

THE SOLUBILIZATION OF HYDROCARBON MIXTURES AS ONE OF THE MECHANISMS OF HYDROPHOBIC POLLUTANTS REMOVAL FROM SOIL

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Abstract

Solubilization of aliphatic hydrocarbons (decane, dodecane, tetradecane, hexadecane) and aromatic hydrocarbons (toluene, o-xylene) mixtures was performed in micellar solutions of nonionic surfactants - ethoxylated alcohol (Rokanol NL6) and alkylpolyglucosides (Triton BG10, AG 6210). The best solubilization efficiency was obtained for Rokanol NL6. Solubilization efficiency of mixture depended on solubility of particular components in micellar solution. The highest solubility was observed for aromatic hydrocarbons (toluene and xylene). Aliphatic hydrocarbons with shorter chain (decane and dodecane) solubilize more effectively than hydrocarbons with longer one (tetradecane and hexadecane). The presence of aromatic compounds in the mixture led to a considerable increase of solubility of more hydrophobic compounds (aliphatic hydrocarbons).

INTRODUCTION

Continuously increasing demand for petroleum and its modified products is directly connected to the necessity for seeking and improving cheap and efficient methods of counteracting its entrance to environment consequences. With regards to high toxicity and the mutagenity of petroleum compounds, not only the efficiency of remediation of water and soil is important, but also the time within which desirable results are achieved.

Soil remediation by washing out hydrophobic pollutants reaches higher efficiency, when surfactant solution instead of water is used. Proper selection of surfactant is very important in achieving a high process efficiency. The most commonly used surfactants are nonionic ones because of their high solubilization capacity and good biodegradability [1-3].

Surfactants (surface active compounds) can enhance the removal of hydrophobic pollutants from porous media by two different mechanisms: micellar solubilization and increased mobilization of residual compounds trapped in porous media by capillary forces. The way of acting is strictly connected with specific properties of surfactants which are a consequence of

their amphiphilic structure. The molecule of surfactant consists of two parts: the hydrophobic one, which is typically a long hydrocarbon chain, and the hydrophilic one, which provides high solubility in water [4]. To minimize the internal energy of the system at low surfactant concentration, molecules adsorb at the air/water or oil/water boundary. After the whole boundary is saturated, the micelles start to form. They are the aggregates of surfactant molecules, frequently of spherical size, where the hydrophobic tails are directed towards the interior of the aggregate whereas the external layer has hydrophilic properties that are composed of ionic or nonionic polar headgroups. The concentration at which micelles forming in the solution begins is called critical micelle concentration (CMC). In the surfactant solutions far above the CMC a deformation of spherical micelles has place with forming cylindrical micelles, lamellar ones or liquid crystals [5].

One of the most important properties of surface active compounds, strictly connected with forming micelles, is micellar solubilization, which is a process defined as spontaneous dissolution of the substance due to forming thermodynamically stable isotropic system. From practical point of view surfactant solution in water can dissolve higher amounts of hydrophobic compounds than pure water due to distribution into two immiscible phases: polar water phase (solvent) and less polar phase - hydrophobic interior of the micelle [4,5].

Properties of hydrophobic solubility play a factor in determining its localization in a micellar aggregate. Strongly hydrophobic compounds, like aliphatic hydrocarbons, solubilize in a hydrophobic interior of the micelle, which is practically pure alkane but of a significantly higher viscosity. Therefore, hydrophobic interior is a small, in respect of volume, region of micellar aggregate, where the packing of surfactant tails is very close. Inasmuch as the closeness of packing is influenced by the balance between attractive and repulsive forces, so a capital fraction of hydrophobic tails stays in contact with the solvent. The region of micellar aggregate, where hydrophobic tails of surfactant and solvent molecules occur is called a palisade layer. An indirect region between the hydrophobic interior of a micelle and palisade layer is a position where compounds of lower than pure alkanes hydrophobicity solubilize, eg. fatty acids, alcohols and esters. Orientation of the molecules of this group of compounds is probably connected with incorporation into the micellar aggregate, as it is similarly in the case of incorporation of surfactant molecules. Moderately polar contaminants, eg. aromatic hydrocarbons, can be solubilized entirely in a palisade layer or, if they are strongly polar, at the surface of the micelle, in a polar layer consisting of solvated hydrophilic groups [6].

