

# Medium influence on spectral characteristics of 1-naphthol

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The rate constants of the internal, radiative, and intercombination conversion, as well as photoprotonation centers, in the 1-naphthol molecule were estimated through quantum-chemical calculation by the PNDO (partial neglect of differential overlap) method. It has been found that besides the processes of quenching due to intercombination conversion, the possibility of protonation of the molecule in the excited state should be taken into account. Protonation centers for the neutral and anion forms of 1-naphthol were determined. Possible values of the acidity constant of the 1-naphthol molecule in the excited state ( $pK^*$ ) range from 0.4 to 2.8.

## Introduction

Protection of environment and arrangement of conditions for its improvement in the ecologically optimal way are among the most important current problems. The environmental protection assumes continuous analytical monitoring of various objects including waters of different genesis, air masses, soils, plants, and biological objects.

Aromatic compounds such as benzol, phenol, their derivatives, benzoic acids, and naphthols fall in the category of widespread, highly toxic environmental pollutants. The toxicity of aromatic compounds is high; they contribute to depletion of the atmospheric ozone layer and kill microorganisms in biological sewage disposal plants. Aromatic compounds are contained in oil and shale oil cracking products and are used in production of phenolformaldehyde resins, caprolactam, numerous dyes and medicines, in pulp and paper industry, food industry, as well as pesticide and plastic production. The amount of anthropogenic toxicants that are annually discharged into water bodies and emitted into the atmosphere is as high as 10–11 billion ton [Ref. 1].

Undoubtedly, phenol is the most thoroughly studied aromatic compound.<sup>2</sup> However, an adverse effect on the environment of other compounds also should be remembered. This paper describes the results of spectral studies of 1-naphthol (phenol of the naphthalene series) in water and binary mixtures of water with triethylamine, ethanol, and potassium oxide hydrate. The additives were used to change the basic properties of water. Naphthols, characterized by significant toxicity, are contained in smoke and water.<sup>3</sup> Besides, naphthols occupy an intermediate position in the series of easily oxidizable ("biologically soft") substances after phenols and alcohols.<sup>3</sup> For analytical monitoring of environmental objects, it is necessary to know some physical, in particular, spectral properties of the monitored substances.

In this paper we study photoprocesses in the 1-naphthol molecule with the use of electronic

absorption spectra, emission spectra, and quantum-chemical calculation.

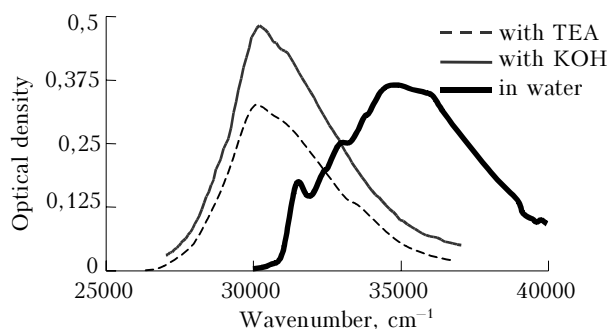
The electronic absorption spectra of 1-naphthole were recorded with an automated instrument based on the SF-26 spectrophotometer. The fluorescence spectra were recorded using the SDL-2 system. The DDS 30 (deuterium) and H1 (halogen) lamps served the sources of excitation. The spectral sensitivity of the spectrofluorimeter was taken into account in the fluorescence spectra. The following concentrations of 1-naphthol were used:  $7 \cdot 10^{-4}$ ,  $7 \cdot 10^{-5}$ ,  $7 \cdot 10^{-6}$  M. The quantum-chemical calculation was performed by the PNDO (partial neglect of differential overlap) method with the spectroscopic parameterization. The program involved the MEP (molecular electrostatic potential) method. This method is especially efficient in analysis of the protonation reaction and formation of hydrogen bonds.<sup>4</sup>

The acidity constants of the 1-naphthol molecule in the ground and excited states differ widely. Analysis of the data from Refs. 5–11 shows that the acidity constant in the ground state ( $pK$ ) for 1-naphthol in water is 9.23, while in the excited state ( $pK^*$ ) it ranges from 2.8 to 0.4, which is likely caused by the complicated procedure of determining the peak of the absorption band for the neutral form. Therefore, it seems important to consider the absorption band corresponding to the anion ( $RO^-$ ) and neutral ( $ROH$ ) forms of the 1-naphthol.

