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A Reversible Separation Method Process Using Nonionic Surfactants

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ABSTRACT

An extraction method for hydrocarbons based on surfactant association structures is presented.

The process utilizes the strong temperature dependence of the micellar association structures in systems of water, hydrocarbons and nonionic surfactants. The extraction is made at the HLB-temperature at which large amounts of water and oil concurrently dissolve to an isotropic solution.

Reduction of the temperature (20°C) causes separation of the hydrocarbon; a corresponding increase gives separation of pure water.

In this article determinations of the purity of the separated phases are reported.

INTRODUCTION

Extraction and separation processes are usually based on the concept of using an organic solvent for extraction followed by a removal of the solvent by distillation. The conditions that govern these processes have by now been extremely well characterized.

The separation by distillation is an energy consuming process and the recent price increases in petroleum commodities make separation mechanisms that use less energy of prime interest. With this contribution we describe the basics of a new extraction and separation process that appears to use extremely small energy amounts.

It is based on the association conditions of nonionic surfactants of the polyethylene glycol alkyl ether type with water and hydrocarbons. An introductory description of these conditions will be given, followed by some analytical results from a preliminary experiment.

Temperature Dependence of Micellar Solutions Containing Nonionic Surfactants

Polyethylene glycol alkyl ethers show a strong temperature dependence of their solubility in water and hydrocarbons. In general, the surfactants are soluble in water at low temperatures and in hydrocarbon at high temperatures (1–4).

At an intermediate temperature they show a balanced solubility; this temperature level has been named the HLB-temperature (Hydrophilic-Lipophilic Balance) by Shinoda (5). At this temperature the phase conditions according to Fig. 1 are found (6–8). A total composition marked A in the figure will separate into three isotropic liquid phases (P, Q and R, Fig. 1). P is an aqueous phase with extremely small amounts of hydrocarbon and surfactant present. Q is the surfactant phase containing large amounts of water and hydrocarbon in addition to less amount of surfactant; typically 6–8% by weight. R is a hydrocarbon solution of some surfactant and water.

A reduction in temperature causes the area for the surfactant phase to move toward compositions with higher water content. After a reduction by approximately 15°C, the area of the surfactant phase will unite with the aqueous corner and a sectorial solubility region is found Fig. 2 (6–8). This means that the former three-phase area now contains only two phases; an aqueous phase and a hydrocarbon phase.

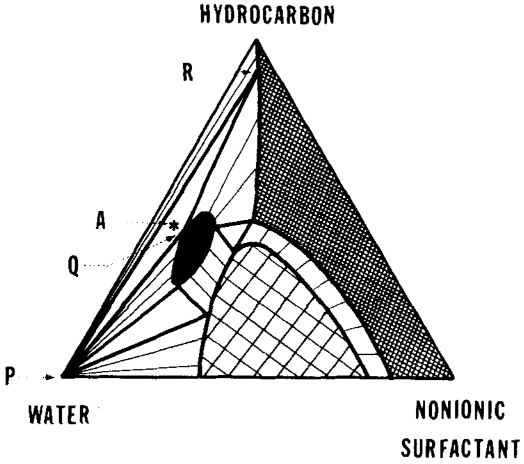

FIGURE 1. At the HLB-temperature 10 g of a total composition A (water (W) 49.1, hydrocarbon (H) 44.7 and nonionic surfactant (NS) 6.2 weight percent) will separate into three phases:

P (W 100, H <0.01 and NS <0.01 weight %)
Q (W 46.1, H 44.0 and NS 9.9 weight %)
R (W 4.3, H 90.7 and NS 5.0 weight %)

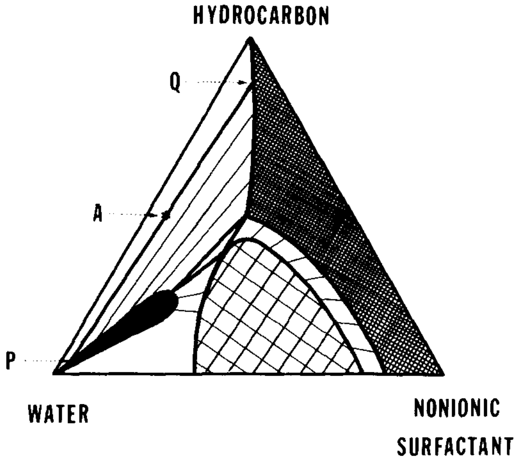

FIGURE 2. After reduction of the temperature (15°C) the three phases are reduced to two phases:

P (W 89.0, H 7.0 and NS 4.0 weight %)
Q (W 7.7, H 85.1 and NS 7.2 weight %)

A corresponding increase in the temperature causes the region of surfactant phase to move toward the hydrocarbon solution area (6–8). After it has joined this area, a two-phase system of water and a hydrocarbon/water/surfactant solution is present (Fig. 3).

