INVESTIGATIONS OF SPECTRAL AND LUMINESCENT PROPERTIES OF NEUTRAL AND IONIC PHENOL AND *PARA*-CHLOROPHENOL FORMS IN AQUEOUS MICELLAR SOLUTIONS

O. N. Tchaikovskaya and I. A. Mikhaleva   UDC 535.37

Special features of the absorption and fluorescence spectra of phenols (phenol and para-chlorophenol) in alkalized and acidified aqueous-micellar solutions are studied. It is established that the absorption band of the anionic phenol form is formed in aqueous-alkali media in the presence of ionogenic surfactants. The fluorescence intensity of the anionic phenol form solubilized in micelles is higher than that in water.

INTRODUCTION

Considerable progress has been made in spectroscopy in the field of theoretical and experimental studies of the influence of intermolecular interactions on optical spectra of molecules [1]. This creates the necessary prerequisites for a more profound understanding of mechanisms of forming spectroscopic characteristics of molecules and molecular complexes in a condensed medium. Since phenol is included in functional groups of many biological systems, it is of interest to study its behavior in structurized media, for instance, in micellar solutions. The urgency of studying the behavior of organic molecules in micellar surfactant solutions is explained by their wide practical application, for example, in detergent production, information recording, modeling of photoprocesses in biological membranes and other biological systems, and increasing the efficiency of photochemical reactions to solve the problem of solar-to-chemical energy conversion [2]. Most often, micellar surfactant solutions are used as a reaction medium and influence significantly the state and physical properties of aqueous and non-aqueous organic reagents thereby causing significant changes in the rate and mechanism of processes occurring in them [3, 4]. Spectral and luminescent characteristics of phenol dissolved in water or binary solvents were studied in [6-8]. In the present work, we investigate the spectral and luminescent characteristics of neutral and ionic phenol and *para*-chlorophenol forms in micellar media.

1. METHODS OF INVESTIGATION

The spectral and luminescent properties of neutral and ionic phenol forms (phenol and *para*-chlorophenol) with concentrations of $5 \cdot 10^{-5}$ M in aqueous-micellar solutions were studied on addition of NaOH (10^{-6}–10^{-1} M) and H_2SO_4 ($7.2 \cdot 10^{-6}$–10^{-2} M). The limiting alkali and acid concentrations were chosen from the following considerations: for the examined NaOH concentrations, transition to the anionic phenol form in water was observed; such acid additions did not change the micelle structure. Deoxidation of working solutions was not required. For different surfactants to be used above the critical concentration of micellization we have chosen sodium dodecylsulfate (SDS) for an anionic reagent, N-cetyl-trimethyl ammonium bromide (CTAB) for a cationic reagent, and polyoxyethylene isooctyl phenol (triton X100 produced by the Loba Chemie Corp.) for a non-ionogenic reagent with concentrations exceeding the critical concentration of micellization. The electronic absorption and fluorescence spectra were routinely recorded with a Specord M40 spectrophotometer and a Hitachi M850 spectrofluorimeter. The pH values of the medium were measured with a pH-673

TABLE 1. Spectral and Luminescent Characteristics of the Neutral Phenol Form

Solvent	λ_{abs}^{max}, nm	$\Delta\nu_{1/2}$, cm^{-1}	ε_{max}, l/M·cm	f	$\tau_0 \cdot 10^8$, s	λ_{fl}^{max}, nm	φ_{fl}
Water	270	3000	1600	0.02	5.6	296	0.22
Water + SDS	271	3200	1630	0.022	5	296	0.16
Water + CTAB	275	3100	2020	0.027	4.2	300	0.21
Water + triton X100	280	3300	2142	0.03	3.8	305	0.026