The absorption band of 1-naphthol in water (Fig. 1) in the region of 30 000–40 000  $cm^{-1}$  is wide with a broaden peak nearby 35 000  $cm^{-1}$ .

The shortwave band of 1-naphthol (40 000–50 000  $cm^{-1}$ ) is characterized by the molar decimal absorption coefficient much higher than that in the longwave band peaking nearby 46 000  $cm^{-1}$ . The quantum-chemical calculation has yielded the spectrum of singlet states of the molecule under study (Table 1). Based on the values of the oscillator strength  $f$ , we can separate four allowed transitions:  $S_1$ ,  $S_2$ ,  $S_7$ , and  $S_8$ . The first three states are of the  $\pi\pi^*$ -type, while the last is a mixture of  $\pi\pi^*$  and  $\sigma\sigma^*$  types. The absorption spectrum in the region of

28 000–40 000  $\text{cm}^{-1}$  is due to two electronic  $\pi\pi^*$  transitions.



**Fig. 1.** Absorption spectrum of 1-naphthol in water, water + KOH (KOH concentration of  $3.57 \cdot 10^{-3}$  M), and water + TEA (TEA concentration of  $0.48 \cdot 10^{-3}$  M); the 1-naphthol concentration is  $7 \cdot 10^{-5}$  M.

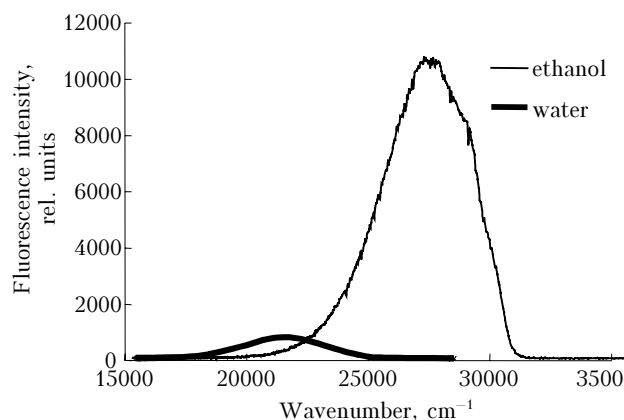
From the absorption spectra of 1-naphthol in the water + KOH and water + TEA (triethylamine) solutions (Fig. 1) it follows that about 80% of 1-naphthol transit into the  $\text{RO}^-$  form. The both forms absorb in the region of 32 000–35 000  $\text{cm}^{-1}$ . The molar decimal absorption coefficient of the anion form is roughly twice as large as that of the neutral form. For the anion form of 1-naphthol, the calculated spectrum of singlet states is also in agreement with the experimental results (Table 1).

Knowing the positions of the absorption bands of the  $\text{RO}^-$  and  $\text{ROH}$  forms of 1-naphthol in water, we can judge the value of the acidity constant in the excited state. The band belonging to the  $\text{RO}^-$  form has a pronounced peak at 30 170  $\text{cm}^{-1}$ . The band corresponding to the  $\text{ROH}$  form is complex, and  $\text{pK}^*$  depends on the position taken for the calculation. Using the Forster cycle, we have estimated the acidity constant  $\text{pK}^*$  from the absorption frequencies; the resulting values are 0.4, 1.4, 2, 2.3, 2.5, and 2.8. The first three values are obtained from the first absorption band, while others are taken from the second band; therefore,  $\text{pK}^*$  of 1-naphthol should be thought ranging from 0.4 to 2.

Consider peculiarities of the fluorescence spectrum of 1-naphthol in water. The excitation wavelength corresponded to the  $\text{ROH}$  form, but fluorescence was observed only from the  $\text{RO}^-$  form.

