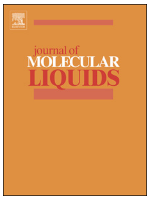
Journal of Molecular Liquids xxx (2013) xxx–xxx

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq



# Differentiating impact of the AOT-stabilized droplets of water-in-octane microemulsions as examined using halogenated fluoresceins as molecular probes

Natalya A. Vodolazkaya *, Yuliya A. Kleshchevnikova, Nikolay O. Mchedlov-Petrossyan

*Department of Physical Chemistry, V. N. Karazin Kharkov National University, Svoboda sq. 4, 61022 Kharkov, Ukraine*

A R T I C L E  I N F O

*Article history:*
Received 9 July 2013
Received in revised form 27 August 2013
Accepted 30 August 2013
Available online xxxx

*Keywords:*
Halogenated fluorescein dyes
Reversed AOT microemulsions
Protolytic equilibria
Vis-spectroscopy
Differentiating impact
'Apparent' ionization constant

A B S T R A C T

The stepwise ionization $H_2R \rightleftarrows HR^- \rightleftarrows R^{2-}$ of six halogenated fluorescein dyes was studied by vis spectroscopy. The 'apparent' $pK_a^a$ values were determined in the reversed Aerosol OT (AOT) microemulsion in *n*-octane at a water:surfactant ratio $W = 20$ and ionic strength of the dispersed aqueous phase at 0.05 M. An expressed shift of the tautomeric equilibria of a neutral (molecular) $H_2R$ form of dyes toward colorless lactone was registered on going from water to the reversed AOT microemulsions. The consideration of the $K_{a1}^a/K_{a2}^a$ ratios of fluorescein dyes in dispersed water pools against those in an aqueous solution allowed the revelation of the essential differentiation impact of the interior of AOT-stabilized droplets on acidity strength. This phenomenon is caused by the peculiarities of the location of the dye species in water pools and by the specific state of dispersed water inside the microdroplets.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

The aim of the present investigation was to examine the solvation properties of dispersed water pools in anionic surfactant-based reversed microemulsions (RME) using a set of halogenated fluorescein dyes, possessing different functional groups (OH, COOH) and dissociating stepwise, as spectroscopical molecular probes.

The anionic surfactant sodium bis-2-ethylhexylsulphosuccinate Aerosol OT, or AOT, is the most effective and well-studied compound for the creation of reversed micelles and microemulsions in apolar solvents [1–5]. AOT-based reversed microemulsions are actually spherical nano-sized inclusions into nonaqueous media, containing an exactly defined small amount of water molecules. The most important value that controls the size, structure, and properties of the RME is the concentration ratio $W = [H_2O] / [AOT]$. The most drastic change of the water content inside the nanopools is observed for $W$ ranging from 4 to 10, which corresponds to the variation of the microemulsion particle diameters varying from 1 to 4 nm. A 'water in oil' nanodroplet, stabilized by anionic surfactant AOT, is schematically presented in Fig. 1.

These RME are used as excellent model systems of biological membranes [6] and nanoreactors for many chemical processes [7]. Therefore the study of the acid-base equilibria in RME has attracted considerable interest [3a]. In our previous studies, we have investigated the row of fluorescein dyes in direct and reversed microemulsions [8].

In this study, we examined six fluorescein dyes (Scheme 1), which are polyfunctional indicators, dissociating in a stepwise manner:

$$H_3R^+ \rightleftarrows H_2R + H^+; K_{a0} \qquad (1)$$

$$H_2R \rightleftarrows HR^- + H^+; K_{a1} \qquad (2)$$

$$HR^- \rightleftarrows R^{2-} + H^+; K_{a2}. \qquad (3)$$

In AOT-based reversed microemulsions, equilibrium (1) for all the investigated dyes takes place in the region of low pH values; the $pK_{a0}$s were not estimated because of turbidity resulting from acidification of the water pools by HCl.

The detailed protolytic equilibria of the dyes are specified in Scheme 2 [8a,9].

The key characteristic of a pH-dependent indicator dye $H_jR^z$, dissolved in organized media, is the so-called 'apparent' ionization constant as defined by Eq. (4) [8,9a]:

$$pK_a^a = pH_w + \log\frac{\left[H_jR^z\right]}{\left[H_{j-1}R^{z-1}\right]}. \qquad (4)$$

---

* Corresponding author.
*E-mail address:* vodolazkaya@univer.kharkov.ua (N.A. Vodolazkaya).