Note. Here λ_{abs}^{max} specifies the wavelength of the absorption band maximum, $\Delta\nu_{1/2}$ is the absorption band half-width, ε_{max} is the extinction coefficient at the wavelength of the absorption band maximum, f stands for the oscillator force, τ_0 is the emission lifetime, λ_{fl}^{max} specifies the wavelength of the fluorescence band maximum, and φ_{fl} is the fluorescence quantum yield under excitation to the absorption band maximum (270 nm).
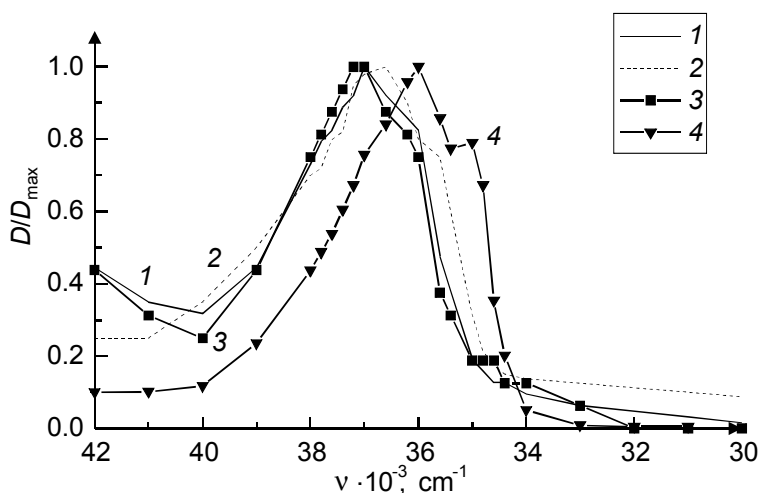

Fig. 1. Absorption spectra of phenol in water (*1*), CTAB (*2*), SDS (*3*), and triton X100 (*4*).

meter [5]. Fluorescence quantum yields were determined from relative measurements [5]. The phenol fluorescence quantum yield in water ($\varphi = 0.22$) was used as a reference one [5]. To calculate the fluorescence quantum yield, we calculated the concentration so that the optical density of the solution equaled 0.1 at the fluorescence excitation wavelength.

Methods of fluorescence analysis, in particular, based on measurements of fluorescence quenching were used to determine the reagent-micelle coupling constants [9]. The fluorescence quenching constants for the examined molecules were calculated based on the Stern–Volmer dependence [5].

2. DISCUSSION OF RESULTS

In the ground electronic state, the acid-alkali balance of phenols is determined by the quantity $pK_a \sim 10$. Therefore, in aqueous solutions at pH ~ 6.5, these compounds are almost completely in the non-dissociated form. Like in water, the long-wavelength phenol absorption band in the micellar media under study is structurized (Fig. 1). As follows from the quantum-chemical calculations done in [7], a reason for the absorption in this wavelength range is the $S_0 \rightarrow S_1$ $\pi\pi^*$-type electronic transition; therefore, the observed band structure is in fact a manifestation of its vibrational structure. The experiments and quantum-chemical calculations suggest that for the hydroxyl-containing solvents, the long-wavelength band is a superposition of the absorption spectra of phenol molecules bound both by oxygen and hydrogen of the OH phenol group with solvent molecules [10]. The absorption band profiles of phenol in water and in the aqueous-micellar anionic surfactant solution coincide (Fig. 1). Their absorptivities are almost the same (Table 1). Such behavior is probably due to

TABLE 2. Position of Vibronic Bands in the Absorption Spectra of Phenol in Different Solvents
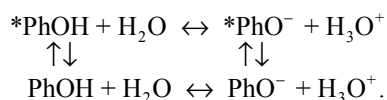
Solvent	$S_0 \rightarrow S_1$ transition, cm^{-1}		
	ν_1	ν_2	ν_3
Water	38310	37590	36630
Hexane + ethanol [10]	37590	36630	35650
Ethanol + acetone [10]	38168	37037	36100
Water + SDS	38200	37200	36300
Water + CTAB	37700	36500	35700
Water + triton X100	37000	36000	35000

TABLE 3. Spectral and Luminescent Characteristics of the Neutral *Para*-Chlorophenol Form