As rather high concentrations of the base and TEA were added to water, the peak of the recorded fluorescence spectrum coincided with the peak of the fluorescence band of 1-naphthol in water (21 740  $\text{cm}^{-1}$ ), that is, 1-naphthol in water exists in the  $\text{RO}^-$  form.

The fluorescence spectra of 1-naphthol in ethanol, obtained at the excitation wavelength corresponding to the neutral form, have a peak nearby  $\sim 27 770$   $\text{cm}^{-1}$ , that is, at shorter wavelengths than in water (Fig. 2). The difference between the peak positions in the spectrum of 1-naphthol in water and ethanol is  $\sim 5 730$   $\text{cm}^{-1}$ , and the Stokes shift is 8 250  $\text{cm}^{-1}$  for the  $\text{RO}^-$  form and 4 480  $\text{cm}^{-1}$  for the  $\text{ROH}$  form.



**Fig. 2.** Fluorescence spectrum of 1-naphthol in water and ethanol; 1-naphthol concentration of  $7 \cdot 10^{-4}$  M, excitation wavelength of 290 nm.

Thus, if the absorption spectrum includes two bands corresponding to the anion and neutral forms, then the fluorescence spectrum is formed by only one band with the peak position remaining unchanged for 1-naphthol both in water and in water with additions of the base or TEA.

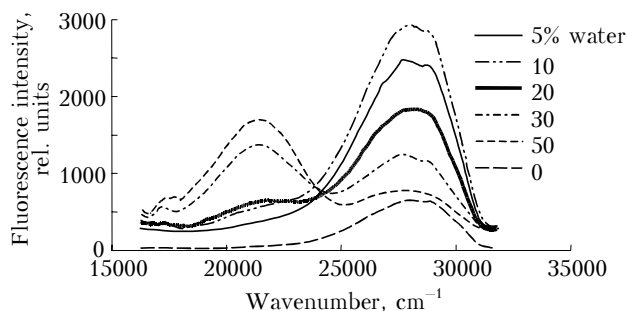
The manifestation of the acid-base balance of 1-naphthol  $\leftrightarrow$  1-naphtholat has been studied in fluorescence spectra in the water–ethanol and ethanol–water binary solutions.

Consider the ethanol–water mixtures. Adding different concentrations of water into the solution of 1-naphthol in ethanol results in gradual transition into the  $\text{RO}^-$  form (Fig. 3).

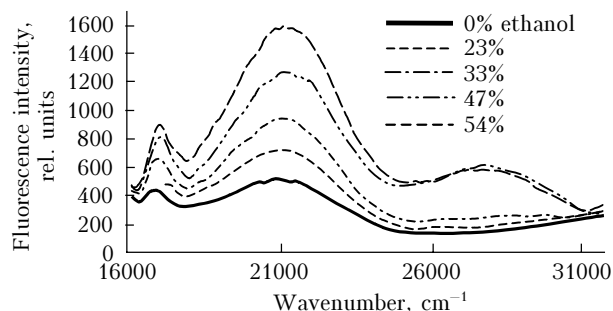
**Table 1.** Characteristics of electronic transitions of 1-naphthol and 1-naphtholat

State	ROH		RO <sup>-</sup>	
	$\nu_{\text{calc/exp}}$ , $\text{cm}^{-1}$	$f_{\text{calc/exp}}$	$\nu_{\text{calc/exp}}$ , $\text{cm}^{-1}$	$f_{\text{calc/exp}}$
$S_1$	31930 / 33160	0.033 / 0.028	29820 / 30120	0.223 / 0.210
$S_2$	34820 / 34750	0.242 / 0.220	31550 / 31060	0.104 / 0.090
$S_3$	37940 / –	0.000 / –	34680 / –	0.000 / –
$S_4$	42210 / –	0.000 / –	38870 / –	0.002 / –
$S_5$	42580 / –	0.003 / –	40750 / 40485	0.055 / 0.050
$S_6$	43070 / –	0.004 / –	41210 / –	0.002 / –
$S_7$	44390 / 43380	0.429 / 0.450	41500 / –	0.000 / –
$S_8$	45240 / –	0.000 / –	42070 / –	0.000 / –
$S_9$	46420 / 46080	1.100 / 0.620	43530 / 42735	0.579 / 0.540
$S_{10}$	46660 / –	0.000 / –	45340 / –	0.033 / –

We have studied how the neutral and anion forms of 1-naphthol depend on the concentration of water. We have found that for the anion form the content of water in the solvation sphere is higher than that in the preset solution. For the neutral form, the content of water in the solvation sphere is practically equal to 100% still at 50% of water in the solution.



