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AN MD SIMULATION STUDY OF REICHARDT'S BETAINES IN SURFACTANT MICELLES: UNLIKE ORIENTATION AND SOLVATION OF CATIONIC, ZWITTERIONIC, AND ANIONIC DYE SPECIES WITHIN THE PSEUDOPHASE

V.S. Farafonov[*,a], A.V. Lebed[*,b], N.O. Mchedlov-Petrossyan[*,c]

V.N. Karazin Kharkiv National University, School of Chemistry, Department of Physical Chemistry, 4 Svoboda sqr., 61022 Kharkiv, Ukraine

a. e-mail: farafonov@karazin.ua, ORCID: 0000-0003-0785-9582
b. e-mail: alebed@karazin.ua, ORCID: 0000-0001-5175-816X
c. e-mail: mchedlov@karazin.ua, ORCID: 0000-0001-6853-8411

Solvatochromic indicators of the pyridinium *N*-phenolate series, also known as Reichardt's betaines, or Reichardt's dyes, are often used for examining not only pure or mixed solvents, but also various colloidal aggregates, such as surfactant micelles, droplets of microemulsions etc. In order to disclose the locus of these molecular probes within the micellar pseudophase, we recently utilized the molecular dynamics (MD) simulations for the standard dye, i.e. 4-(2,4,6-triphenylpyridinium-1-yl)-2,6-diphenylphenolate, and three other dyes of this family of higher and lower hydrophobicity. Both zwitterionic (colored) and protonated (cationic, colorless) species were involved into the research, as these compounds are also used as acid-base indicators for micellar systems. In the present paper, we extended this investigation further. MD modeling was applied to another three dyes incorporated in sodium *n*-dodecyl sulfate and cetyltrimethylammonium bromide micelles. The following compounds were examined: (i) the most hydrophobic dye, bearing five *tert*-butyl groups, 4-[2,4,6-tri(4-*tert*-butylphenyl)pyridinium-1-yl]-2,6-di(4-*tert*-butylphenyl)phenolate, (ii) a dye with a hydrocarbon loop around the oxygen atom, 4-(2,4,6-triphenylpyridinium-1-yl)-*n*-(3,5-nonamethylene)phenolate, and (iii) the dye with additional carboxylate group attached to the phenyl group opposite to the phenol, 4-(4-carboxylatophenyl-2,6-diphenylpyridinium-1-yl)-2,6-diphenylphenol. The orientation and solvation of the cations, zwitterions (both colored and colorless), and the anion of the last-mentioned dye in micelles appeared to be dissimilar, depending on the molecular structure and ionization state. The results were compared with those obtained previously for the standard betaine dye. In some cases, the most probable orientation of the dyes in their colorless form was opposite to that of the standard Reichardt's dye, i.e., their OH group is directed towards the center of the micelle.

Keywords: solvatochromism, polarity, sodium dodecyl sulfate, cetyltrimethylammonium bromide, localization, orientation, hydration, molecular dynamics simulation.

Introduction

Solvatochromic indicators of different molecular structure are widely used for examining surfactant micelles and other self-assembled aggregates [1–4]. Pyridinium *N*-phenolates [5], also known as Reichardt's betaine dyes, exhibit a strongly-expressed negative solvatochromism and are repeatedly utilized for the aforesaid purpose, in particular also for evaluating the polarities of micellar pseudophases [6–8].

Moreover, these dyes are in fact also acid-base indicators with colored-to-colorless transition (Fig. 1), and can serve for estimating the interfacial electrostatic potential of surfactant micelles [6,8]. In relation to this, the problem of the locus of these dyes within the micellar pseudophase is of key importance. Unfortunately, the abilities of experimental methods, e.g., NMR spectroscopy, for solving this problem are limited. For a more detailed review on the application and instrumental investigation of these dyes, the reader is addressed to ref. [9, 10].
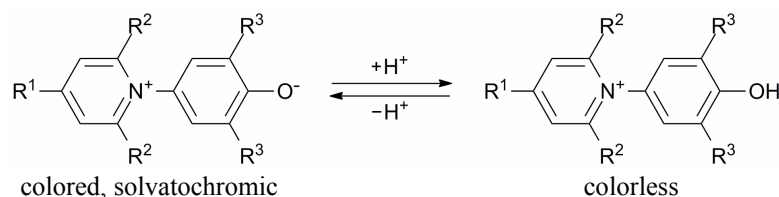

Figure 1. Molecular structure of solvatochromic pyridinium *N*-phenolate dyes.