Solvent	λ_{abs}^{max}, nm	λ_{fl}^{max}, nm	φ_{fl}
Water	280	305	0.06
Water +SDS	283	310	0.1
Water + CTAB	275	315	0.07
Water + triton X100	285	305	0.012

the fact that phenol in these systems has similar surroundings. From Fig. 1 (curve *3*) we can see that the spectra differ in the range 33,000–35,000 cm^{-1}. A special feature of the spectrum in the SDS aqueous-micellar solution is indicative of the fact that a number of molecules can be in the dissociated form. Thus, SDS micelles facilitate the formation of anion phenolates in the ground state. The shift of the phenol absorption band maximum in the triton X100 aqueous-micellar solution relative to that in the water solution is indicative of the fact that the phenol molecule has different surroundings. In [10], a similar absorption band was registered (see Table 2) for the hexane + ethanol mixture, when the phenol molecule was mostly in nonpolar surroundings. The absorption band profile of phenol in the CTAB solution is closest to the phenol spectrum in the ethanol + acetone mixture, when the phenol molecule exhibits both donor and acceptor properties. This situation arises when phenol forms a complex with two solvent molecules. Unlike phenol, the long-wavelength absorption band of *para*-chlorophenol in micellar media is smoothed. Therefore, any conclusions on the molecule surroundings from the spectra are impossible. Phenols in aqueous solutions in the presence of the triton X100 micellar phase cause the neutral form fluorescence quantum yield to decrease by an order of magnitude (Tables 1 and 3). A reason for the low *para*-chlorophenol fluorescence quantum yield is that the intercombination conversion is the dominating deactivation channel for the first excited singlet state [3]. We assume that this channel also remains the main deactivation channel for the *para*-chlorophenol fluorescent state in aqueous-micellar solutions.

Phenols in the ground state are weak acids. Their acidity increases with the pH value under excitation to the singlet state, thereby causing dissociation in aqueous solutions, which in its turn produces excited phenolate ions:

$$\begin{array}{ccc} *PhOH + H_2O & \leftrightarrow & *PhO^- + H_3O^+ \\ \updownarrow & & \updownarrow \\ PhOH + H_2O & \leftrightarrow & PhO^- + H_3O^+. \end{array}$$

Generally, a similar reaction scheme is expected to take place in the micellar phase. In this case, an exchange by molecules of different types, including excited ones, is possible between the two phases. On addition of alkali, the absorption spectra of phenol in the SDS aqueous-micellar solutions pass through the isobath point, which points to the PhOH $\leftrightarrow$ PhO$^-$ balance in the ground state. Moreover, compared to the aqueous solutions, transition to the anionic form starts at a higher NaOH concentration. The same situation takes place with *para*-chlorophenol (Fig. 2). In the CTAB aqueous-alkali solutions, the frequency of the absorption maximum for the anionic phenol form is shifted toward lower frequencies as compared to its absorption in SDS solutions and in water (Table 4). For excited solutions, we detected fluorescence of only non-dissociated phenol form (Table 4). In the presence of micelles of the cationic surfactant (Fig. 3),

TABLE 4. Wavelengths of Absorption and Fluorescence Band Maxima of the Neutral and Ionic Phenol Forms