Solubilization of hydrocarbons was an object of several scientist's research. Abriola et al. [7] showed that efficiency of solubilization decreases with increasing amount of



ethyleneoxy groups in surfactant molecule (with increasing hydrophilicity of surfactant). Diallo et al. [8] observed linear decrease of molar solubilization ratio (MSR) and micelle-water partition coefficient (K_{MW}) for aliphatic hydrocarbons with the increase of hydrophilic-lipophilic balance (HLB). The same trend was observed by Pennel for dodecane solubilization [9]. The increase of solubilization efficiency was connected with the increase of micelle core volume caused by the increase of length of surfactant hydrocarbon chain. Because alkanes are solubilized in the micelle hydrophobic core, its volume decides about solubilization efficiency. Peña and Miller [10] concluded that the efficiency of the process decreases linearly with the increase of the length of the solubilize chain (octane, nonane, decane and undecane). Diallo et al. [8] concluded that, in contradiction to aliphatic hydrocarbons, which MSRs decreased with the HLB increase, aromatic hydrocarbons showed different dependence. At the beginning MSRs increased with the increase of HLB, achieving the maximal value at HLB=15. However, further increase of HLB caused decrease of solubilization efficiency. This decrease one can explain by reduction of micelle core volume. Whereas the initial increase of solubilization efficiency with the HLB increase is connected with occurrence of interactions between ethyleneoxy groups and aromatic hydrocarbon molecules, what enables solubilization of more hydrophobic compounds (aliphatic hydrocarbons) in the palisade layer of micelle. Attwood and Florence [11] claimed that micelles can reorganize by incorporating both solubilize molecules and more surfactant monomers. It leads to situation where the presence of second dissolved substance (pollutant) can cause further aggregate reorganization and makes solubilization of other compounds possible, till they achieve solubility concentration typical for one-component system [12]. From the practical point of view, it is very important to broaden the knowledge about solubilization of a mixtures of model contaminants despite the need for investigating a single compound solubilization. This approach is strictly connected with a fact that majority of petroleum products are mixtures of broad spectrum of hydrocarbons, often of a very complicated structure.

The main purpose of this investigation was to study efficiency of solubilization of multicomponent hydrocarbon mixtures in nonionic surfactant solutions, to estimate length of solubilize chain and presence of aromatic compound influence.

EXPERIMENTAL PROCEDURES

Solubilization of non-branched aliphatic hydrocarbons (decane, dodecane, tetradecane, hexadecane – Lancaster Synthesis) and aromatic hydrocarbons (toluene, o-xylene – Lancaster



Synthesis) mixtures was run in aqueous micellar solutions of nonionic surfactants belonging to following groups: ethoxylated alcohols (Rokanol NL6) and alkylpolyglucosides (Triton BG10, AG6210). Rokanol NL6, which was obtained from PCC Rokita, is a polydisperse mixture of synthetic polyethoxylated alcohols (C₉-C₁₁) with the average number of ethyleneoxy groups equaling 6. Triton BG10 and AG 6210 (Brenntag Polska) are 60-70% solutions of C₈-C₁₀ alkylpolyglucosides. Surfactants were used as received from the supplier, without further purification, but the surfactant concentration in solutions were recalculated for 100% of active substance.