In a set of previous papers, we made an attempt to reveal probable location and, thus, the nature of the microenvironment of several dyes within the micelles of cationic and anionic surfactants via molecular dynamics (MD) modeling [9–11]. Some most widely used pyridinium *N*-phenolates were already involved in the research project, such as the standard betaine dye **I**, 4-(2,4,6-triphenylpyridinium-1-yl)-2,6-diphenylphenolate ($R^1 = R^2 = R^3 = C_6H_5$) and three other compounds with different hydrophilicity/hydrophobicity: **II** ($R^1 = R^2 = C_6H_5$; $R^3 = H$), **III** ($R^1 = R^2 = C_6H_5$; $R^3 = Cl$), and **IV** [$R^1 = R^2 = C_6H_5$; $R^3 = C(CH_3)_3$] [9, 10]. Both colored (phenolate) and colorless (phenolic) forms were considered in micelles. The MD simulations allow to state that the dyes with $R^3 = C_6H_5$ and $C(CH_3)_3$ are somewhat deeper penetrated into the micelles, as compared to the other two more hydrophilic compounds. However, all species, both colored and colorless (protonated) ones, are situated near the water/micelle interface, with the O⁻ or OH groups directed toward the water phase.

In order to reveal the consequences of more substantial structural changes, we decided to extend the MD studies with following betaine dyes, also used for studying micellar solutions of surfactants [12]: **V,** 4-[2,4,6-tri(4-*tert*-butylphenyl)pyridinium-1-yl]-2,6-di(4-*tert*-butylphenyl)phenolate [$R^1 = R^2 = R^3 = 4$-$C(CH_3)_3$–C_6H_4], **VI,** 4-(2,4,6-triphenylpyridinium-1yl)-*n*-(3,5-nonamethylene)phenolate ($R^1 = R^2 = C_6H_5$, $R^3 = $ –$(CH_2)_9$–), and **VII,** 4-(4-carboxylatophenyl-2,6-diphenylpyridinium-1-yl)-2,6-diphenylphenol ($R^1 = 4$- ⁻OOC–C_6H_4, $R^2 = R^3 = C_6H_5$). The molecular structures are given in Fig. 2A. For convenience, they will be denoted as RD-PhtBu, RD-cyclo9, and RD-COOH, respectively, while the standard dye will be called RD-Ph for notation consistency. All dyes were simulated in both zwitterionic and cationic (protonated) forms. Due to the presence of the second acidic group, RD-COOH can exist in third, fully deprotonated anionic form, Fig. 2B. Thus, it was simulated in all three forms. Importantly, for this dye, it is the anionic form that is colored and solvatochromic because only this form possesses a negatively charged deprotonated phenolate group.
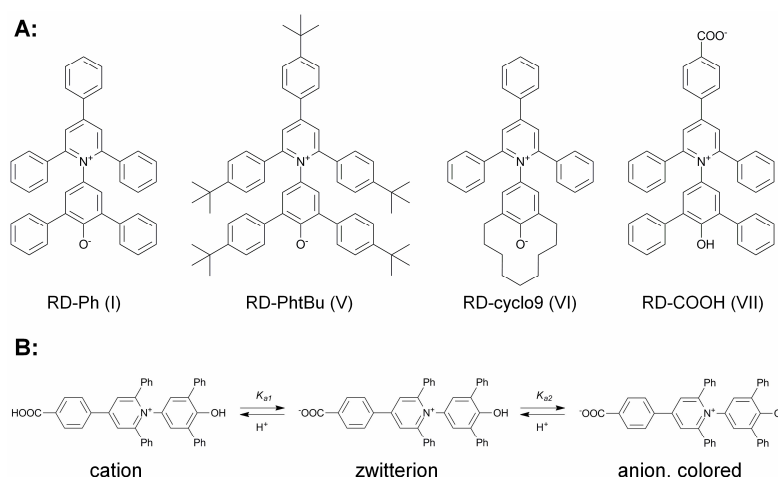

Figure 2. A: The standard betaine dye (**I**) and three related dyes studied in the present work: highly hydrophobic (**V**); with a hydrocarbon loop (**VI**); with an additional ionic group (**VII**). **B:** Protolytic equilibria of RD-COOH.

Simulation methodology

The simulations were carried out at standard conditions with the use of Berendsen thermostat and barostat. The 3D periodic boundary conditions were imposed. Time step equaled 2 fs for cells with SDS and 1.6 fs for that with CTAB. It appeared necessary to reduce the time step for the long-chain surfactant because the value of 2 fs lead to accumulation of constraints errors and simulation crash. Electrostatic interactions were computed with the PME method, while van der Waals interactions were cut-off at 1 nm.

