material. Further, the sulfonates were composed of a wide range of individuals. The oil layers contained small proportions of oil-soluble sulfonates of higher equivalent weight as shown.

The C_{17}-C_{21} Pennsylvania gas oil oxidized products on sulfonation behaved similarly to the C_{26} fraction. The use of greater proportions of sulfur trioxide (see Experiments 23 and 24) favored the formation of lower equivalent weight material and thus polysulfonation.

Additional data also suggest that the use of the continuous system may favor polysulfonation.

Sulfonation of the oxidized products from the C_{27} naphthenic fraction and the Pennsylvania heavy neutral proceeded as expected.

Sulfur balances obtained for similar sulfonation experiments (2) show that from 35-50% of the sulfur reacting appears as sulfonates, from 20-25% appears as sulfur dioxide while the remainder appears as sodium sulfate. The relatively large proportion of sodium sulfate found is expected because of the oxygen present in the cyclic ether molecules. The sulfur trioxide must dehydrate the ethers to form water which reacts with sulfur trioxide to form the corresponding salt. Aromatic and olefinic hydrocarbons also react with sulfur trioxide to produce an equivalent amount of sulfur dioxide as a by-product and some sodium sulfate.

Work is underway to attempt to prepare sulfonates having a more desirable proportion of monosulfonates of a more desirable equivalent weight range. The sulfonates from the C_{27} naphthenic fraction also need to be evaluated as surfactants.

CORE TESTS

The results obtained from core tests using various mixtures of sulfonates as dilute slugs are shown in Table 3. The core tests were made using horizontal Berea sandstone cores 61 cm long x 5.04 cm in diameter. The flow rate was 0.3 m per day. The cores were cast with a low-melting alloy in steel tubes and after being saturated with 2% NaCl brine followed by saturation with oil and flooding with 2% brine were ready for the tests. The slug for study was prepared by making a solution containing 0.5% of the desired active sulfonate in 1.0% Na_2CO_3 solution. The sulfonates used were restricted to mixtures of PRL 7A (see Experiment 23, Table 2, Equivalent weight 298) and TRS 16 (Witco Chemical Co. equivalent weight 455), depending on the equivalent weight desired. The buffer solution used in all runs consisted of 500 ppm Xanflood dissolved in brine containing 200 ppm of NaCl. In all experiments 60% pore volume of the buffer solution was used.

The data for the first four runs listed in Table 3 show that when working with matched η_{min}-EACN Systems (each having a low interfacial tension), the oil recovery rose from 17 to 77% as the slug size was increased from 18 to 100% pore volume. The term η_{min} (refers to the surfactant solution) is the carbon number of the alkane against which the surfactant gives minimum interfacial tension. EACN (Equivalent

Alkane Carbon Number – referring to the crude oil) is the carbon number of the pure alkane which exhibits minimum interfacial tension against the surfactant solution that also yields minimum tension against the crude oil itself.

Examples of systems in which the η_{min} and EACN values were mismatched are shown in Runs 5 and 6. In each case, the interfacial tension was relatively high and the oil recovery was poor. (NOTE: In Run 3, made at a similar slug pore-volume, the oil recovery was 67% when a matched system was used.)

Three additional examples of the advantage of using matched systems are shown by the data of the final three runs listed in Table 3. Thus, to achieve maximum oil recovery when working with dilute slugs, the equivalent weight of the sulfonate used in the slug should be selected to match the EACN of the oil in place.

The advantage of matched over mismatched systems is shown by the data of Figure 2 where oil recovery is plotted against sulfonate injected (mg of active sulfonate per g of rock). The data show the advantage of matching the properties.

During the collection of the data it was noted that wide variations in EACN occurred when oil samples underwent weathering. Because of this effect, it was necessary to determine accurately the EACN of a given oil sample before matching/mismatching it with a given surfactant. (For the case of Runs 9 and 5, hexadecane (50% by weight) was added to artificially "weather" the oil. When using pure hydrocarbons as diluents, experience has shown that lower interfacial tensions and higher recoveries result than with undiluted crude oil samples. Such behavior can be noted by comparing Runs 9 and 4 (undiluted) in Figure 2 and the interfacial tension data in Table 3.)

Properties of the cores used in the various runs presented in Table 3 are summarized in Table 4.

The same core test procedure has been used to evaluate high concentration slugs prepared from conventional petroleum sulfonates and alcohol co-surfactants. The maximum sulfonate efficiency of a commercial high concentration slug in an equivalent Berea core test is in the range of 1.2-1.5. The equivalent enhanced recovery efficiency using low concentration Penn State sulfonate is as high as 3.4 in the same type of core tests using matched η_{min}-EACN (surfactant-oil) system. It should be emphasized that this level of efficiency with low concentration slugs was achieved without co-surfactants and without viscosity control in the slug.

CONCLUSIONS

1. Both paraffinic and naphthenic feedstocks can be converted to sulfonates by means of a single two-step procedure involving vapor phase oxidation and sulfonation.

2. The oxidation step is best carried out under mild conditions (low temperature, air as the oxidant, excess steam or nitrogen as a diluent and heat absorber).