Solubilization experiments were carried out by mixing hydrocarbon mixture with nonionic surfactant solutions (10 g/dm³ - 50 g/dm³) in 10 cm³ glass vials sealed by caps fitted with septa. The vials containing 5 cm³ of surfactant solution and 0.5 cm³ of organic phase were agitated for 24 h in an IKA Vibrax VXR orbital shaker at 1500 rpm. After equilibration was complete the vials were centrifuged for 15 min at 5000 rpm in MPW 350R centrifuge. Samples were then stored at constant temperature (25°C) for 96 h, to allow the complete phase separation. From the aqueous phase in each vial 1 cm³ of the lower phase was taken and dissolved in 2-propanol. The hydrocarbons concentration in water/2-propanol solution was determined chromatographically. Gas chromatography analysis was performed on a Chrompack CP 9001 gas chromatograph (Varian Inc.) equipped with flame ionization detector (FID). A 30 m long capillary column of internal diameter 0.32 mm – Chrompack CP-Sil 8CB was used. The injector and detector temperature was 250°C. The analysis temperature was changed from 140 to 250°C.

RESULTS

Micellar solubilization of aliphatic hydrocarbon mixture (decane, dodecane, tetradecane, hexadecane) and aliphatic-aromatic hydrocarbon mixture (dodecane and toluene) in three different synthetic surfactants solutions is presented in Figures 1 and 2. Each data point represents the average concentration obtained from three independent experiments. As nonionic surfactants, two alkylpolyglucosides (Triton BG10 and AG6210) and one ethoxylated alcohol (Rokanol NL6) were used. The application of these nonionic surfactants in soil remediation is common due to their resistance to ions present in soil and due to good biodegradability. For all surfactants solutions, the linear increase of solubilization efficiency with increase of surfactant concentration in solution was observed. Moreover, the higher slope



of the solubilization curve means achieving the higher efficiency with smaller amounts of surfactant used.

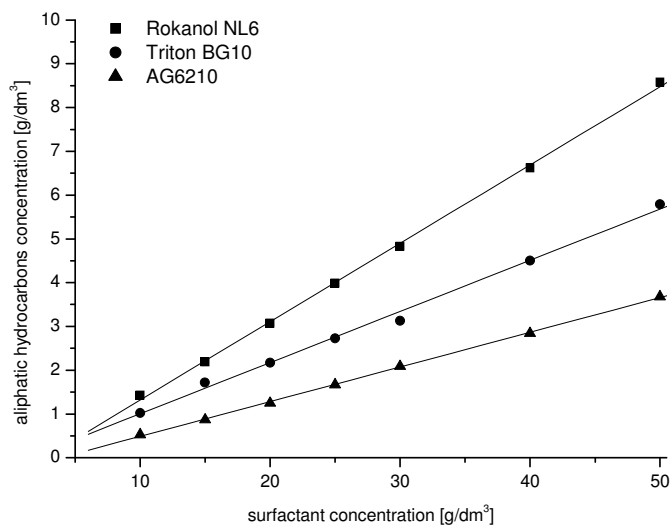


Fig. 1. Micellar solubilization of 4-component mixtures of hydrocarbons (decane, dodecane, tetradecane, hexadecane) in nonionic surfactant solutions.

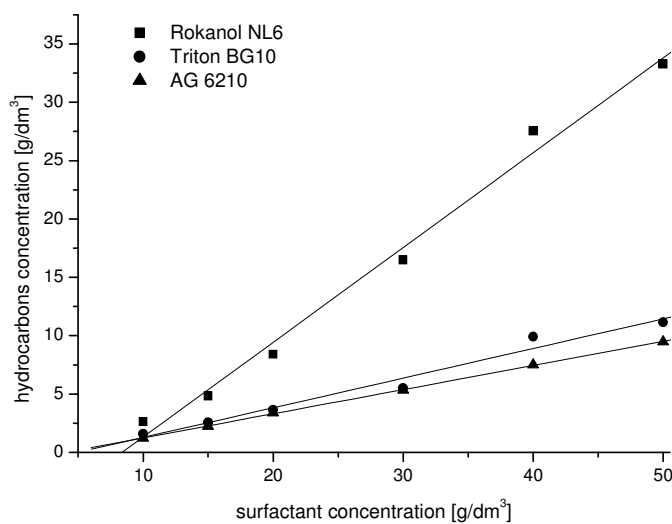


Fig. 2. Micellar solubilization of 2-component mixtures of hydrocarbons (dodecane, toluene) in nonionic surfactant solutions.

