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Note

# Degree of counterion binding on water in oil microemulsions

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**Abstract**

An ion-exchange process has been used to prepare HOT from NaOT (sodium bis(2-ethylhexyl)sulfosuccinate), where the $Na^+$ counterion has been replaced by $H^+$. The acidity function, $H_0$, of the aqueous core of HOT-based microemulsions decreases with $W$ from $H_0 \approx 0.6$ at $W > 20$ to $H_0 = -1.4$ at $W = 2$. On the basis of the $H_0$ acidity function of the aqueous core and the dependence of $H_0$ on acid concentration, we have been able to determine the degree of counterion binding ($\beta$) in microemulsions with a value of $\beta \approx 0.92$ which is practically independent of the water content of the system.

*Keywords:* Microemulsion; Acidity function; Neutralized charge; Counterion binding

## 1. Introduction

Microemulsions are thermodynamically stable systems consisting of two immiscible liquids separated and stabilized by a monolayer of surfactant [1,2]. In the case of water-in-oil (W/O) type microemulsions, the interactions between the surfactant and the two solvents result in the formation of nanometer-sized water pools in an apolar solvent. The study, in this unique nanoenvironment, of chemical reactions such as acid-catalyzed reactions, electron-transfer reactions, and biochemical reactions is particularly interesting and depends to a great extent on the properties of the aqueous core [3–8]. The surfactant sodium bis(2-ethylhexyl)sulfosuccinate (NaOT) has been extensively used to form microemulsions since it allows a large amount of water to be solubilized compared to other surfactants [9]. The relation between water and NaOT concentrations is given by the parameter $W$, $W = [H_2O]/[NaOT]$ which is directly proportional to the size of the nanodroplet.

As $W$ increases, the properties of water in the microemulsion resemble those of bulk water [10]. However, interactions of water molecules with the counterions and headgroups of the NaOT can be observed at any $W$ value [11,12]. Levinger and co-workers [13] have recently shown that a proton gradient exists inside NaOT microemulsions leaving the interior neutral while the interfacial region is acidic. In order to make the use of water-in-oil microemulsions compatible with strongly acidic media, we performed an ion-exchange process in which the $Na^+$ counterion of NaOT was replaced by $H^+$. The resulting surfactant is able to form microemulsions and solubilize large amounts of water (with $W$ values similar to those obtained in the presence of NaOT), providing us with microemulsions with acidic water pool where the surfactant itself is the source of reactive counterions.

Ion distribution between the interface and the interior of the water pool has been the focus of interest of many researchers due to its considerable importance for the study of reactions in which at least one of the species is ionic and the reaction proceeds at the interface [14,15]. The Poisson–Boltzmann equation (PBE) has allowed some authors to study the effect of $W$ on the degree of counterion binding [16–19]. However, the number of experimental studies providing information about ion distribution in the water pool of microemulsions is scarce. The most commonly used technique is the so-called "chemical trapping" method [20] that provides $\beta$ values different from those reported in theoretical studies [21].

The pseudophase ion-exchange (PPIE) formalism has been applied in bimolecular reactions between an organic substrate and an ion of charge opposite to that of the interphase. The knowledge of the properties of aqueous charged interphases,

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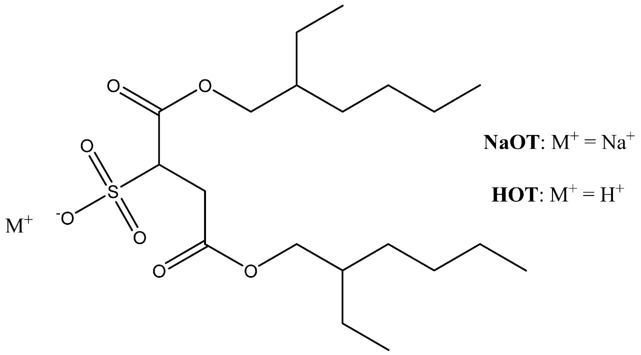

Scheme 1.

and mainly the fraction of neutralized charge ($\beta$), plays a key role in understanding chemical reactivity in microemulsions and other colloidal aggregates. The aim of this work is to determine the value of $\beta$ in water/HOT/isooctane microemulsions. The acid nature of these microemulsions and their changes with the size of the water core were previously studied in our laboratory, using Hammett's acidity function [22]. We will use these $H_0$ values previously obtained to determine the $H^+$ concentration in the microemulsion and once we have obtained the local $H^+$ concentration we can calculate the $\beta$ value [6]. As will be shown below, our experimental results are in quite good agreement with those calculated by the Poisson–Boltzmann method.