The initial configurations are micelles of 60 SDS monomers or 80 CTAB monomers with a solubilized dye molecule inside. These numbers correspond to the aggregation numbers for these surfactants [13,14]. For each system, three different initial configurations were prepared, and for each of them, a 50 ns simulation was performed. The first 10 ns of the trajectories were treated as equilibration and thus omitted. GROMACS 5.0 software [15] was employed. The preparation of initial cells involved several stages and is in detail described in our previous papers [9,10].

The potential models for the dyes were built in the same way as the model for the standard dye [9,10]. For deriving the atomic point charges, we followed the standard OPLS-AA methodology. It consists of quantum-chemical computation of the electrostatic potential around the molecule of interest on the Hartree-Fock level of theory in 6-31G(d) basis set in vacuum and the following fitting of it with a set of point charges via CHELPG algorithm [16]. The RED Server was employed in order to facilitate the process: this web-service automatically performs both steps for a given molecule, providing the final point charges to the user [17].

For the surfactants, the OPLS-AA models developed by us were taken [18,19], while for water, the SPC model was used.

Results and discussion

For each system, the state of the dye molecule in the micelle was comprehensively characterized. The localization of the molecule was described by means of distribution functions of the distance (DFDs) between micelle center of mass (COM) and the O and N atoms of the dye molecule. In order to indicate the location of the surface layer, DFDs between micelle COM and surfactant head groups S or N atoms were plotted as well. The graphs are shown in the Appendix, Fig. A1.

For zwitterionic forms of the RD-cyclo9 and RD-PhtBu dyes, the N peak is located behind the O one that corresponds to the inclined orientation of the molecule, having the pyridinium part immersed into the micelle deeper than the phenolate part. This resembles the locus of the standard dye. For cationic forms, peaks almost coincide or, in the case of RD-PhtBu, the opposite order of peaks is observed.

The behavior of RD-COOH is quite different. Its colorless zwitterionic form is inclined having the OH group immersed into micelle, while in both charged forms, the peaks either coincide or the O atom is somewhat advanced toward the bulk (aqueous) phase.

RD-PhtBu is immersed into micelles notably (>0.3 nm) deeper than the other dyes, which proves the increased hydrophobicity of this dye.

The orientation of the dye molecules was described in terms of the distribution of the angle θ that is formed by three points: $\angle$ (micelle COM, dye N atom, dye O atom), Fig. 3. Values more than 90° indicate that the molecule is inclined with the O atom pushed toward the volume phase, while values less than 90° show deeper immersion of this atom into the micelle compared to the N atom. The latter orientation will be further called 'inverted'.
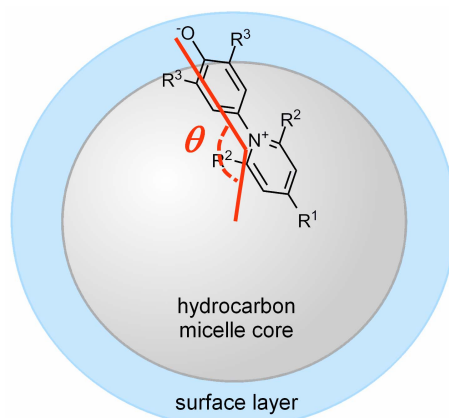

Figure 3. Definition of the angle θ that characterizes the inclination of the dye molecules.

The distribution functions of θ, pertinent to each system, are shown in Fig. 4. The colored zwitterionic form of RD-cyclo9 is oriented exactly in the same way as that of the standard dye, RD-Ph. However, this does not mean identical orientation of their protonated forms: for the former dye, the 'inverted' orientation is not observed, in contrast to the latter dye. The reason is likely that the two phenyl rings make the phenolate part more hydrophobic than the $(CH_2)_9$ chain makes. The picture with RD-PhtBu is more complicated. The zwitterionic form can reside in the same orientation as the RD-Ph and RD-cyclo9. However, it has a second orientation that is more populated than the abovementioned one: the molecule is aligned along the micelle radius with the O atom directed toward the volume

phase. Further, after protonation, the molecule inverts its orientation and relocates the phenolate part from the surface to micelle interior.