Comparing results of aliphatic hydrocarbon mixture solubilization, the best results were obtained for Rokanol NL6 (Fig. 1). Hydrocarbons solubility in solutions of this

surfactant was 8.6 g/dm^3 at surfactant concentration of 50 g/dm^3 . In solutions of alkylpolyglucosides solubilization proceeded with lower efficiency. Solubility of hydrocarbons in solutions of Triton BG10 at surfactant concentration 50 g/dm^3 was only 5.8 g/dm^3 . It was about 30% less than in Rokanol NL6 solutions. Much lower solubilization efficiency was observed for AG 6210, only 3.7 g/dm^3 of hydrocarbons were solubilized, when surfactant concentration was 50 g/dm^3 .

Similar results were observed for the aliphatic-aromatic hydrocarbon mixture (dodecane and toluene). The highest solubilization efficiency was observed for Rokanol NL6 solutions (Fig. 2). At surfactant concentration 50 g/dm^3 , the concentration of solubilized hydrocarbons was 33.3 g/dm^3 . Hydrocarbons solubility obtained in Triton BG10 and AG 6210 solutions was significantly lower. For the first mentioned surfactant it was 11.2 g/dm^3 , and respectively 9.5 g/dm^3 – for the second. Summarizing the solubilization efficiency in Triton BG10 solutions was about 70% lower than in Rokanol NL6 solutions. Data obtained for alkylpolyglucosides differed inconsiderably – higher by about 20% efficiency was obtained in Triton BG10 solutions. The application of alkylpolyglucosides in soil remediation is advisable, due to their very low toxicity to microorganisms present in soil and very good biodegradability which can be attributed to the fact that the breakdown of the glucoside bonds are enzymatically controlled by different glucosidases present in the environment.

In the Table 1 weight and molar solubilization ratios for solubilization of particular compounds of hydrocarbon mixture are presented. The weight solubilization ratio (WSR), which expresses the ratio of the amount of solute solubilized to the amount of surfactant present in the form of micelles, was calculated from the slope of the solubility curve. The molar solubilization ratio (MSR), presented in the Table 1 in brackets, was calculated from WSR. For solubilization in alkylpolyglucosides, only weight solubilization ratios are presented, because of undefined molecular weight of these surfactants, necessary to calculate molar solubilization ratios.



Table 1. Weight and molar solubilization ratios for particular compounds of hydrocarbon mixtures. Molar solubilization ratios (MSR) presented in brackets.

hydrocarbon/surfactant	Rokanol NL6	Triton BG10	AG 6210
aliphatic hydrocarbons mixture			
decane	0.051 (0.151)	0.035	0.021
dodecane	0.051 (0.126)	0.031	0.019
tetradecane	0.035 (0.074)	0.024	0.018
hexadecane	0.039 (0.072)	0.026	0.018
aliphatic-aromatic hydrocarbons mixture			
dodecane	0.350 (0.863)	0.124	0.082
toluene	0.461 (2.102)	0.129	0.124
aliphatic-aromatic hydrocarbons mixture			
decane	0.157 (0.473)	-	-
dodecane	0.176 (0.445)	-	-
toluene	0.214 (0.832)	-	-
xylene	0.171 (0.595)	-	-

Comparing the solubilization ratios one can see, that the highest ratios were obtained for solubilization in solutions of Rokanol NL6. These values were over 2-times higher than for solubilization in AG 6210. These conclusions are in accordance with earlier described observations, that the hydrocarbons solubility was the highest in Rokanol NL6 solutions.