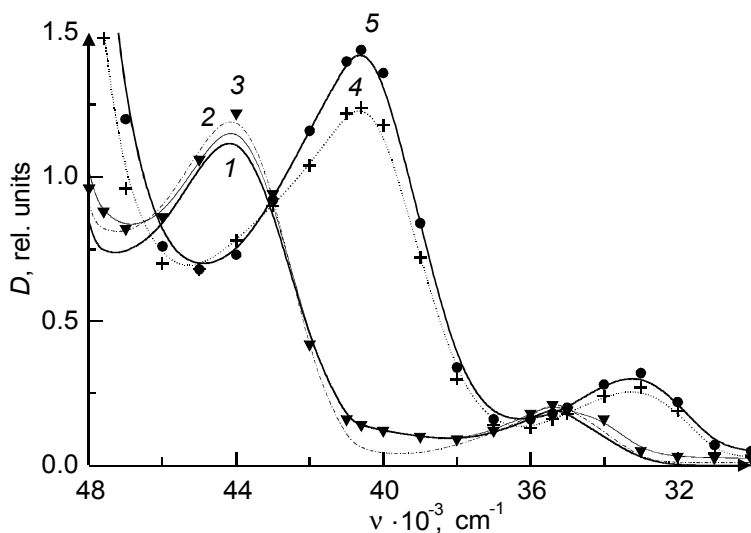| Solvent	Anionic form		Neutral form
	λ_{abs}^{max}, nm	λ_{fl}^{max}, nm	λ_{fl}^{max}, nm
Water + 5·10^{-2} M NaOH	287	340	–
Water + SDS + 5·10^{-2} M NaOH	287	–	300
Water + CTAB + 5·10^{-2} M NaOH	292	340	–
Water + triton X100 + 5·10^{-2} M NaOH	292	Special feature at $\lambda = 340$ nm	300

Fig. 2. Absorption spectrum of *para*-chlorophenol in the SDS aqueous-micellar solution on addition of alkali with concentrations of 0 (*1*), 10^{-5} (*2*), 10^{-4} (*3*), 5·10^{-3} (*4*), and 10^{-2} M (*5*).

transition of phenols to the anionic form in both ground and excited states occurs at lower alkali concentrations in comparison with aqueous solutions. The anionic emission band in the CTAB aqueous-alkali solutions is detected already at NaOH concentrations of 5·10^{-4} M for phenol and 10^{-3} M for *para*-chlorophenol (Fig. 3*b* and Table 5). The low fluorescence quantum yield of the anionic phenol forms and the absence of the isobath point in the fluorescence spectra did not allow us to evaluate quantitatively the acid-alkali balance in the excited state and to determine the *pK$_a$** value for the dissociation reaction [10]. For phenols, the bimolecular constant of interaction with the alkali (Table 6) in the system with CTAB is larger than that in water. This proves again the fact that transition to the anionic form in the ground and excited states in the presence of the CTAB micelles occurs at lower alkali concentrations, while the fluorescence intensity of anionic forms is higher than of aqueous solutions [6]. The Stern–Volmer dependence for phenols in water and aqueous-micellar solutions on addition of alkali is nonlinear in character. It is commonly assumed that in this case, the fluorescence is quenched due to both diffusion collisions and formation of complexes with solvent molecules. The broadening of the fluorescence band of the neutral *para*-chlorophenol form in the triton X100 aqueous solutions is observed together with its shift toward longer wavelengths without changes in its intensity (Fig. 5) as the alkali concentration increases. With increasing pH value, no anionic phenol forms were observed in the fluorescence spectra of the media with triton X100.

The analysis of the absorption and fluorescence spectra of phenols in the acidified micellar media demonstrated that there is hardly any acid influence as compared to the alkali. The interaction of phenols with the acid is much weaker than that with the alkali (Table 6). At surfactant concentrations above the critical micellization level, no quenching of *para*-chlorophenol fluorescence in acidified solutions was observed in comparison with aqueous solutions. It then follows that most *para*-chlorophenol molecules are solubilized by micelles and are therefore inaccessible to the molecules of additives.