For RD-COOH, the following picture is found. For all forms, the orientation parallel to the micelle surface is pertinent. However, when the phenolate group is protonated, it starts to bury into the micelle core that leads to inclination of the molecule. In the limiting case, the molecule is oriented roughly along the micelle radius with the carboxyl group advanced toward the volume phase and the neutral OH group immersed into the micelle; this orientation is more probable for the zwitterionic form.
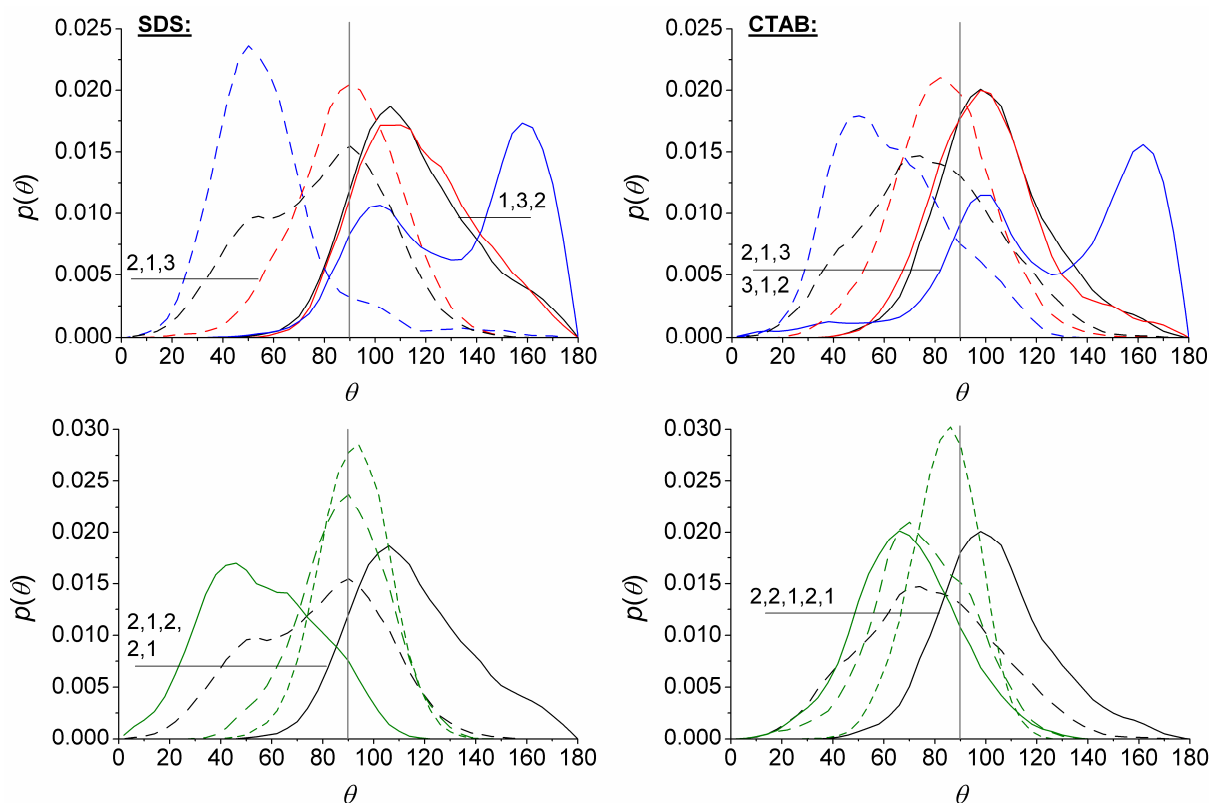

Figure 4. Distribution functions of θ. Top row: 1 — RD-Ph, 2 — RD-cyclo9, 3 — RD-PhtBu; bottom row: 1 — RD-Ph, 2 — RD-COOH. Solid curves are for zwitterionic forms, dashed curves are for cationic ones, short-dashed curves are for the anionic one. Left: SDS micelles, right: CTAB micelles. The data for RD-Ph are from ref. [9].

The listed information is collected and depicted in Fig. 5. Summarizing, some tendencies about the orientation of Reichardt dyes molecules can be derived from the presented data and the data on previously studied dyes:

1. An ionized carboxylate or phenolate group always stays on the micelle surface in contact with water molecules. This is easily explained by presence of high-energy ion-water interactions in this case;

2. A neutral phenolic group in most cases also stays on the micelle surface. However, it can be made immersed into the hydrocarbon core by placing large outstretched hydrophobic substituents in *ortho*- position to it or by attaching a carboxyl group to the opposite side of the molecule. The reason likely is that the carboxylic group interacts with water stronger than the phenolic one, thus the former 'wins' the competition for contact with water molecules;

3. The hydrophobic part of the molecule, which does not contain ionized groups except pyridinium ring, can be oriented differently (lay on the micelle surface or stay perpendicular to it) and samples these orientations in turn. This is somewhat counterintuitive, because a large hydrophobic moiety is expected to immerse into the micelle interior. The explanation is that the total hydrophobic surface area of the micelle+dye complex is similar in both cases, and covering dye molecule from water in the micelle will simultaneously reveal to water an equal area of the hydrophobic micelle core.

