# The effect of the nature of the surfactant on the location of 6-R-2,2,4-trimethyl-1,2-dihydroquinolines in micelles

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The locus of solubilization of 6-R-2,2,4-trimethyl-1,2-dihydroquinoline molecules (R = Me, OEt) in sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) has been determined by comparing the UV spectra of micellar solutions of the dihydroquinolines and their solutions in solvents of various polarities. The parameter $R_{pv}$ (defined as the ratio of the absorbance of the long-wave band maximum to that at the adjacent valley) decreases with an increase in the solvent polarity in the order: *n*-heptane > 2-propanol > ethanol > $H_2O$. In SDS micellar solutions, $R_{pv}$ is close to the corresponding value in water and does not depend on [SDS]. In CTAB micellar solutions, $R_{pv}$ is essentially greater than in water and increases with [CTAB]. Thus, the solubilized dihydroquinoline molecules in SDS micelles reside in the Stern layer, and in CTAB micelles they are located both in the interior of the micelle and in the Stern layer; in this case the micelle packing begins from the core.

**Key words:** 1,2-dihydroquinolines, location in micelle; UV spectra.

When studying the solubilization of substances in micellar solutions, information about location, distribution, and orientation in micelles is of great importance for understanding both the kinetic and equilibrium aspects of the solubilization processes themselves, and the physicochemical behavior of the solubilized species. The lifetime of a solubilized species in micelles is long enough for rapid interchange or distribution between several possible states, although some locations or orientations are preferable.[1]

The issue of the site of the solubilization of aromatic molecules such as benzene and its alkyl derivatives has continued to be in dispute.[2—7] The methods for determining the location of aromatic compounds in micelles have been developed using these systems. For this purpose, the most commonly used methods are NMR[2] and UV spectroscopy.[5—7] In the present work, analysis of the UV spectra has been used to locate dihydroquinolines in micelles of the anionic surfactant, sodium dodecyl sulfate (SDS), and the cationic surfactant, cetyltrimethylammonium bromide (CTAB).[5,7]

## Experimental

2,2,4,6-Tetramethyl-1,2-dihydroquinoline (**1**) (Voikov Chemical Plant) was vacuum sublimed before use; 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline (**2**) was vacuum distilled before use. SDS (Shostka Chemical Plant) was twice recrystallized from ethanol, and CTAB (Serva) was recrystallized from ethanol. To solubilize it, the mixture of dihydroquinoline in the surfactant solution was sonicated for 15 min at 40 °C and then kept at room temperature for 24 h.

UV spectra were obtained with a Beckman 50 DUO spectrophotometer.

## Results and Discussion

The method used by us was proposed by Mukerjee;[5,7] and is based on the fact that the UV-absorbance of the long-wave band of many aromatic compounds depends on the medium polarity. Several parameters have been suggested to characterize this dependence.[5,7] From the practical point of view, the most convenient polarity-sensitive parameter is $R_{pv}$, defined as the ratio of $a_p/a_v$, where $a_p$ is the absorption in a long-wave maximum, and $a_v$ is the absorption in an adjacent valley. To evaluate the polarity of the microenvironment of a solubilized molecule the dependence of $R_{pv}$ for a given substance is plotted *vs* the dielectric constant (*D*) of the known solvents (usually, water, methanol, ethanol, 2-propanol, *n*-heptane). Then the value of $R_{pv}$ in the micellar solution is determined and the average polarity of the microenvironment of the given substance in the micelles is evaluated from the calibration curve.

The results of spectral measurments of dihydroquinolines in solvents of different polarities and in micellar solutions are presented in Table 1. It is worth noting that the absorption spectra of the dihydroquinolines under study correspond to the spectra of the neutral form in solutions of both surfactants and in water. The

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**Table 1.** $\lambda_{max}$ and $R_{pv}$ for dihydroquinolines **1** and **2** in homogeneous solutions as a function of dielectric constant ($D$) and in micellar solutions as a function of surfactant concentration ([S])