**Fig. 3.** Fluorescence spectrum of 1-naphthol in ethanol with different water additions; the 1-naphthol concentration in all cases is  $7 \cdot 10^{-4}$  M, the excitation wavelength is 290 nm. The intensity of the ethanol curve is decreased tenfold.



**Fig. 4.** Fluorescence spectrum of 1-naphthol in water with different ethanol additions; the 1-naphthol concentration is  $7 \cdot 10^{-4}$  M; the excitation wavelength is 290 nm;

Now consider the water–ethanol mixtures. When ethanol of different concentrations was added to water, the fluorescence intensity in the both forms of 1-naphthol increased. For the anion form, the increase is significant already at small ethanol additions, and for the neutral form, it becomes

marked upon addition of more than 30% ethanol (Fig. 4). The ethanol molecules in the water–ethanol binary mixture likely affect the fluorescence intensity of the neutral form weaker than that of the anion form. At 47% ethanol, the fluorescence intensity of the neutral form saturates, while that of the anion form increases. The increase is likely caused both by the increase of the medium basic properties and the decrease of the rate constant of intercombination conversion as the ethanol molecule forms a complex with the  $RO^-$  form. The increase of the fluorescence intensity for the neutral form supposes that in the medium a proton is added to oxygen of the  $RO^-$  form.

The increase of the fluorescence intensity for the anion form in the ethanol+water and water+ethanol mixtures is likely connected with the composition of the solvation sphere, which includes water and alcohol molecules. In the case of the solvation sphere that contains both water and ethanol molecules, the fluorescence intensity of the anion form is higher than in the case of the solvation sphere that consists of only water molecules. Goryaeva et al.<sup>12</sup> noted that, due to distribution of the negative anion's charge between oxygen and the system of  $\pi$  electrons and the charge of the aromatic core, the first coordination sphere is formed by several hydrogen atoms of hydroxyl groups. To discuss the composition of the solvation sphere of the anion form in the excited state, we have to know the charge distribution of the anion in this state. The experimental data (Table 2) show that the solvation sphere for the anion form has a mixed composition.

Analysis of the recorded fluorescence spectra of the neutral and anion forms of the 1-naphthol molecule allows us to speak not only about the possibility of protonation of the neutral form of 1-naphthol, but also about deprotonation of 1-naphthol in the excited state. To find the most probable centers of interaction of 1-naphthol and 1-naphtholat with water molecules, we consider the MEP data.

In the ground, first and second singlet states of the neutral form of 1-naphthol, protonation proceeds only via the 11th atom. Protonation of 1-naphthol in the states  $S_1$  (via the 8th and 9th atoms) and  $S_2$  (via the 5th–8th atoms) is likely possible as well, but the MEP values in these cases are low (see Table 2).

**Table 2.** MEP for the neutral and anion forms of 1-naphthol

Atom	$S_0$		$S_1$		$S_2$	
	ROH, kJ/mol	$RO^-$ , kJ/mol	ROH, kJ/mol	$RO^-$ , kJ/mol	ROH, kJ/mol	$RO^-$ , kJ/mol
3	—	−367.44	—	−298.6	—	−290.24
4	−2.54	—	—	—	—	—
5	—	−403.99	—	—	−24.68	—
6	—	—	−12.36	—	−22.68	—
7	−3.76	—	—	517.82	−19.87	−518.83
8	−4.35	—	−21.36	—	—	—
9	−3.95	—	−20.84	—	—	—
10	—	—	−11.47	—	−18.43	—
11	−107.06	−733.44	−92.19	−646.92	−97.01	−647.27

For the anion form of 1-naphthol, besides protonation via the 11th atom, protonation via the 3rd and 4th atoms in the ground state and via the 3rd–4th and 7th–10th atoms in the first and second singlet states is also possible (see Table 2).