The final point is an inspection of the local environment of the dye molecule or, in other words, its microenvironment. For this sake, the previously described approach was employed [9-11]. The atoms located in 0.4 nm vicinity of either whole dye molecule or its chosen atom were distributed into 3 categories, namely, micelle hydrocarbon core, surfactant headgroups, and water; the average number of atoms in each category was computed. The proportion between the amounts of these atoms provides general information about the medium the dye molecule is located in. The obtained numbers are depicted in Fig. 6.
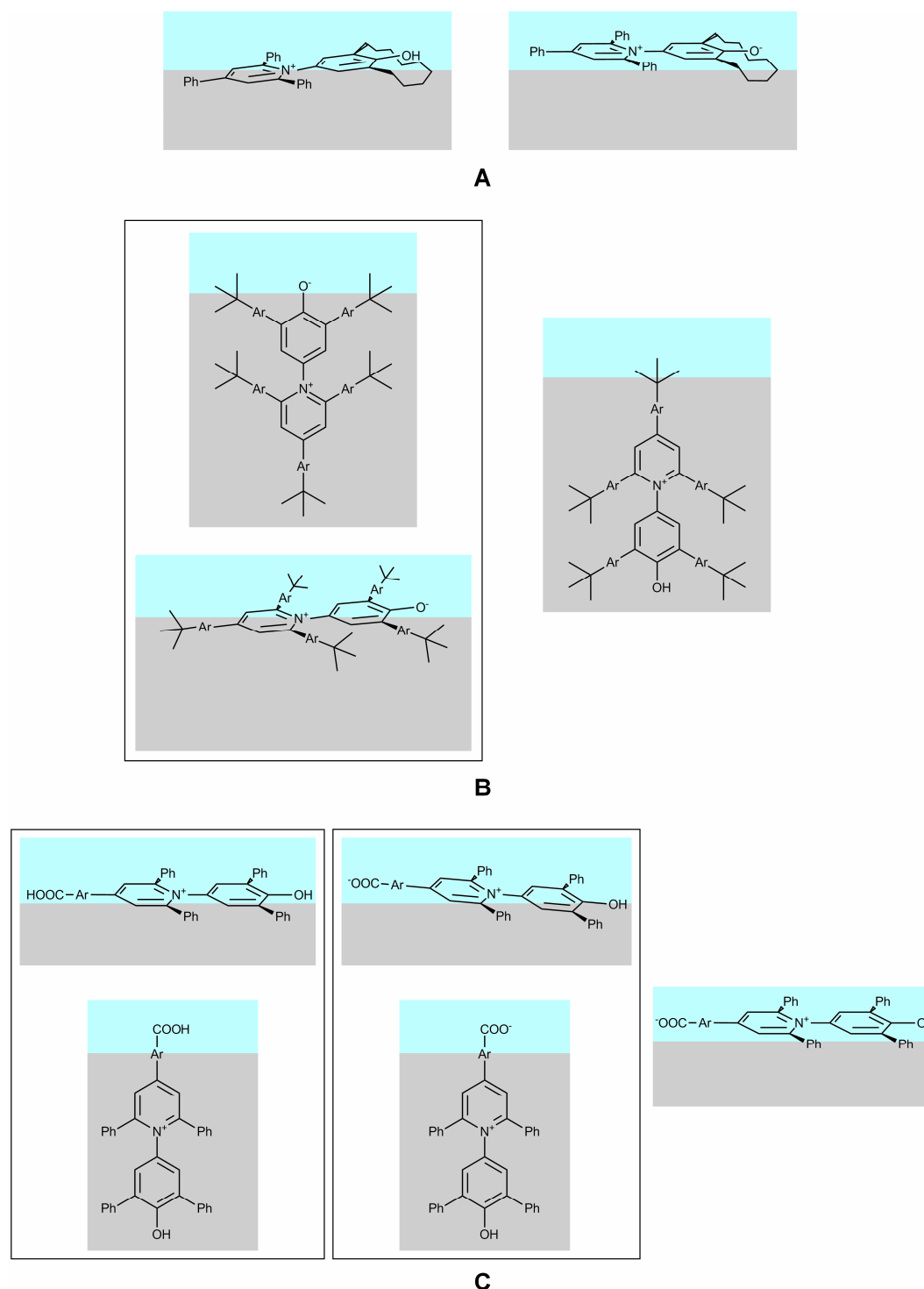