3. The sulfonation step readily occurs at about room

temperature and may be carried out either batch-wise or continuously. The sulfonates appear to be largely alkyl sulfonates containing unsaturation or a hydroxyl group. Some polysulfonates are present.

4. Slugs containing 0.5% of active sulfonate have been used successfully in achieving high oil recoveries in core tests. The importance of matching the η_{min} of the slug to the EACN of the oil in place has been noted. Differences of as little as 1 or 2 between slug η_{min} and oil EACN can reduce the oil yield to one half or less than that achieved with a matched slug η_{min}-oil EACN. Changes of 1 to 2 in oil EACN can easily result from poor handling techniques or weathering.

REFERENCES

1. Ashcraft, T. L. and R. K. Saunders: Paper SPE 6119 presented at SPE-AIME 51st Annual Fall Meeting, New Orleans, Oct. 3-6, 1976.

2. Huang, Liuching, M.S. Thesis, Dept. of Chemical Engineering, The Pennsylvania State University, March 1979.

Table 1

VAPOR PHASE OXIDATIONS

Experiment No.	1	2	3	4	5	6	7	8	9
Feedstock	C_{26} Paraf. Fract.			C_{27} Napththenic Fraction		C_{19} PA Gas Oil		PA Heavy Neutral	
Feed to Reactor, Mole %									
Feedstock	4.5	4.4	12	6.3	6.2	27.8	19.2	16.7	6.9
Oxygen	3.9	11.5	13.3	11.4	13.6	27.8	25.0	33.3	13.8
Nitrogen	14.9	----	----	----	----	----	----	----	51.7
Steam	76.7	84.1	74.7	82.3	80.2	44.4	55.8	50.0	27.6
Oxygen/Feed Mole Ratio	0.87	2.6	1.1	1.8	2.2	1.0	1.3	2.0	2.0
Oxygen/Feed Weight Ratio	0.08	0.23	0.10	0.08	0.19	0.12	0.15	0.09	0.09
Steam/Feed Weight Ratio	0.84	0.94	0.30	0.62	0.62	0.11	0.19	0.33	0.15
Temperature, °C	320	345	400	390	410	400	370	380	390
Feed Conversion, %	34	66	48	67	67	44	42	82	75
Wt. % Feed to Liq. Prod.	103	91[+]	96	102	98	86	86	75[+]	86[+]
Liquid Prod. Comp., %									
Oxys	33	53	34	47	51	30	41	55	58
Olefins	3	9	12	17	15	16	4	20	12

Table 2

SULFONATIONS OF LIQUID OXIDIZED PRODUCTS

Experiment No.	21	22	23	24	25	26	27
Semibatch (s) or Continuous (c)	S	S	S	C	S	S	S
Feedstock, Oxid. Prod.	C_{26} Paraf. Frac.		C_{19} PA Gas Oil		C_{27} Naphthenic Frac.		PA Heavy Neutral
Solub. 98% H_2SO_4, vol. %	44	65	48	55	65	67	85
Charge: Basis 100 Parts by Weight of Oxidized Feed							
Feedstock	100	100	100	100	100	100	100
SO_3 Reacted	27	50	24	92	28.5	62	19
Product: Basis 100 Parts by Weight of Oxidized Feed							
Sulfonate	45	65	42.3	120.5	42	70.2	50.3
Oil	67.4	55	54.7	48.2	72.7	69.1	65.7
Salt	22.2	--	--	46.4	--	27.6	27.8
Product Compositions, wt. %							
Sulfonate			*				
Active Sulfonate	72.4	75	60.6	66.7	57.3	51.1	62.0
Oil	8.8	1.1	1.1	7.1	4.8	6.7	19.2
H_2O	25.4	23.9	28.0		33.2	40.1	17.0
Salt	--	1.1	10.2		2.3	--	2.0
Eq. Wt. Found (expected)	316(472)	298(472)	298(371)	255(371)	380(480)	326(570)	353(570)
Oil							
Active Sulfonate	4.0	6.5	17.0	--	6.4	17.8	13.2
Oil	95.0	82.8	83.0	--	86.3	79.0	80.6
H_2O	0	0	0.0	--	0.0	0.5	0.4
Salt	1.0	0.6	--	--	0.6	--	2.0
Eq. Wt. Found	943	759	680	--	901	--	654
Solub., 98% H_2SO_4, vol. %	26	40	--	30	54	61	74
Conversion of Reactive Intermediates, %	67	70	>85	>90	40	70	50

* PRL 7–A

Table 3

CORE TESTS

Slug Content: 0.5% active sulfonate in 1% aqueous Na_2CO_3 solution

Core Dimensions: 61 cm x 5.04 cm.   Flow Rate: 0.3 m/day   Buffer Size: 60% PV   Buffer: 500 ppm Xanflood in 200 ppm NaCl Brine

