Micelles of Oxyethylated Isononylphenols in Aqueous Solutions and Hydrophilic–Lipophilic Balance

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ABSTRACT: We have measured the self-diffusion coefficients and calculated the effective hydrodynamic radii of micelles of ethoxylated isononylphenols in aqueous solutions in the presence of sodium chloride, as well as in their binary mutual mixtures, when approaching cloudy conditions. These cloudy conditions were created by an increase in temperature, a change in the concentration of an electrolyte in the solution, or a mutual ratio of neonols in their binary mixtures. The results are discussed within the concept of the hydrophilic–lipophilic balance.

INTRODUCTION

The properties of nonionic surfactant solutions are largely determined by the concentration, temperature, and the presence of organic or inorganic salts or cosurfactants in the solution. At a concentration of a surfactant $C < \text{critical micelle concentration (CMC)}$, the solution is a molecular monomeric solution; at $C > \text{CMC}$, micelles are formed whose size and shape change with increasing concentrations of nonionic surfactants in the solution. Under certain conditions, the phenomenon of turbidity is observed due to a change in the solubility of nonionic surfactants in water, an increase in temperature, or a change in the properties of the solvent (water). Change in the properties of the solvent may occur by the addition of salts, alcohols (with salting-out, or, conversely, salting-in action), or aqueous solutions of nonionic surfactants. The solubility of nonionic surfactants is determined by the hydrophilic–lipophilic balance (HLB), which depends on the ratio of the alkyl and oxyethylene parts of the molecules of individual nonionic surfactants, and can be changed when mixtures of the surfactants are used.

The loss of solubility leads to the formation of dehydrated aggregates from nonionic surfactant molecules that are released into a separate phase of the solution—the phase enriched in nonionic surfactant molecules and, accordingly, depleted in water. The initially uniform transparent micellar solution of nonionic surfactants breaks down into two components—enriched and depleted nonionic surfactant phases. The depleted nonionic surfactant phase is a true molecular solution of a nonionic surfactant in water with a concentration at the level of the critical micelle concentration. As soon as aggregates of the nonionic surfactant-enriched phase reach a size of about $10^2 \text{ nm}$, clouding of the solution is visually observed due to incoherent light scattering. Further evolution of the solution is associated with different phase densities—the density of nonionic surfactants differs from the density of water—therefore, due to the phenomenon of sedimentation, the phases are spatially separated.

Nonionic surfactants are used in the cloud point extraction (CPE) method based on different solubilities of recoverable compounds in the enriched and depleted nonsurfactant phases of the solution. To select the optimal conditions for CPE, it is necessary to study the properties of nonionic surfactant solutions. In this work, the goal was to experimentally determine the sizes of micelles and aggregates in a wide range of parameters of aqueous solutions of nonionic surfactants. A homologous series of ethoxylated isononylphenols was taken as the object of the study, which made it possible to study the dependence of micelle sizes on the properties of individual nonionic surfactants and on the composition of their mixtures.

Experimental studies were carried out on the dynamics of changes in the size of micelles and aggregates of neonols in aqueous solutions when approaching cloudy conditions. The temperature and concentration of an electrolyte (sodium chloride) in the solutions of individual neonols were varied; measurements were also made in reciprocal binary mixtures of neonols, using the NMR diffusion method to measure the self-diffusion coefficients of micelles, and calculating neonol aggregates within the framework of the two-state model. 

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as they approached turbidity conditions. Then, using the Stokes–Einstein relation, the so-called effective hydrodynamic radii of micelles and aggregates were calculated with corrections for their interaction with each other. The results are discussed in the framework of the HLB concept.

## RESULTS AND DISCUSSION

The dynamic and structural properties of aqueous solutions of neonols were studied in detail by us earlier. Relations were obtained expressing the dependence of the cloud point on the number of oxyethylene groups in neonol molecules at a constant concentration of neonols in solutions with C = 1 wt %. The hydration of oxyethylene chains was studied and it was shown that 3 to 4 water molecules bound to one oxyethylene group. The sizes of micelles of water-soluble neonols AF9-8,9,10,12 were determined by NMR and dynamic light scattering analyses in the temperature range from 25 °C to the corresponding cloud points. It was found that the effective hydrodynamic radii of micelles of individual neonols AF9-8,9,10,12 at C = 1 wt % in aqueous solutions monotonically increase with temperature. When approaching the cloud points, dehydration of oxyethylene groups begins and aggregates are formed whose effective hydrodynamic radii in solutions of all neonols from AF9-8 to AF9-12 are ≈35 nm.

**Micelle Sizes in the Presence of Electrolytes.** The effect of electrolytes on the size of neonol micelles in aqueous solutions at a constant temperature of 25 °C was studied using sodium chloride as an example. Note that the temperature 25 °C is below the cloud point of all water-soluble neonols (Table 1). Figure 1 shows the results of measuring the diffusion coefficients in aqueous (D2O) solutions of neonols AF9-9,10,12 depending on the concentration of sodium chloride in the solution. A significant, within the 1 order of magnitude, decrease in the diffusion coefficient of micelles upon the addition of NaCl is observed.