Deactivation of the state  $S_1$  for the neutral and anion forms proceeds due to intercombination conversion  $k_{ST}$  (Table 3). The constant of internal conversion rate  $k_{ic}$  does not influence quantum yield of fluorescence due to its small value. The quantum yield of fluorescence for 1-naphthol molecule in the neutral and anion forms was, respectively, 0.02 and 0.04. Since the rate constants of intercombination conversion and radiative conversion  $k_r$  differ by an order of magnitude, the quantum yield of fluorescence depends on the properties of the medium.

**Table 3. Nonradiative and radiative constants for 1-naphthol and 1-naphtholat**

State	$k_r \cdot s^{-1}$		$k_{ic} \cdot s^{-1}$		$k_{ST} \cdot s^{-1}$	
	ROH	RO <sup>-</sup>	ROH	RO <sup>-</sup>	ROH	RO <sup>-</sup>
$S_1$	$1.2 \cdot 10^7$	$1.3 \cdot 10^8$	$9.5 \cdot 10^2$	$7 \cdot 10^4$	$7 \cdot 10^8$	$2.7 \cdot 10^9$
$S_2$	$2.1 \cdot 10^8$	$6.2 \cdot 10^7$	$1.1 \cdot 10^4$	$2.8 \cdot 10^4$	$7 \cdot 10^8$	$2.2 \cdot 10^9$

The main channel of nonradiative deactivation of the 1-naphthol molecule is the intercombination conversion and protonation of the neutral form via the 11th atom. Protonation of the neutral form in the state  $S_1$  via the 8th–9th atoms and in the state  $S_2$  via the 5th–8th is also possible but with low probability. For the anion form of 1-naphthol, protonation proceeds not only via the 11th atom, but also in the state  $S_1$  via the 3rd–4th and 7th–10th atoms and in the state  $S_2$  via the 3rd–4th and 7th–10th atoms.

The possibility of determining the composition of the solvation sphere of a molecule in binary solvents has been considered when studying the dependence of the fluorescence intensity on the composition of the binary solvent.

## References

1. Ya.I. Korenman, *Aromatic Compounds – Ecological and Analytical Problems* (Khimiya, St. Petersburg, 1999), 60 pp.
2. O.N. Tchaikovskaya, V.T. Kuznetsova, I.V. Sokolova, and N.V. Sul'timova, *Zh. Fiz. Khim.* **74**, No. 10, 1806–1809 (2000).
3. V.A. Filov, ed., *Noxious Chemical Substances. Halogen and Oxygenated Organic Substances* (Khimiya, St. Petersburg, 1994), 400 pp.
4. G.V. Maier, V.Ya. Artyukhov, and O.K. Bazyl', *Excited Electronic States and Photochemistry of Organic Compounds* (Nauka, Novosibirsk, 1997), 232 pp.
5. A.N. Terenin, *Photonics of Dye Molecules* (Nauka, Leningrad, 1967), 615 pp.
6. P. Wan and D. Shukla, *Chem. Rev.* **93**, 571–584 (1993).
7. *Chemical Encyclopedia* (Sov. Entsiklopediya, Moscow, 1990), Vol. 3, 600 pp.
8. C.A. Parker, *Photoluminescence of Solutions* (Elsevier, Amsterdam, 1968).
9. N.D. Sokolov, *Hydrogen Bond* (Nauka, Moscow, 1981), 287 pp.
10. G.V. Maier and V.I. Danilova, *Quantum Chemistry, Structure, and Photonics of Molecules* (Tomsk State University, Tomsk, 1984), 218 pp.
11. S.P. McGlynn, T. Azzumi, and M. Kinoshita, *Molecular Spectroscopy of the Triplet State* (Pentice Hall, Englewood Cliffs, NJ, 1969).
12. E.M. Goryaeva, A.V. Shablya, and V.L. Ermolaev, *Opt. Spektrosk.* **90**, No. 4, 577–585 (2001).