0167-7322/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.molliq.2013.08.018

Please cite this article as: N.A. Vodolazkaya, et al., J. Mol. Liq. (2013), http://dx.doi.org/10.1016/j.molliq.2013.08.018

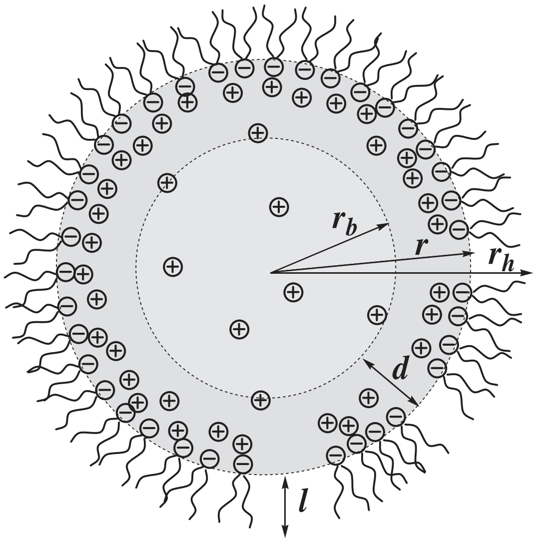


**Fig. 1.** Schematic illustration of a reversed water-in-oil AOT-stabilized microemulsion: $r$—radius of aqueous droplet, surrounded by a monolayer of surfactant molecules; $r_h = r + l$, where $r_h$—hydrodynamic radius, $l$—the length of the hydrocarbon tail of a surfactant; $r = r_b + d$, where $r_b$—radius aqueous droplet, $d$—region of 'surface' water (hydrated polar groups of surfactant).

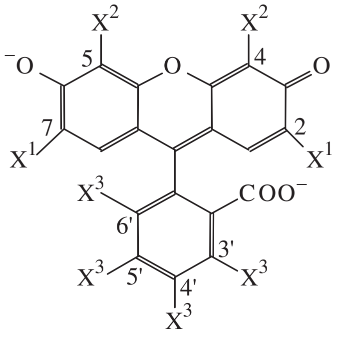
The ratio of equilibrium concentrations of $H_jR^z$ and $H_{j-1}R^{z-1}$ can be determined by vis-spectroscopy. The $pH_w$ values refer to the aqueous solutions within the RME. They are determined with a glass electrode in the bulk aqueous buffer solutions before introducing them into the AOT solution. A more strict standardization of pH in RME is presently hindered. In addition, the location of the indicator species within the dispersed phase is a priori not so clear [3a,10].

The pH value is a poorly defined parameter in nanoscopically-confined water of RME, because the traditional concept of acidity breaks down in a nanosystem that includes fewer than $10^7$ water molecules [2d]. Furthermore, according Poisson–Boltzmann distribution in the case of an anionic surfactant like AOT the maximum concentration is near the surface for $H^+$ ions [3,11] and pH-gradient takes place inside water pools of RME [2,5c,8b,12,13].

According to the electrostatic theory, the apparent $pK_a^a$ value under conditions of complete binding of the indicator couples by the pseudophase depends on the electrostatic surface potential of the electrostatic potential of the locus (normally the Stern layer in the direct micelles/microemulsions), $\Psi$, in the following manner [8,9a]:

$$pK_a^a = pK_a^w + \log\left( {}^w\gamma^m_{H_{j-1}R^{z-1}} / {}^w\gamma^m_{H_jR^z} \right) \qquad (5)$$

Here $pK_a^w$ is the thermodynamic $pK_a$ value in water, the ${}^w\gamma_i^m$ quantities are transfer activity coefficients of the corresponding species from



| Dye | X1 | X2 | X3 |
|---|---|---|---|
| Fluorescein [1] | H | H | H |
| 2,7-Dichlorofluorescein [1] | Cl | H | H |
| 2,4,5,7-Tetrabromofluorescein (Eosin) | Br | Br | H |
| 2,4,5,7-Tetraiodofluorescein (Erythrosin) | I | I | H |
| 3′,4′,5′,6′-Tetrachlorofluorescein | H | H | Cl |
| 3′,4′,5′,6′- Tetrabromofluorescein | H | H | Br |
| 4,5-Dibromofluorescein | H | Br | H |
| 2,4,5,7-Tetraiodo-3′,4′,5′,6′-tetrachlorofluorescein (Rose Bengal B) | I | I | Cl |
| 2,7-Difluorofluorescein [1] | F | H | H |
| 2,4,5,7-Tetrafluorofluorescein [1] | F | F | H |
| 3′,4′,5′,6′-Tetrafluorofluorescein [1] | H | H | F |
| 2,7,3′,4′,5′,6′-Hexafluorofluorescein [1] | F | F | F |

**Scheme 1.** Dianionic structure $R^{2-}$ of fluorescein and its derivatives. [1]These dyes were investigated earlier at our laboratory and the data were published in [8b,c].

Please cite this article as: N.A. Vodolazkaya, et al., J. Mol. Liq. (2013), http://dx.doi.org/10.1016/j.molliq.2013.08.018

Download English Version:

https://daneshyari.com/en/article/5411860

Download Persian Version:

https://daneshyari.com/article/5411860

Daneshyari.com