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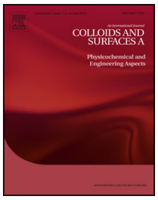

Study of influence of ionic additives to AOT reverse microemulsions by liquid chromatography, IR and UV–visible spectroscopy

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HIGHLIGHTS

- Binding constants of o-NA with AOT reverse micelles are higher in the presence of acetate ions.
- Retention factors of solutes in reverse micellar chromatographic system are less in the presence of acetate.
- Addition of salts results in the changes of ratio of the bound, free and trapped water fractions in the reverse micelles.

GRAPHICAL ABSTRACT

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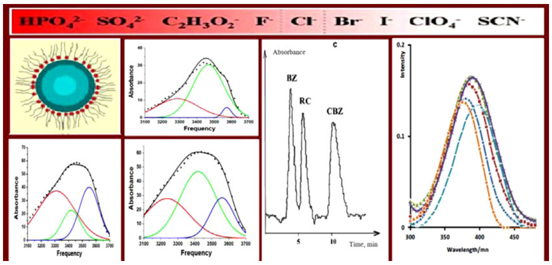

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ABSTRACT

Reverse micellar mobile phases based on sodium bis(2-ethylhexyl) sulfosuccinate (AOT) were used as mobile phases in HPLC. The chromatographic behavior of the model compounds was studied on the basis of reverse micellar mobile phases modified by salt additives. Structural changes of water pools of reverse micelles depending from AOT concentration in the presence or absence of structure-making and structure-breaking ions was investigated by IR-Spectroscopy. The O—H stretching vibrational absorption spectra in the region of 3000–3800 cm^{-1} were fitted into three subpeaks with a Monte Carlo method. The binding of o-nitroaniline (o-NA) to the micelles of AOT was determined by UV–visible spectroscopy. The different influence of kosmotropic and chaotropic anions on the binding constant K_b was revealed.

1. Introduction

Reverse micelles have been the subject of a large number of experimental and theoretical investigations during the last two decades. They are powerful models for complex biological water cavities and wall pores in solid media [1,2]. These reverse micelles may be considered as microreactors for enzyme catalysis and drug delivery, therefore they are intensively studied in biochemistry and colloid chemistry [3].

One of the most commonly studied surfactants is sodium bis(2-ethylhexyl) sulfosuccinate (AOT), which forms spherical nanometer-sized molecular aggregates in nonpolar solvents without help of cosurfactant [4–8]. The hydrocarbon part of the AOT molecules are oriented toward the exterior of the aggregate, while the sulfonate headgroups with the sodium counterion are localized

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in the interior of the reverse micelle. Therefore AOT based reverse micelles are used as a membrane–mimetic system since reverse micelles represent one of the normal membranous structures in cells. The biological processes occurring in a reverse micellar system mimic those involved in the in vivo membranous environment [9]. The interior dimensions of reverse micelles are similar to confined water found in cavities in biological systems [10].

Water confined into the nanometer-scale cavities behaves anomalously, e.g. enzymes entrapped in reverse micelles achieve their optimal efficiency when the reversed micelle reaches a particular size. This means, that the enzyme activity is dependent on the molecular ratio of water to surfactant W_0 [11–13]. Water in the core of reversed micelle reveals at least two structures. Water that is close to the periphery of the micelle or in direct contact with the barrier molecules i.e. surfactants, differs from water nearer the center of the reversed micelle. At that both of these structures differ from free, chemically pure water [11]. Introducing of additives of ions into the water pockets of reverse micelles is especially important because of influence of ion–water interactions on the structure of water, viz. kosmotropic ions bind water in the first hydrated layer and order the structure of water. Chaotropic ions retain molecules of water in the second hydrated layer and disrupt the structure of water [14–16].

The structure of reversed micelles is studied by several methods: UV–visible spectroscopy, IR-spectroscopy, small angle neutron scattering, nuclear magnetic resonance, differential scanning calorimetric method, dynamic light scattering, etc. [4–8,17–29]. Investigation of the microenvironment in reverse micelles using optical probes in UV–visible spectroscopy provides a unique possibility to study the properties of water aggregates close to the ionic center of the surfactant. This means, that an additional information on the nature of the water in the polar core of the reverse micelle may be received [7,8,17–20]. Infrared spectroscopy is also a suitable method to characterize microstructure in the AOT microemulsions [4–6,21–23]. Three types of water: bound, trapped and free water exist in reverse micelles according to Gaussian curve fitting of the broad peaks obtained for water OH by IR spectroscopic technique [6,22,23]. Reverse micellar solutions may be successfully used as mobile phases in Water-in-Oil Microemulsion Liquid Chromatography (MELC), because they reveal high solubilisation ability for hydrophilic and hydrophobic compounds. Unfortunately, this method did not find a great development after the first pioneering articles notwithstanding very interesting structure of reverse micelles and there are only scanty literary data about application of reverse microemulsions in liquid chromatography in the last decade [30–33]. Our recent investigations show that many interesting information may be obtained on the basis of data of liquid chromatography and UV–visible spectroscopy [34].