## 2. Experimental

HOT was prepared from NaOT by ion exchange using Amberlite IR 120 (plus) resin. HOT surfactant was initially prepared as a synthetic intermediate in the $Na^+$ counterion exchange process [23]. We checked the extent of $Na^+/H^+$ exchange by two methods: atomic absorption spectroscopy which showed the absence of $Na^+$ in the HOT sample (the residual $Na^+$ content is consistent with a degree of $Na^+/H^+$ exchange of greater than 99%), and acid/base titration, which also indicated that the extent of $Na^+/H^+$ exchange is greater than 99%.

Mass spectra were recorded on a Bruker Microtof ESI-TOF mass spectrometer in high-resolution mode using electrospray ionization in the negative mode. The solutions were infused into the ESI source at flow rates of 0.2 mL/min. Comparison of the mass spectra of NaOT and HOT-based microemulsions shows not HOT decomposition after 7 days of preparation of the microemulsion (see supporting material).

All other reagents used were purchased from Aldrich at the highest level of purity available and were used without further purification. Absorption spectra were recorded on a Varian Cary 500 spectrophotometer fitted with thermostatically controlled cell holders at 25.0 °C.

Determination of the acidity function is described in a previous paper using 2-nitroaniline as indicator [22]. Experiments were carried out keeping the surfactant concentration constant, $[\text{HOT}] = 1.00$ M, and varying the water content in the range $W = 1$ to 30.

Table 1
Variation of $H_0$ and $[H^+]_{\text{calc}}$ with $W$ in HOT/isooctane/water microemulsions

| $W$ | $H_0$ | $[H^+]_{\text{calc}}$ | $W$ | $H_0$ | $[H^+]_{\text{calc}}$ |
|---|---|---|---|---|---|
| 1 | −1.40 | 4.020 | 16 | 0.62 | 0.249 |
| 2 | −0.77 | 2.004 | 17 | 0.64 | 0.235 |
| 3 | −0.47 | 1.332 | 18 | 0.67 | 0.223 |
| 4 | −0.24 | 0.997 | 19 | 0.69 | 0.212 |
| 5 | −0.06 | 0.787 | 20 | 0.70 | 0.203 |
| 6 | 0.00 | 0.647 | 21 | 0.72 | 0.194 |
| 7 | 0.24 | 0.551 | 22 | 0.73 | 0.186 |
| 8 | 0.27 | 0.482 | 23 | 0.75 | 0.179 |
| 9 | 0.34 | 0.429 | 24 | 0.76 | 0.172 |
| 10 | 0.40 | 0.388 | 25 | 0.77 | 0.166 |
| 11 | 0.45 | 0.354 | 26 | 0.78 | 0.160 |
| 12 | 0.49 | 0.325 | 27 | 0.79 | 0.155 |
| 13 | 0.53 | 0.302 | 28 | 0.80 | 0.150 |
| 14 | 0.56 | 0.282 | 29 | 0.81 | 0.146 |
| 15 | 0.59 | 0.264 | 30 | 0.82 | 0.142 |

## 3. Results and discussion

Water/HOT/isooctane microemulsions constitute a system with a strongly acidic character. An efficient method for determining the acidity of the water pool and its variation with $W$ is the use of the $H_0$ acidity function. The $H_0$ acidity function of the dispersed phase of the microemulsion is of crucial importance in understanding the properties of this system as a reaction medium. In a recent paper, we reported the $H_0$ values obtained at different values of $W$ [23]. Table 1 shows the influence of $W$ on the acidity function, which increases abruptly as the water content in the microemulsion increases and remains practically constant above $W = 10$. A large variation in the $H_0$ values can be observed between $W = 1$ and 10. The decrease in the size of the water pool at constant surfactant concentration (and therefore constant $H^+$ ion concentration) leads to an abrupt increase in acidity.

Literature values of the $H_0$ acidity function for aqueous solutions of strong acids increase much more rapidly than the stoichiometric acid concentration [24]. These differences result from variations of the activity coefficients of the species involved in equilibrium with changing acid concentration [24]. A plot such as that shown in Fig. 1 can be obtained from the $H_0$ values for different acids. Based on these reference values we can easily relate a $H_0$ value to its equivalent ($[H^+]$) acid concentration in aqueous solution.

The acid with a higher degree of similarity to the HOT headgroup is the methanesulfonic acid. However, as illustrated in Fig. 1, except at high acid concentrations ($[H^+] \sim 7$–8 M), no significant differences can be found in the values of the proton concentration in aqueous solution at a fixed value of $H_0$ using HCl, HBr, $HNO_3$ and $CH_3SO_3H$. Taking into account the $H_0$ values in Table 1, we can conclude that the acidic medium of the aqueous core of water/HOT/isooctane microemulsions is equivalent to an acid concentration between 0.5 and 5 M. The calculated $H^+$ concentration values, $[H^+]_{\text{calc}}$, have been interpolated for different values of $H_0$ in HOT microemulsions by using a simple polynomial fit (solid line, Fig. 1). Table 1 displays the variation of $[H^+]_{\text{calc}}$ with $W$.