Figure 5. Observed preferential orientations of Reichardt's dyes relative to the micelle surface. **A:** RD-cyclo9; **B:** RD-PhtBu; **C:** RD-COOH. Gray zones depict the micelle cores and blue zones depict the Stern layer. In the bottom row, the anion is colored, whereas in all other cases, the zwitterions are colored and solvatochromic. For some structures, two highly populated orientations are observed and shown.
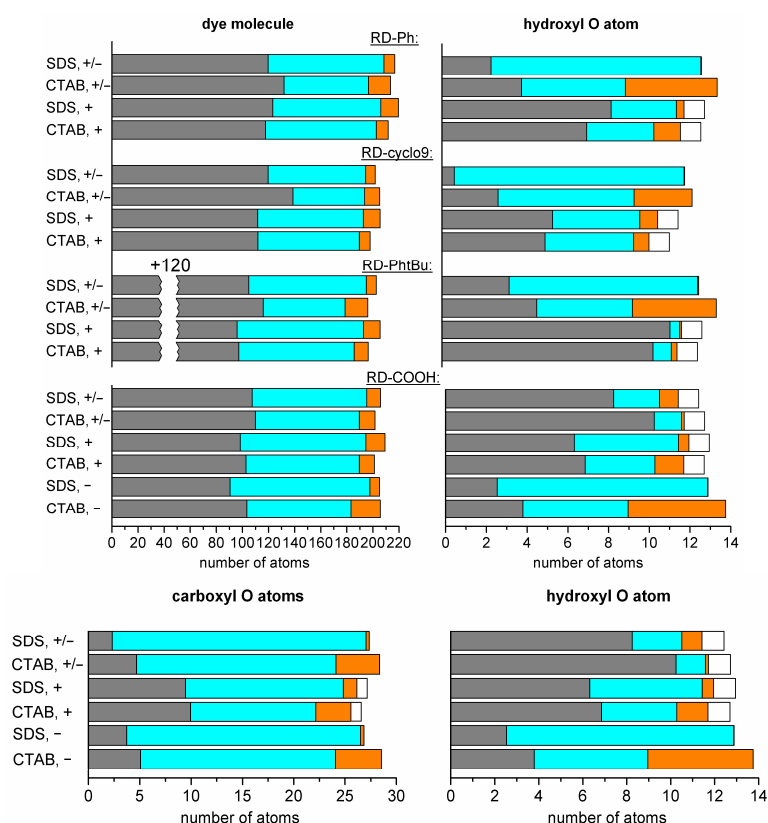
Figure 6. Average numbers of atoms of three categories in the microenvironment of the whole dye molecule and its O atoms. The sections of bars correspond to (left to right): the micelle core atoms (gray), the water atoms (cyan), the headgroup atoms (orange), the covalently bonded H atom (white). The microenvironment of the RD-COOH hydroxyl O atom is shown twice for convenience. The data for RD-Ph are from ref. [9].

Considering the whole molecule, the microenvironment of RD-cyclo9 is similar to that of RD-Ph in all cases. The same is true for RD-PhtBu, except the largely increased amount of hydrocarbon around the molecule that can be attributed to its relatively big size. The oxygen atom of RD-cyclo9 is in all cases better hydrated as compared to RD-Ph. However, the situation is somewhat surprising for RD-PhtBu. In its zwitterionic form, the O atom resides in roughly the same medium as that of RD-Ph, but the protonation leads to complete isolation of water. It can be explained with the fact that the 'inverted' orientation became populated. The negligible water content corresponds to short moments when some exposure to water takes place.

The microenvironment of the whole RD-COOH molecule remains almost constant upon change of the protonation state or the surfactant. Quantitatively, its composition is close to that of the RD-Ph zwitterion in SDS micelles. The carboxylic group is well hydrated in all cases, but protonation heavily decreases its hydration. The hydroxyl group is strongly hydrated only in the anionic form when it is dissociated. In other cases, it is forced to immerse into the micelle core because the carboxylic group, which is located on the opposite side of the molecule, has a tendency to be situated on the micelle surface. This tendency is stronger for the ionized COO⁻ group, thus in this case the OH group becomes almost completely screened from water.

Conclusions

MD simulations of three solvatochromic Reichardt's dyes in micelles of ionic surfactants, namely, sodium *n*-dodecyl sulfate and cetyltrimethylammonuim bromide, were performed. The results show that structural changes actually are able to drastically affect the locus of the dye molecule. The states of RD-cyclo9 and RD-Ph are similar in micelles of both kinds, with hydroxyl group of the former being a little better hydrated.