TABLE 5. Absorption and Fluorescence Band Maxima of the Neutral and Ionic *para*-Chlorophenol Forms

Solvent	Anionic form		Neutral form
	λ_{abs}^{max}, nm	λ_{fl}^{max}, nm	λ_{fl}^{max}, nm
Water + $5 \cdot 10^{-2}$ M NaOH	300	355	–
Water + SDS + $5 \cdot 10^{-2}$ M NaOH	301	355	–
Water + CTAB + $5 \cdot 10^{-2}$ M NaOH	301	350	–
Water + triton X100 + $5 \cdot 10^{-2}$ M NaOH	303	–	310

TABLE 6. The Stern–Volmer Constant of Phenol Fluorescence Quenching by the Alkali and Acid, M^{-1}

Solvent	Alkali	Acid
	Phenol	
Water	$1.6 \cdot 10^3$	2.3
Water + SDS	$7 \cdot 10^2$	0.6
Water + CTAB	$8.4 \cdot 10^3$	0.9
Water + triton X100	32	No quenching
	Para-chlorophenol	
Water	$4.7 \cdot 10^3$	0.5
Water + SDS	$1.5 \cdot 10^2$	Fluorescence buildup
Water + CTAB	$8 \cdot 10^3$	Fluorescence buildup
Water + triton X100	No quenching	Fluorescence buildup
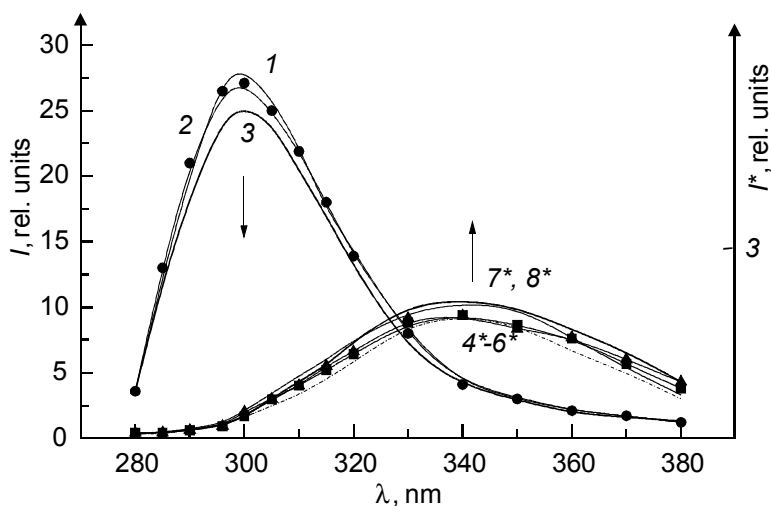
Fig. 3. Fluorescence spectra of phenol in the CTAB aqueous-micellar solution on addition of alkali with concentrations of 0 (*1*), $5 \cdot 10^{-5}$ (*2*), 10^{-4} (*3*), $5 \cdot 10^{-4}$ (*4**), 10^{-3} (*5**), $5 \cdot 10^{-3}$ (*6**), 10^{-2} (*7**), and $5 \cdot 10^{-2}$ M (*8**).