For future discussion it is essential to observe the fact that lowering the temperature results in most of the surfactant being dissolved in the aqueous solution while practically all of it is found in the hydrocarbon solution at elevated temperatures. These conditions form the basis for an extraction and separation process according to the following description.

The Extraction and Separation Process

The extraction step should take place at the HLB-temperature. An aqueous solution of the surfactant that is brought into contact with the hydrocarbon will spontaneously dissolve the latter into the surfactant phase.

Separation of the hydrocarbon takes place at reduced temperature, when the hydrocarbon phase with some dissolved water and surfactant spontaneously separates.

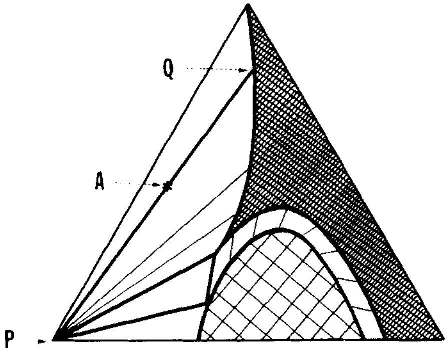

FIGURE 3. After increase of the temperature (15°C) the two phases have the composition:

P (W 100, H <0.01 and NS <0.01 weight %)
Q (W 9.0, H 80.0 and NS 11.0 weight %)

The aqueous phase may then be used directly for a new extraction at the HLB-temperature. If there is a need to separate the water in pure form this can be achieved by raising the temperature.

The following preliminary experiments were made in order to test the validity of the proposals.

EXPERIMENTAL

Materials

The surfactant was penta ethylene glycol dodecyl ether (Nikkol >98% according to gas chromatography), the decane was Aldrich Gold Label 99+% purity and the water was doubly distilled.

Phase Conditions

The water and decane in a 1:1 ratio were mixed with 7% by total weight of the surfactant and left to equilibrate at different temperatures. For the cases where stable emulsions were encountered separation of these was achieved by fast freezing and thawing.

The content of water and surfactant in the separated oil phase was determined by IR directly on the samples using calibration curves from spectra of samples with known content of water and surfactant. The amount of water was determined from the absorbence of its symmetric deformation vibration at 1640 cm^{-} , the amount of surfactant using the CO stretching vibration at 1118 cm^{-} .

For samples with low water content, a confirmatory determination was made using Karl Fischer titration.

RESULTS AND DISCUSSION

The cloud point of aqueous solutions of the surfactant was observed at 31°C. Three phases illustrating the conditions in Fig. 1 were found at 36°C. This temperature is denoted as the HLB-temperature in this investigation.

Reduction of the temperature to different levels and separation gave the water and surfactant contents according to Table 1.

The table shows only traces of water to be present in the separated hydrocarbon at reduced temperatures. Values of 0.02 to 0.01 percent of water appear to be at a reasonably low level.

The surfactant content was higher. The reduction from 36°C to the lowest value 12°C gave a content of 0.37% by weight.

The rest of the surfactant should be found in the aqueous phase. An estimation of the level can be made assuming equal amounts of aqueous and hydrocarbon phase. For this condition, a surfactant concentration of 13.63% should be in the aqueous phase. The concentration ratio will be 0.027.

The surfactant was added to 7% by weight on the total. The concentration of 0.37% in the hydrocarbon phase means that of the 7%, 0.19% will be lost. This in turn means a loss of 2.6% of the surfactant at each separation step. If no surfactant is added, one half of it will be lost after 26 consecutive extractions.

The analysis of the water separated at 60°C showed less than 0.01% by weight of surfactant and even less of the hydrocarbon.

TABLE 1

Surfactant and Water Content in the Oil Phase Separated at Lower Temperatures. HLB-t. = 36°C

Temperature °C	Time, hours	Surfactant, weight %	Water, weight %
30	48	1.3	0.5
25	16	1.0	0.02
20	3	0.6	No det.
20	19	0.6	No det.
17.5	1.5	0.5	0.01
12	1	0.37	No det.

CONCLUSIONS

The preliminary analysis of a new reversible extraction and separation method for hydrocarbon showed the water content to be extremely low in the separated hydrocarbon. The amount of surfactant was low, 0.4%, but not negligible.

The water separated at higher temperatures was extremely pure with only traces of hydrocarbon and surfactant.

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