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Demulsifying Power of Salts of Sulfated Ethoxylatated Nonylphenol and Their Combination with Certain Petroleum Sulfonates

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قدرة أملاح نونيل فينول المتكبرتة الأثوكسالية على الاستحلاب وامتزاجها مع سلفونات زيت بترول محددة

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لقد تم في هذا البحث دراسة تأثير ادخال مجموعة كبريتات في جزيّ مستحلب ايثوكسيلات نونيل فينول على فعاليته في ازالة الاستحلاب. وقد أظهرت أملاح الصوديوم للأثير المحتوي على مجموعات الكبريتات المحضر قدرة عالية على ازالة الاستحلاب . ويناقش البحث أيضا ظاهرة مزج هذه الأملاح مع سلفونات بترولية ذات وزن جزئي منخفض تم تحضيرها بسلفنة زيت غاز فراغي.

Abstract: *The influence of the introduction of a sulfate group into a molecule of nonylphenol ethoxylate emulsifier on its demulsification activity was studied. A great demulsifying power was shown by sodium salts of the produced sulfated ether. The feature of combining these salts with a low molecular weight petroleum sulfonate, obtained via sulfonation of a vacuum gas oil, is discussed .*

INTRODUCTION

The Efficiency of ethoxylated alkylphenols as demulsifiers to break crude oil emulsion is a function of both the alkyl side chain length and polyglycol chain length (number of ethylene oxide groups - nEO)[1,2]. The greatest demulsifying power was shown by the ethoxylated alkylphenols with C_9 - C_{12} alkyl side chain of (nEO) of about 20. The introduction of a sulfate group into two molecules of an ethoxylated alkylphenols has a significant effect on surface and demulsifying activities. The sulfate group in its influence of surface activity was found to be equivalent to approximately five moles of ethylene oxide, while in its influence on demulsifying activity was equivalent to 7-10 moles of ethylene oxide depending on crude oil nature[2].

In an investigation on the effects of crude oil components on demulsifying efficiency[3], it was noted that petroleum surfactants have marked effects on demulsifying power of a block copolymer of ethylene oxide .

The present work deals with the influence of the introduction of a sulfate group into a molecules of nonylphenol ethoxylate (NPE) emulsifier on its demulsifying activity. The feasibility of formulating a demulsifier combination containing a salt of sulfated NPE together with a low-molecular weight petroleum sulfonate, was studied as well .

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EXPERIMENTAL

The Sodium Salt of Sulfated NPE + H_2O

The preparation of this surfactant, starting with NPE emulsifier, consists of two steps; sulfation of NPE and neutralization of the sulfoether with caustic soda[2] according to the following reactions

$RC_6H_4(OCH_2CH_2)_nOH + H_2SO4 \rightarrow RC_6H_4(OCH_2CH_2)_nOSO_2OH + H_2O$

$RC_6H_4(OCH_2CH_2)nOSO_2OH + NaOH \rightarrow RC_6H_4(OCH_2CH_2)_nOSO_2ONa + H_2O$

Thus, the sufation was carried out with concentrated sulfuric acid taken in molar ratios of 1:1 -1:3 at a temperature of 40 °C for 2 hours . The resulting sulfated mass was diluted with acetone and neutralized with 30% caustic soda solution to phenolphthalein end point.

The acetone solution of the sulfoether, together with the sodium sulfate precipitated in the residue, was dried with anhydrous sodium sulfate, after which the sodium sulfate was filtered off, the acetone was driven off from the filtrate, and the residue was brought to a constant weight.

The Petroleum Sulfonate

This sulfonate product was prepared starting with vacuum gas oil of Az zawiyah Refinery. The group-chemical composition, determined by adsorptive chromatography on silica gel, showed that it contains 47.5% by weight aromatic hydrocarbons. The gas-oil was sulfonated with gaseous SO_3 , diluted with nitrogen at 55°C. The amount of reacted SO_3 was 1.2% by weight of the gasoil, corresponding to approximately 13% degree of sulfonation . The sulfonated gasoil had a content of sulfonic acids of 7.5% by weight. After neutralization with 10% aqueous caustic soda, the reaction mass was treated with aqueous isopropyl alcohol to extract the petroleum sulfonate .

Demulsification Properties

The change in emulsification properties of surfactants was evaluated via determining the stability of a direct emulsion, formed using toluene and water in a ratio of 20:80 and containing same concentration of different surfactants. The stability was evaluated by measuring the time needed for complete separation of the two phases at room temperature[4].

RESULTS AND DISCUSSION

Table1 includes results of the influence of molar ratio of NPE: concentrated sulfuric acid on the content. A high degree of purity of sodium salts of sulfated NPE was achieved using the molar ration of 1:3.

Table 1. Sulfation of NPE by concentrated H_2SO_4 at 40 °C.

NPE : H_2SO_4	Contents of sulfated NPE
(molar ratio)	in the products (wt.%)
1:1	55.1
1:3	95.2

The changes in emulsification properties of NPE, due to introducing sulfate group in the molecule, can be seen from the data of Table 2 .

Thus, in the presence of NPE as the surfactant, a highly stable emulsion was formed. However, a partial or complete replacement of this surfactant by the sulfated one caused a great decrease in stability of the direction of mono hydrophile surfactant.

Elucidation of the influence of incorporating the petroleum sulfate in the demulsifier composition was done using a product containing 65.4% by weight of sodium sulfonate, the remaining being unreacted

Table 2. The changes in emulsification properties of NPE as a result of its sulfation.

Surfactant	Concentration of the surfactant in the aqueous phase (wt.%)	Stability of 20:80 (toluene\water emulsion) (hours)
NPE	0.5	>24.0
NPE	1.0	>24.0
70% NPE+30% salt of sulfated NPE.	1.0	6.0
30% NPE+70% salt of sulfated NPE.	1.0	1.8
Salt sulfated NPE	1.0	1.5

gasoil, and having a surface activity value of 210 erg. $1/cm^2$ .g.

Results showed that a composition containing 80% of salt of sulfated NPE and 20% of the petroleum sulfonate exhibited higher demulsifying power than showed by any of the component taken separately.

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