The state of the zwitterionic form of RD-PhtBu is also similar to that of RD-Ph, but for the latter the orientation along the micelle radius is highly typical besides the orientation parallel to the micelle

surface. Oppositely, in the cationic form of RD-PhtBu, the phenolate part is immersed into the micelle core and completely screened from water.

RD-COOH in all forms can be situated parallel to the micelle surface, but in the cationic and zwitterionic forms, the molecule stays roughly parallel to the micelle radius with the OH group immersed into the micelle and having negligible contact with water.

These observations should be taken into account when using the dyes of this family for examining of surfactant micelles and related colloidal species.
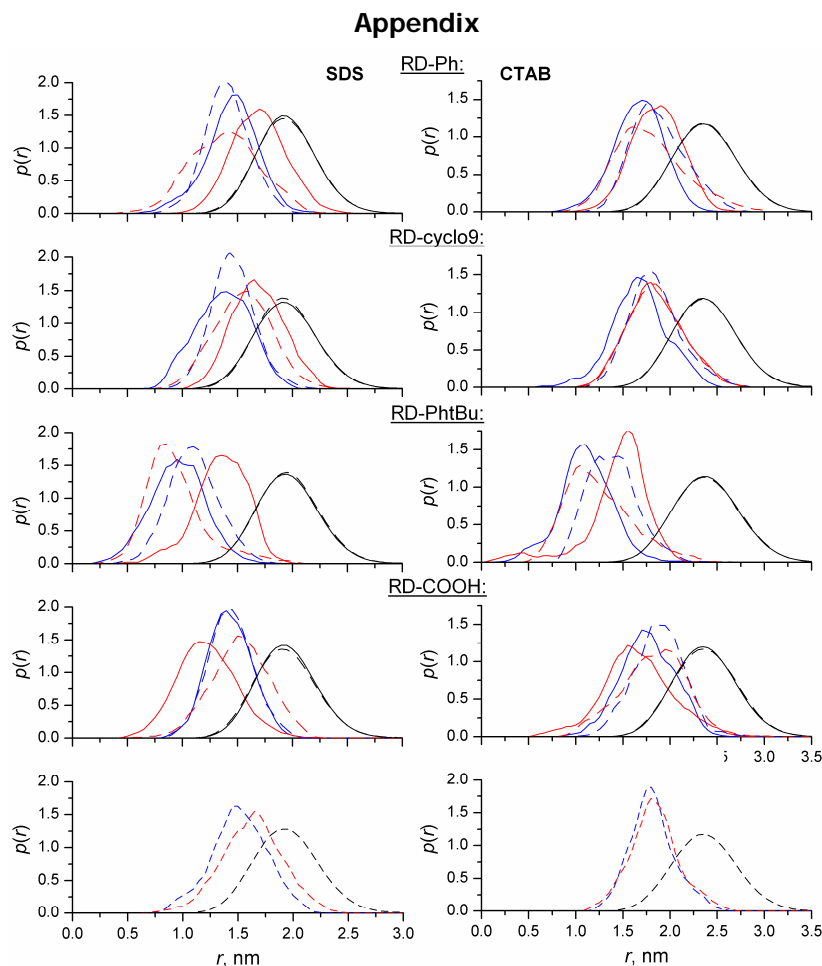
Appendix

Figure A1. Distribution functions of distances micelle COM – N, micelle COM – O, micelle COM – surfactant S (N) for three betaine dyes in SDS (left) and CTAB (right) micelles. Solid curves are for the zwitterionic forms, dashed curves are for the cationic ones. The short-dashed curves in the bottom row are for the anionic form of RD-COOH. The data for RD-Ph are from ref. [9].

Acknowledgements

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В.С. Фарафонов*, А.В. Лебедь*, Н.О. Мчедлов-Петросян*. МД моделирование бетаинов Райхардта в мицеллах ПАВ: Различная ориентация и сольватация катионных, цвиттер-ионных и анионных форм красителей в псевдофазе.

* Харьковский национальный университет имени В.Н. Каразина, химический факультет, площадь Свободы, 4, Харьков, 61022, Украина