Simultaneously we can observe small decrease in solubilization efficiency with the increase of hydrocarbon chain length. This dependence is especially visible for solubilization in Rokanol NL6 solutions. In examined range of surfactant concentrations $0.46 \div 2.51 \text{ g/dm}^3$ decane, $0.38 \div 2.52 \text{ g/dm}^3$ dodecane, $0.35 \div 1.76 \text{ g/dm}^3$ tetradecane and $0.24 \div 1.78 \text{ g/dm}^3$ hexadecane solubilized. In all surfactants solutions the lowest solubility for hexadecane and tetradecane, and the highest – for decane and dodecane were obtained. The calculated values of WSR and MSR (Tab. 1) confirm the above conclusion. For example for decane and dodecane in Rokanol NL6 solutions, WSR were 0.051, while for tetradecane and hexadecane only 0.035 and 0.039, respectively. If it is about MSR, for decane it was 0.151, while for dodecane 0.126. Much lower values of MSR were obtained for tetradecane and hexadecane – 0.074 and 0.072 respectively. The increase of chain length of hydrocarbon molecules caused decrease of solubilization efficiency, what is strictly connected with the increase of their



hydrophobicity and molar volume, which determines the amount of moles of the compound can have place in the micelle. For example, dodecane had over twice higher MSR than hexadecane, which is characterized by the molar volume higher by 50% than dodecane.

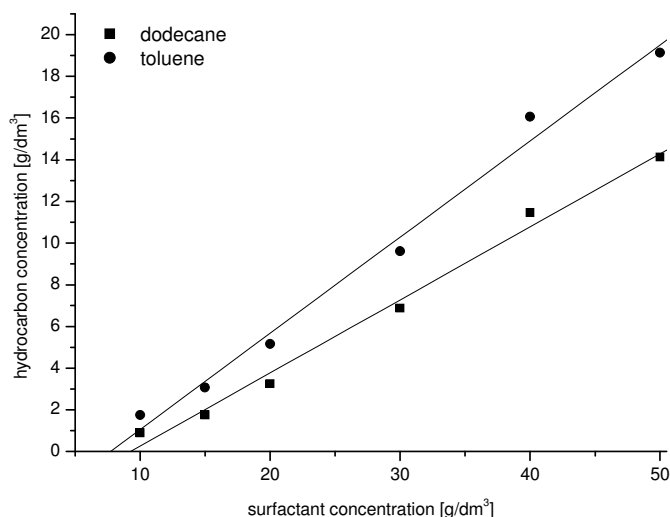


Fig. 3. Micellar solubilization of particular hydrocarbons (2-component mixture) in Rokanol NL6 solutions.

The situation seems to differ in the case of 2-compound mixture containing aromatic hydrocarbon. Toluene solubility in surfactant solutions was higher than the solubility of dodecane (Fig. 3). In Rokanol NL6 solutions 19.2 g/dm³ of toluene and 14.1 g/dm³ of dodecane solubilized at surfactant concentration 50 g/dm³. Similar differences were obtained for Triton BG10 and AG 6210 solutions. The increase of dodecane solubility in comparison to the mixture containing only aliphatic hydrocarbons was also observed (14 g/dm³ and only 2.5 g/dm³, respectively). It was partially connected with the fact that only two hydrocarbons were in this mixture (dodecane and toluene); in 4-component mixture dodecane had to compete about the place in micelles with three other hydrocarbons (decane, tetradecane, hexadecane). However the increase of solubilization efficiency was much higher than we could expect. The total concentration of solubilized dodecane and toluene at surfactant concentration of 50 g/dm³ was 34 g/dm³, what means almost quadruple increase of the solubility in comparison to 4-component mixture (8.6 g/dm³). Moreover, the dodecane solubility was higher than the total solubility of 4-component mixture (14 g/dm³ and 8.6 g/dm³, respectively). This considerable increase of solubilization efficiency was probably caused by the presence of aromatic compound in mixture.

In order to examine the influence of aromatic compounds on the solubility of aliphatic hydrocarbons, the solubilization of 4-component mixture (decane, dodecane, toluene, xylene) in micellar solutions of Rokanol NL6 was proceed. The results of the solubility of particular components of this mixture are presented in Fig. 4.