Thus, from the results presented here it follows that the use of micellar media has allowed us to change the chemical reactivity of phenols in comparison with aqueous media. The interaction of phenol and *para*-chlorophenol with the alkali in aqueous-micellar solutions that characterizes the donor molecular properties turned out to be stronger than the interaction with the acid. In the anionic form, phenols in the ground and excited states are observed in aqueous-alkali solutions in the presence of the cationic surfactant.
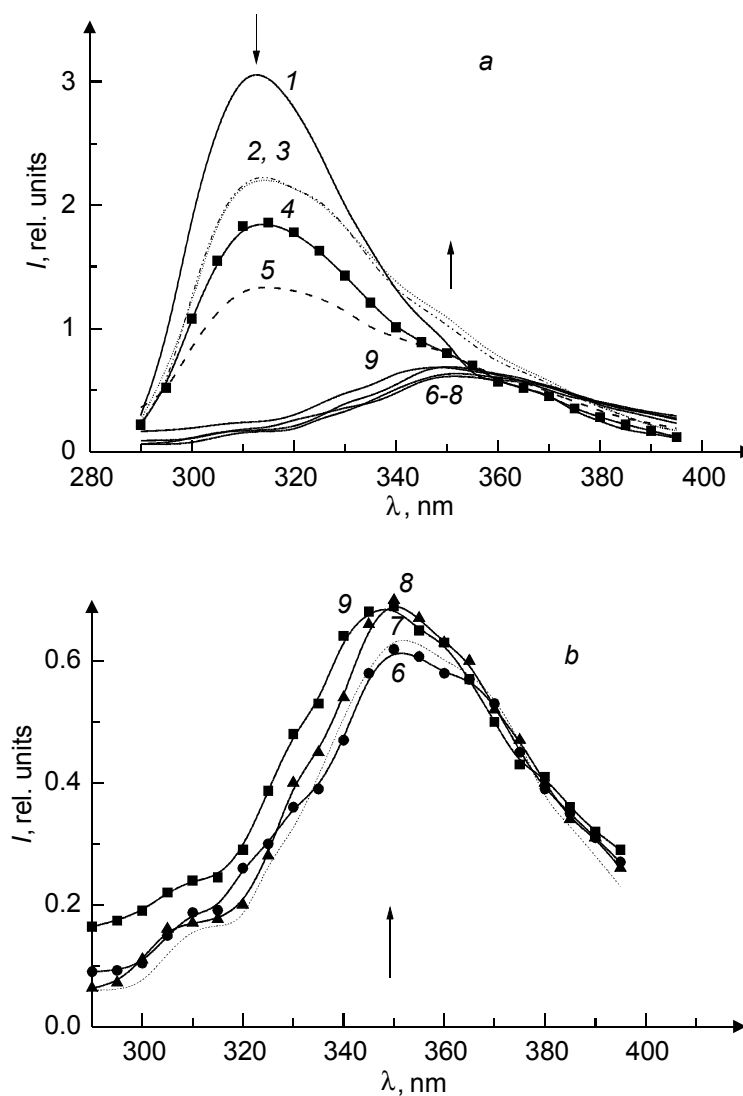
Fig. 4. Fluorescence spectra of *para*-chlorophenol in the SDS aqueous-micellar solution on addition of alkali with concentrations of 0 (*1*), 10^{-5} (*2*), $5 \cdot 10^{-5}$ (*3*), 10^{-4} (*4*), $5 \cdot 10^{-4}$ (*5*), 10^{-3} (*6*), $5 \cdot 10^{-3}$ (*7*), 10^{-2} (*8*), and $5 \cdot 10^{-2}$ M (*9*).

REFERENCES

1. B. Valeur, Molecular Fluorescence, WALEY-VCH GmbH, Weinheim (2002).
2. M. K. Kadirov and E. S. Nefedyev, Izv. Ross. Akad. Nauk, Ser. Khim, No. 5, 1055 (2003).
3. G. V. Melnikov and A. V. Kosarev, Zh. Prikl. Spektrosk., **69**, Nos. 1–2, 32 (2002).
4. K. L. Mittal, ed., Micellization, Solubilization, and Microemulsions, Plenum Press, New York and London (1976).
5. J. R. Lakowicz, Principles of Fluorescence Spectroscopy, Kluwer Academic Plenum Publishers, New York (1999).
6. O. N. Tchaikovskaya, R. T. Kuznetsova, I. V. Sokolova, and N. B. Sultimova, Zh. Fiz. Khim., **74**, No. 10, 1806 (2000).
7. O. K. Bazyl, V. Ya. Artyukhov, G. V. Mayer, and I. V. Sokolova, Khim. Vys. Energ. **34**, No. 1, 35 (2000).
8. Shi Zhou, M. E. Sigman, M. M. Ghosh, and R. Dabestani, Envir. Sci. Technol., **31**, 3581 (1997).

9. V. A. Ponomareva and E. E. Zaev, Zh. Prikl. Spektrosk., **33**, 448 (1980).
10. Yu. P. Morozova, O. N. Chaikovskaya, and O. K. Bazyl, Izv. Vyssh. Uchebn. Zaved., Fiz., No. 1 (2003).
11. N. Lasser and J. Feitelson, J. Phys. Chem., **79**, No. 14, 1344 (1975).