Aggregation properties of p- and n-functionalized calix[4]resorcine in water/oil emulsion in the presence of sulfate reducing desulfo bacter bacteria

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Abstract. This paper presents a comparative study of the aggregation properties of P- and N-functionalized calix[4]resorcines in “water/oil emulsion + Desulfobacter culture”. It has been shown that both compounds under study displayed aggregation properties in low concentration range. Nevertheless, their structural features affect the aggregation process. Moreover, the beginning of aggregation of N-functionalized calix[4]resorcine with petroleum hydrocarbons molecules and microorganism cells shifted to lower concentration zones than the one of P-functionalized calix[4]resorcine. However, P-functionalized calix[4]resorcine was characterized by a wider interval at which the structuring of the water/oil emulsion is observed.

1. Introduction

It is well known that interfacial phenomena are essential in petroleum extraction and recovery. The combination of hydrophilic and hydrophobic groups in surfactants lead to widely regulate their properties [1–3]. In general terms, Calix[4]resorcines can be defined as macrocyclic cavity systems with different interesting properties [4–6]. Thus, the presence of hydrophilic and hydrophobic groups in their composition, as well as the possibility of functionalization their lower and/or upper rims with functional fragments may allow them to acquire surface-active properties (surfactants) [7], which may be of great importance in oil biodegradation processes for controlling the reactivity of substances. Previously, the aggregation properties of P- and N-functionalized calix[4]resorcines I–II (Figure 1) were studied on model systems that mimic the composition of hydrocarbons that are found in larger quantities in oil [7, 8]. The purpose of this work is to compare the characterization of the aggregation properties of P- and N-functionalized calix[4]resorcines I–II in a system of “50 % OFWW (oil field wastewater) – 50 % oil – 10 % of a Desulfobacter culture medium”.

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2. Methodology

In order to compare the aggregation properties characteristics, N-functionalized calix[4]resorcine, substituted on the upper rim of the molecule by aminomethyl fragments [9] and P-functionalized calix[4]resorcine, substituted on the lower rim of the molecule by aryldiethoxyphosphoryl fragments [10] were taken as objects of study.

During the research process we created a system of “50 % OFWW (oil field wastewater) –50 % oil –10 % culture medium Desulfobacter” in which compounds I or II were introduced in various concentrations. In parallel, control experiments were carried out without the addition of compounds I and II. Further, the system "50 % OFWW (oil field wastewater) – 50 % oil – 10 % culture medium Desulfobacter” is designated as "water/oil emulsion- Desulfobacter”.

The aggregation ability of P- and N-functionalized calix[4] resorcines was determined according to the composition-properties diagrams using two independent methods:

• conductometric method based on measuring electrical conductivity of the studied compounds solutions \( G = f(C) \);

• spectrophotometry method based on measuring the optical density of the studied compounds solutions \( A = f(C) \).

All measurements were taken at 25 °C. The temperature was maintained using a thermostat with an accuracy of ±0.1°C. The concentration of the studied compounds varied within \( 10^{-3} - 10^{-6} \text{ mol/l} \). Solutions of the studied compounds were prepared immediately prior to studies using the dilution method. The electrical conductivity of the studied compounds solutions was measured on an LM-301 conductometer (standard cell LM-3000). The measurement of the optical density of the compounds solutions was carried out on an SF-16 instrument at wavelengths of \( \lambda = 280 \text{ nm} \) and \( \lambda = 288 \text{ nm} \), which characterize the presence of a calix-resorcinal structure [11].

3. Results and discussions

The change in electrical conductivity of “water/oil emulsion-Desulfobacter” system when adding compounds I–II d (Figure 2–3) shows that the aggregation of both compounds occurs in 2 stages. At \( C_I = 0.012 \cdot 10^{-3} \text{ mol/l} \) and \( C_{II} = 0.023 \cdot 10^{-3} \text{ mol/l} \) (0.03 g/l), the dependences \( G=f(C) \) show a clear bend, indicating a change in the physicochemical properties of the systems and the beginning of their structuring process. The intense bending next point of the graph corresponds to \( C_I = 0.093 \cdot 10^{-3} \text{ mol/l} \) (0.1 g/l) and \( C_{II} = 0.184 \cdot 10^{-3} \text{ mol/l} \) (0.25 g/l), at which form new bonds with micellar system. The change in optical density in the “water/oil emulsion-Desulfobacter” system when adding compound I also indicates that the structure of the solution changes at 2 points (Figure 4–5). Thus, compound I-II exhibits aggregation properties at low concentrations.
Both compounds can be attributed to ionic surfactants, in which already at low concentrations an intense increase in electrical conductivity occurs, apparently due to an increase in the number of protonated calixresorcines molecules to a bend corresponding to the critical concentration of association. In the area of these concentrations, spontaneously form associates by the head-to-tail type of electrostatic mechanism, most likely, in the form of ionic micelles. After this, the mobility of the ions decreases and, consequently, the conductivity will decrease.

Figure 2. "water/oil emulsion – Desulfobacter" system electrical conductivity dependence on the concentration of the compound I.

Figure 3. "water/oil emulsion – Desulfobacter" system electrical conductivity dependence on the concentration of the compound II.

Figure 4. "water/oil emulsion – Desulfobacter" system optical density dependence on the concentration of the compound I.
Figure 5. water/oil emulsion – Desulfobacter” system optical density dependence on the concentration of the compound II.

However, for compound I, the process of changing the physicochemical characteristics of the solution occurs at lower concentrations. Obviously, the presence of a lone electron pair in nitrogen atom of the amino groups will contribute to the formation of hydrogen bonds with hydroxyl groups, turning compound I into a zwitterion [12]. Protonated forms of amino groups lead to the formation of a charged lower rim, which facilitates association. In addition, the presence of a lone electron pair in nitrogen atom of the amino groups will contribute to the formation of bonds with the constituent parts of oil that carry acceptor groups, as well as with negatively charged cells of microorganisms. Obviously, therefore, the concentration at which the structuring of the solution begins in the presence of compound I should be lower.

In compound II, the localization of a positive charge in phosphorus atom transforms it into a cation-active surfactant, which will bind the negative charge of sections of the molecules of petroleum hydrocarbons. The upper hydrophobic resorcinol part of molecule rim will encapsulate those parts of the oil molecules or individual molecules of oil fractions that are compatible with it in size, as well as the cells of microorganisms. Obviously, the encapsulation process requires higher concentrations of compound II. In this case, hydroxyl groups can also interact via hydrogen bonds.

4. Conclusion
We have presented a comparative study of the aggregation properties of P- and N-functionalized calix[4]resorciners in the “water/oil emulsion + Desulfobacter culture” and have demonstrated that both compounds reveal aggregation properties in low concentration range. However, the concentration at which the structuring of the solution begins in the presence of compound I is lower, which is explained by structural features and different ways of interacting with molecules of petroleum hydrocarbons and microbial cells of compounds I–II.

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