| Solvent | $D$ | $[S]\cdot10^2$ /mol $L^{-1}$ **1** | **2** | | | |
|---|---|---|---|---|---|---|
| | | | $\lambda_{max}$/nm | $R_{pv}$ | $\lambda_{max}$/nm | $R_{pv}$ |
| *n*-Heptane | 1.9 | | 348 | 10 | 360 | 11.7 |
| 2-Propanol | 18.3 | | 349 | 7 | 360 | 8.5 |
| EtOH (95 %) | 26.3 | | 348 | 4.7 | 359 | 5.3 |
| 2-Propanol —$H_2O$ (1:3) | 64.1 | | 334 | 3.8 | | |
| $H_2O$ | 78.5 | | 333 | 2.8 | 345 | 2.9 |
| CTAB | | 1.1 | $353^a$ | 4.0 | $363^c$ | 4.5 |
| CTAB | | 0.55 | $353^a$ | 3.4 | $362^c$ | 3.5 |
| CTAB | | 0.44 | $351^a$ | 3.3 | $361^c$ | 3.6 |
| CTAB | | 0.33 | $351^a$ | 3.6 | $361^c$ | 3.5 |
| CTAB | | 0.22 | $347^a$ | 3.3 | $357^c$ | 3.5 |
| SDS | | 10 | $337^b$ | 2.9 | $350^d$ | 2.4 |
| SDS | | 5 | $337^b$ | 3.0 | $350^d$ | 2.5 |
| SDS | | 4 | $337^b$ | — | $350^d$ | 2.7 |
| SDS | | 3 | $337^b$ | 2.7 | $350^d$ | 2.6 |
| SDS | | 2 | $337^b$ | 2.8 | $350^d$ | 3.0 |

[a] [**1**] = $2.35\cdot10^{-4}$ mol $L^{-1}$; [b] [**1**] = $2.30\cdot10^{-4}$ mol $L^{-1}$; [c] [**2**] = $3.10\cdot10^{-4}$ mol $L^{-1}$; [d] [**2**] = $2.84\cdot10^{-4}$ mol $L^{-1}$.

absorption due to the cation in the region of about 300 nm is absent. Both the position of the absorption peak and $R_{pv}$ depend on the solvent and the nature of the surfactant. In water and SDS micelles, $\lambda_{max}$ is shifted in comparison with solutions of **1** and **2** in heptane, alcohols, and CTAB. An analogous shift has been also observed earlier for benzene.[7] However, the longer hydrocarbon chain in CTAB in comparison with SDS, and the presence of a polar group in CTAB lead to an overall shift for benzene of $\Delta\lambda_{max} \leq 1$ nm. In the case of dihydroquinolines this shift is of about 15 nm (see Table 1). This difference is associated with the ability of **1** and **2** to form hydrogen bonds with water. The proximity of the absorption maximum in water and in SDS, on the one hand, and in heptane and CTAB, on the other hand, indicates that dihydroquinoline molecules form hydrogen bonds with $H_2O$ in SDS micelles.

The experimental results on the dependence of the parameter $R_{pv}$ on the medium polarity are presented in Fig. 1 and Table 1. The dependences of $R_{pv}$ on $D$ of compounds **1** and **2** have breaks, unlike those of benzene and its derivatives for which this dependence is close to linear. This break corresponds to the transition from water-free solvents to mixtures that contain water.

The experimental values of $R_{pv}$ and $\lambda_{max}$ in SDS solutions do not depend on the surfactant concentration. In this case, $R_{pv}$ is practically equal to $R_{pv}$ in water, and $\lambda_{max}$ in the SDS solution is 5 nm higher than in water. This implies that the polarity of the microenvironment of solubilized molecules in SDS is only a little different from that in water. Nevertheless, some increase in $\lambda_{max}$ in micellar solutions seems to indicate that the orientation of dihydroquinoline molecules **1** and **2** in SDS is such that the contribution of hydrogen bonds to the position of the absorption band decreases. Based on these data it may be concluded that in SDS solutions the molecules of **1** and **2** are located preferably in the Stern layer. The observed decrease in $R_{pv}$ for compound **2** with the increase in [SDS] is due to its instability in water and dimerization. After 24 h exposure of **2**, prod-