Сольватохромные индикаторы ряда пиридиний *N*-фенолятов, также известные как бетаины Райхардта или красители Райхардта, часто используются для изучения не только чистых или смешанных растворителей, но также и разнообразных коллоидных агрегатов, таких как мицеллы поверхностно-активных веществ, капли микроэмульсий и др. Чтобы выявить локализацию этих молекулярных зондов в мицеллярной псевдофазе, мы недавно использовали молекулярно-динамическое (МД) моделирование для стандартного красителя, 4-(2,4,6-трифенилпиридиний-1-ил)-2,6-дифенилфенолята и трех других красителей этого семейства с более высокой и низкой гидрофобностью. В исследовании были рассмотрены как цвиттер-ионные (окрашенные), так и протонированные (катионные, бесцветные) формы, поскольку эти соединения также используются в качестве кислотно-основных индикаторов для мицеллярных систем. В настоящей работе мы продолжили это исследование. МД моделирование было применено для еще трех красителей в мицеллах *н*-додецилсульфата натрия и цетилтриметиламмоний бромида. Были исследованы следующие соединения: (i) самый гидрофобный краситель с пятью трет-бутильными группами, 4-[2,4,6-три(4-трет-бутилфенил)пиридиний-1-ил]-2,6-ди(4-трет-бутилфенил) фенолят, (ii) краситель с углеводородной петлей вокруг атома кислорода, 4-(2,4,6-трифенилпиридиний-1-ил)-*н*- (3,5-нонаметилен)фенолят и (iii) краситель с дополнительной карбоксильной группой, присоединенной к бензольному кольцу, противоположному феноляту, 4-(4-карбоксилатофенил-2,6-дифенилпиридиний-1-ил)-2,6-дифенилфенол. Ориентация и сольватация катионов, цвиттер-ионов (как окрашенных, так и бесцветных) и аниона последнего красителя в мицеллах оказались многообразными, в зависимости от структуры молекул и состояния ионизации. Результаты сравнивались с результатами, полученными ранее для стандартного индикатора. В некоторых случаях наиболее вероятная ориентация красителей в их бесцветной форме противоположна по сравнению со стандартным индикатором Райхардта, т.е. их OH-группа направлена к центру мицеллы.

Ключевые слова: сольватохромизм, полярность, додецилсульфат натрия, бромид цетилтриметиламмония, локализация, ориентация, гидратация, молекулярно-динамическое моделирование.

В.С. Фарафонов*, О.В. Лебідь*, М.О. Мчедлов-Петросян*. МД моделювання бетаїнів Райхардта у міцелах ПАР: Відмінна орієнтація і сольватація катіонних, цвітер-іонних і аніонних форм барвників у псевдофазі.

* Харківський національний університет імені В.Н. Каразіна, хімічний факультет, майдан Свободи, 4, Харків, 61022, Україна

Сольватохромні індикатори ряду піридиній *N*-фенолятів, також відомі як бетаїни Райхардта або барвники Райхардта, часто застосовуються для дослідження не тільки чистих або змішаних розчинників, але також і різноманітних колоїдних агрегатів, таких як міцели поверхнево-активних речовин, краплі мікроемульсій тощо. Щоб виявити локалізацію цих молекулярних зондів у міцелярній псевдофазі, ми нещодавно застосували метод молекулярно-динамічного моделювання для стандартного барвника, 4-(2,4,6-трифенілпіридиній-1-іл)-2,6-дифенілфеноляту та трьох інших барвників цього сімейства з більшою та меншою гідрофобністю. У дослідженні розглянуті як забарвлені, так і протоновані (катіонні, безбарвні) форми, оскільки ці сполуки також використовуються як кислотно-основні індикатори для міцелярних систем. У даній роботі ми продовжили це дослідження. МД моделювання застосоване для ще трьох барвників у міцелах *н*-додецилсульфату натрію і цетилтриметиламоній броміду. Досліджені наступні сполуки: (i) найбільш гідрофобний барвник, що містить п'ять трет-бутильних груп, 4- [2,4,6-три(4-трет-бутилфеніл)піридиній-1-іл]-2,6-ди(4-трет-бутилфеніл) фенолят, (ii) барвник із вуглеводневою петлею навколо атома Оксигену, 4-(2,4,6-трифенілпіридиній-1-іл)-н-(3,5-нонаметилен) фенолят та (iii) барвник із додатковою карбоксильною групою, приєднаною до бензенового кільця навпроти феноляту, 4-(4-карбоксилатфеніл-2,6-дифенілпіридиній-1-іл)-2,6-дифенілфенол. Орієнтація і сольватація катіонів, цвітер-іонів (як забарвлених, так і безбарвних) та аніону останнього барвника в міцелах виявилися різноманітними залежно від молекулярної структури та стану іонізації. Результати порівнювалися з результатами, отриманими раніше для стандартного барвника. У деяких випадках найбільш вірогідна орієнтація барвників у їхніх безбарвних формах протилежна до стандартного барвника Райхардта, тобто їх OH-група спрямована до центру міцели.

Ключові слова: сольватохромізм, полярність, додецилсульфат натрію, бромід цетилтриметиламонію, локалізація, орієнтація, гідратація, молекулярно-динамічне моделювання.

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35