The goal of the proposed work was to study the influence of different ionic additives introduced in the water nanocages of reverse micelles by using water-in-oil microemulsion chromatography, infrared and ultraviolet-visible spectroscopy in order to reveal the changes in: (i) chromatographic retention factor of model compounds; (ii) binding of a molecular probe to AOT reverse micelles; (iii) structural changes of water pools of reverse micelles.

2. Experimental

2.1. Model compounds

Nembutal (NB), benzonal (BZ), barbital (BR), phenobarbital (PB), carbamazepine (CBZ), resorcinol (RC), caffeine (Caff), theophilline (Th), hydroquinone (HQ) and pyrogallol (PL) were used as samples.

2.2. Apparatus and conditions

Liquid chromatographic (HPLC) analyses were carried out with a micro-column liquid chromatograph “Milichrom-4” equipped with an isocratic pump and a variable wavelength UV detector. Detection of compounds was carried out at ambient temperature. Detection wavelengths were 250 and 280 nm. The chromatographic column was Silasorb C_2 (5 μm, Lachema, Brno, Czech Republic). Mobile phases were prepared on the basis of water, hexane and AOT. Sodium bis(2-ethylhexyl) sulfosuccinate (98%) was obtained from Fluka and was used without further treatment. Butanol was selected as co-surfactant. Sodium acetate and potassium perchlorate were used as mobile phase additives. Flow-rate of the mobile phase was 50 μL/min.

UV–vis absorption spectra were recorded in a UV–visible spectrophotometer Optizen POP using cells with 1 cm path length. Binding constants of o-NA with AOT micelles were calculated by absorption data of o-NA at wavelengths of 376 and 398 nm in hexane (0.0 M and 0.1 M AOT). Concentrations of free and bound o-NA were determined by equation systems at intermediate concentrations of AOT.

IR absorption spectra were recorded in a IR spectrophotometer Specord 75 equipped with a 1 cm path length quartz windows. All the IR spectra of different H_2O:AOT molar ratio W were obtained between 4000 and 400 cm^{-1} at room temperature. To study the microstructure of the solubilized water, the O—H stretching vibrational absorption spectra in the region of 3000–3800 cm^{-1} were fitted into three subpeaks. The curve fitting was performed by using Origin 6.5. Gauss function was chosen to fit the overlapped peaks. Gaussian curve fitting was achieved with a Monte Carlo method.

2.3. Preparation of the reverse microemulsions

Reverse microemulsions were prepared on the basis of AOT, hexane, water, water solutions of salts sodium acetate and potassium perchlorate. Transparent one-phase solutions were achieved through gentle shaking. For systems of low water content, the solutions became one phase quickly. All spectroscopy experiments were performed on stable, one-phase systems at room temperature.

3. Results and discussion

3.1. Chromatographic study

The nature of the model compounds is different from anionic barbiturates to week polar resorcinol and cationic caffeine. The structure of the analytes is illustrated in Fig. 1. The elution strength of microemulsion mobile phases were improved by fixed quantity of n-butanol in order to elute simultaneously solutes with different polarity.

The compatibility of the salts to the chromatographic system was taken into account in their selection process. Therefore acetate and perchlorate were selected from kosmotropic and chaotropic anions respectively. As to cations, kosmotropic sodium ions were chosen in case of acetate, but chaotropic potassium cations were selected in conjunction of perchlorate in order to provide wholly kosmotropic or entirely chaotropic nature of the selected salts.

Increasing of water content in the mobile phase or increase of W causes a decreasing of retention factor of the model compounds (Table 1, columns 1,2). The additives of water presumably are expended on both modification of residual silanol groups on C_2 stationary phase and increasing of size of water pools of the reverse micelles. Hence decreasing of retention factor with increasing of water content in the micellar mobile phase may be explained by

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