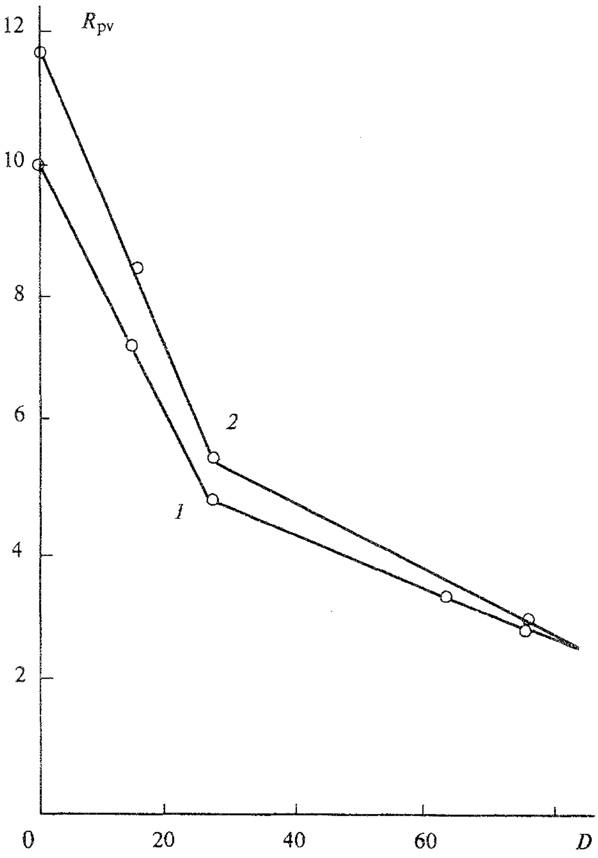

**Fig. 1.** Dependence of $R_{pv}$ on the dielectric constant ($D$) of the solvent for compounds **1** (*1*) and **2** (*2*).

ucts that absorb in a valley adjacent to $\lambda_{max}$ are formed. As can be seen from Table 1, the rate of this reaction increases with the increase in [SDS], which is characteristic of micellar catalysis. It can be noted that in freshly prepared solutions $R_{pv}$ does not depend on [SDS] and is close to the corresponding value in water. However, one cannot be sure that in these solutions the equilibrium distribution of the solubilized molecules is established.

The dependence of both $\lambda_{max}$ and $R_{pv}$ on [CTAB] is observed in CTAB solutions, namely, when the surfactant concentration decreases (that is, as the filling of the micelles with the solubilizate increases), the absorption band shifts to short waves and $\lambda_{max}$ is considerably higher than in water. When [CTAB] decreases, $R_{pv}$ decreases from a value close to $R_{pv}$ in ethanol (when [CTAB] = $1.1 \cdot 10^{-2}$ mol $L^{-1}$) to a value somewhat smaller than that in a 2-propanol—water mixture (see Table 1). Thus, the average polarity of the microenvironment in CTAB solutions increases as the concentration of dihydroquinolines in the micelles increases. It is worth noting, that in the solubilization of **1** and **2** in CTAB micelles the $R_{pv}$ values are close to those in aqueous solutions of alcohols, and $\lambda_{max}$ are close to the corresponding values in water-free organic solvents.

These results can be interpreted by assuming that the solubilized molecules have two preferential locations: inside the micelle and on the micelle-water interface. The observed $R_{pv}$ and $\lambda_{max}$ are averaged over these two positions. In this case, the filling of the CTAB micelles starts from the core. Unlike dihydroquinolines, benzene and its homologs at low concentrations are located on the interface of the CTAB micelles and penetrate inside the micelles as their concentrations increase. In SDS, the filling of micelles begins from the core.[2,3]

Thus, the results obtained demonstrate not only the effect of the nature of surfactant on the location of dihydroquinoline molecules in micelles, but confirm the known fact that different solubilized species may have different locations and orientations in micelles.

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# Rearrangement of *O*-perfluoroisobutenylacetone oxime. The structure of 2,2-bis(trifluoromethyl)-5-methyl-$\Delta^4$-pyrrolin-3-one

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Dehydrofluorination of *O*-(β-hydroperfluoroisobutyl)acetone oxime affords 2,2-bis(trifluoromethyl)-5-methyl-$\Delta^4$-pyrrolin-3-one; the molecular structure of the latter was unambiguously established by X-ray diffraction method.

**Key words:** *O*-perfluoroisobutenylacetone oxime, rearrangement; 2,2-bis(trifluoromethyl)-5-methyl-$\Delta^4$-pyrrolin-3-one, the X-ray crystal structure.

Previously,[1] after dehydrofluorination of *O*-(β-hydroperfluoroisobutyl)acetone oxime (**1**), a crystalline compound (m.p. 139—140 °C) was isolated, to which the structure of 3,3-bis(trifluoromethyl)-5-methyl-$\Delta^4$-pyrrolin-2-one (**2**) was assigned. It is the author's opinion that unstable *O*-perfluoroisobutenylacetone oxime (**3**)

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