Run No.	Sulfonate Eq. Wt.	η_{min} Slug	EACN Oil	Interfacial Tension Slug vs Oil dynes/cm	Slug Size % PV	Oil Recovery %	Sulfonate Efficiency Frac. Oil Rec. mg sulf./g rock
				Matched (η_{min} – EACN) Systems			
1	403	10.3	10.3	1.8×10^{-3}	18	17	2.2
2	403	10.3	10.3	1.8×10^{-3}	32	44	3.4
3	403	10.3	10.3	1.8×10^{-3}	63	67	2.6
4	410	10.7	10.7	9.8×10^{-4}	100	77	2.0
5	395	10	12	3.7×10^{-2}	63	45	1.7
6	403	10.3	11.5	1.2×10^{-2}	60	37	1.4
				Matched (η_{min} – EACN) Systems			
7	395	10	10.3	3.6×10^{-3}	63	66	2.4
8	425	11.5	11.5	9.8×10^{-4}	64	64	2.4
9	425	12	12	8.8×10^{-4}	64	76	3.1

Table 4

PROPERTIES OF CORES USED IN TABLE 3

Run No.	Oil in Place %	Core Porosity %	Permeability Darcys	Slug	Oil	Buffer
		Matched (η_{min} – EACN) Systems				
1	35	20.6	0.229	1.5	5.5	8.5
2	32.2	19.7	0.244	1.4	5.4	5.5
3	34.1	20.5	0.143	1.5	5.4	8.0
4	32.9	21.3	0.321	1.4	5.9	8.0
		Mismatched (η_{min} – EACN) Systems				
5	31.6	20.4	0.293	1.5	5.0	7.5
6	34.6	22.2	0.296	1.6	9.6	7.6
		Matched (η_{min} – EACN) Systems				
7	33.9	21.0	0.266	1.6	4.4	8.8
8	26.9	20.4	0.294	1.6	9.0	8.1
9	28.5	19.9	0.172	1.6	4.4	9.0

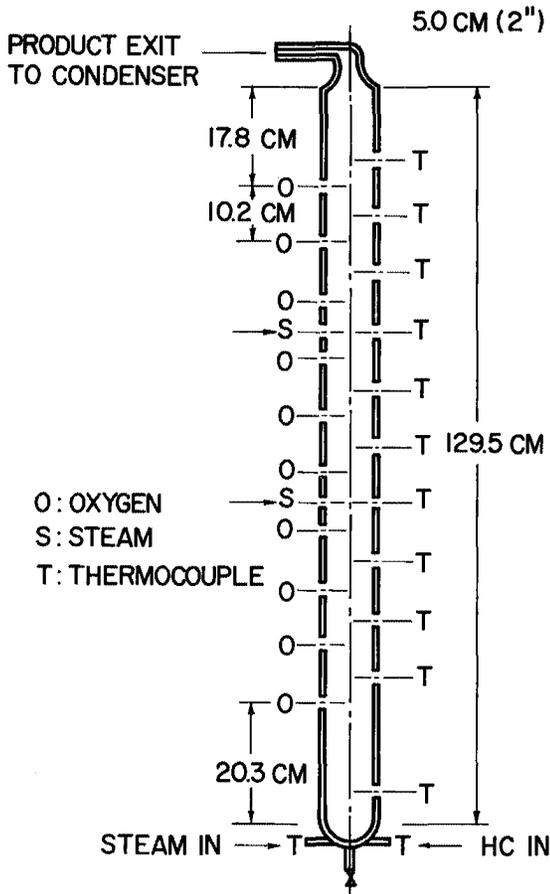Under the column heading "Viscosity, cp" spanning Slug, Oil, Buffer.

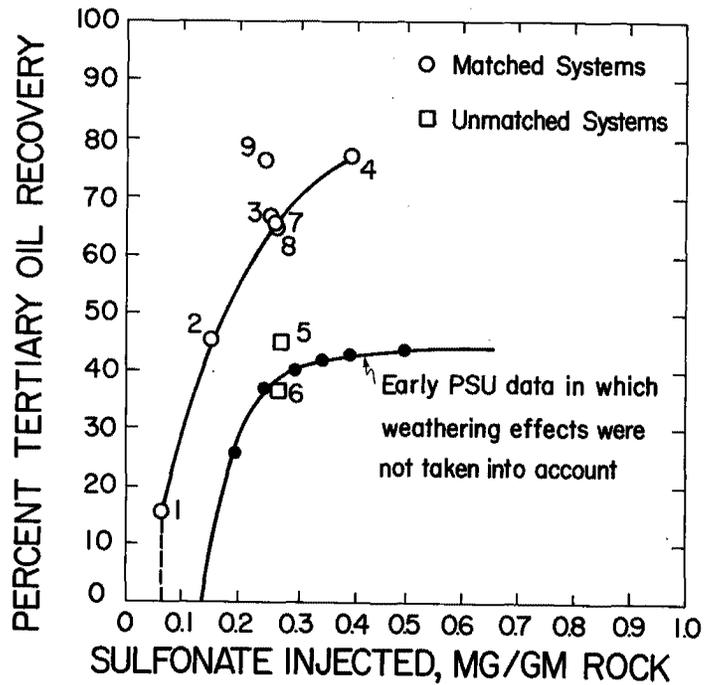Fig. 1 - Steam-moderated oxidation reactor.

Fig. 2 - Matching/mismatching effects on tertiary oil recovery for dilute surfactant solutions.