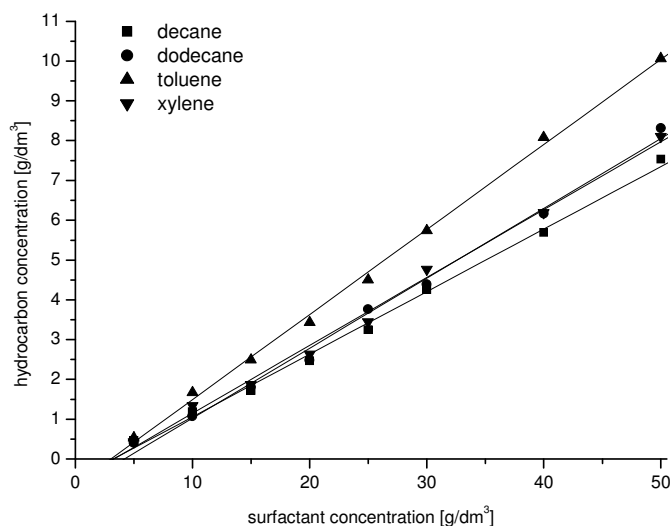


Fig. 4. Micellar solubilization of particular hydrocarbons (4-component mixture) in Rokanol NL6 solutions.

Similarly to previous results, toluene solubility in micellar solutions was the highest from among all four components of the mixture (10.1 g/dm³ at surfactant concentration 50 g/dm³). Xylene solubility was approximate to the solubility of dodecane and decane (about 8 g/dm³). Considerable increase of decane and dodecane solubility in presence of aromatic hydrocarbons was also observed. In the solution of Rokanol NL6 at concentration of 50 g/dm³ 7.5 g/dm³ of decane and 8.3 g/dm³ of dodecane solubilized. In the case of aliphatic hydrocarbon mixture it was only about 2.5 g/dm³. Therefore, over triple increase of the concentration of both aliphatic hydrocarbons was obtained. An increase in efficiency of solubilization of aliphatic hydrocarbons in the presence of the aromatic compounds is also confirmed by the weight and molar solubilization ratios. MSRs for decane and dodecane were over three-times higher in the mixture with aromatic compounds (0.47 and 0.45, respectively) than in the mixture of aliphatic compounds only (0.15 and 0.13, respectively).

CONCLUSIONS

Solubilization efficiency of hydrocarbon mixture depended on solubility of its particular components. One concluded that, hydrocarbons with shorter chain, like decane and dodecane, solubilize more effectively than hydrocarbons with longer one (tetradecane and hexadecane). It was observed for both groups of surfactants, ethoxylated alcohols and alkylpolyglucosides. It is probably connected with higher hydrophobicity of long chain hydrocarbons, as well as with the size of their molecules. We can suppose that this is related to the competition of different hydrocarbons for the place in micelles and the more privilege seems the hydrocarbon be the more it's chain length approximate to the length of surfactant hydrophobic part. In the case of Rokanol NL6 the length is 9 to 11 carbon atoms in chain, hence preferential solubilization of decane and dodecane.

The highest solubility in micellar solutions was observed for aromatic hydrocarbons (toluene and xylene). Hydrophobicity of these compounds is much lower than in the case of aliphatic ones so they can solubilize in palisade layer, not only in hydrophobic core of micelle (in contrast to aliphatic hydrocarbons). The presence of aromatic compounds in the mixture also leads to a considerable increase of solubility of more hydrophobic compounds (aliphatic hydrocarbons) in a micellar surfactant solution. This increase is probably caused by the fact that less hydrophobic compounds (toluene, xylene) solubilize in a palisade region of a micellar aggregate, what decreases the interfacial tension between water and hydrocarbon and then enables aliphatic hydrocarbons to solubilize also in this region, not only in a hydrophobic core [6]. Some of reports explain this fact is due to formation of hydrogen bonds between aromatic hydrocarbon and water molecules [13]. The next advantage of solubilization of aromatic hydrocarbons in the palisade layer of micelle is the fact of enlargement the aggregate size, what enables solubilization of larger amounts of hydrophobic compounds.

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