The reason for the decrease in D of micelles when NaCl is added may be a change in the viscosity of the solution or a change in the size of the micelles. The viscosity of the solvent, a solution of NaCl in D2O, was determined using the published data on the viscosity of aqueous (H2O) NaCl solutions and introducing a correction that takes into account the different viscosities of H2O and heavy D2O water.

![Figure 2](https://dx.doi.org/10.1021/acsomega.0c04041)

**Figure 2.** Hydrodynamic radii of micelles in aqueous solutions of neonols in the presence of sodium chloride: (1) AF9-9, (2) AF9-10, and (3) AF9-12. The measurements were performed at a constant concentration of neonols C = 1 wt %. Solid symbols correspond to aggregates at the cloud point. t = 25 °C.

![Figure 1](https://dx.doi.org/10.1021/acsomega.0c04041)

**Figure 1.** Micelle diffusion coefficients in aqueous solutions of neonols: (1) AF9-9, (2) AF9-10, and (3) AF9-12 depending on the concentration of sodium chloride in the solution. The measurements were performed at a constant concentration of neonols, C = 1 wt %, t = 25 °C.
micelles on the concentration of sodium chloride is close to exponential.

Using the values of the effective hydrodynamic radii of micelles, one can estimate the aggregation numbers by comparing the masses of micelles and surfactant molecules

\[ N_{agg} = \frac{M}{m} \]  (1)

The mass of micelles in the approximation of their spherical shape can be related to the density of neonols \( \rho \) and the volume of the micelle

\[ M = \rho \times V_{mic} = \rho \times \frac{4}{3} \pi R_{mic}^3 \]  (2)

The results of calculation of aggregation numbers depending on the concentration of sodium chloride in solutions of neonols AF9-9, AF9-10, and AF9-12 are shown in Figure 3.

![Figure 3. Aggregation numbers in aqueous (D_2O) 1 wt % neonol solutions: (1) AF9-9, (2) AF9-10, and (3) AF9-12 depending on the concentration of sodium chloride in the solution.](image)

The aggregation numbers in the absence of salt in 1 wt % solutions of neonols AF9-9, AF9-10, and AF9-12 are equal to 1813, 327, and 123, respectively. This means that these micelles are not spherical but ellipsoidal or spherocylindrical. With the increase in the concentration of sodium chloride, the aggregation numbers increase, remaining in the range of \( 10^2 - 10^3 \), and then abruptly increase to \( \sim 200,000 \) when approaching the concentration of turbidity. These dependencies can be explained by the fact that the solubility of nonionic surfactants in water decreases both with a decrease in the degree of oxyethylation and with the introduction of salts with a salting-out effect into the solution, for example, sodium chloride. The decrease in solubility leads to the increase in the size of micelles and aggregates; the sharp increase in the size and number of aggregations when approaching turbidity conditions is explained by the complete loss of solubility and the formation of aggregates from dehydrated surfactant molecules.

**Mixed Micelles in Binary Mixtures of Neonols.** We studied mixed micelles in binary mixtures of neonols AF9-9, AF9-10, and AF9-12 with neonol AF9-6 at various ratios, but with a constant total concentration of 1 wt %. Diffusion decays of the spin-echo signals in all samples at any ratios of components are single exponential, as shown in Figure 12, indicating a high NMR exchange rate both between the monomeric and micellar states and between the nonionic surfactant micelles. The results of measurements of diffusion coefficients in mixtures of neonols AF9-9, AF9-10, and AF9-12 with neonol AF9-6 in aqueous D_2O solutions are shown in Figure 4.

![Figure 4. Diffusion coefficients of mixed micelles in aqueous (D_2O) solutions of neonols: (1) AF9-9, (2) AF9-10, and (3) AF9-12 with neonol AF9-6 depending on the ratio of neonols in a mixture at a constant total concentration of neonols C = 1 wt %, t = 25 °C.](image)

The sizes of micelles and the degree of polydispersity of the composition of neonol micelles in aqueous solutions of neonols can be estimated by dynamic light scattering. We performed measurements of mean values for the sizes (Z-average size), and a width parameter (polydispersity index—PDI) of micelles in 1 wt % aqueous (H_2O) solutions of individual neonols AF9-12, AF9-8, and AF9-6, and their binary mixtures. In all samples, one maximum is observed in the size-distribution curve for light scattering intensity, as shown in Figure 5. Therefore, all micelles have the same composition, determined by the ratio of components. The PDI both in solutions of individual neonols and in their mixtures is in the range of 0.1–0.3.

The radii of micelles, calculated according to the results of NMR diffusion using the Stokes–Einstein relation (eq 14) taking into account the hydrodynamic interaction of micelles (eq 15), are shown in Figure 6. The necessary values of the dynamic viscosity of heavy water were taken from the reference manual. Let us estimate the aggregation numbers in mixed micelles based on the composition of the mixture and using the values of the effective hydrodynamic radii of mixed micelles. Similarly to eq 1, for the mass of micelles and the effective mass of nonionic surfactant molecules

\[ N_{agg} = \frac{M}{m^*} \]  (3)

The mass of micelles, in the approximation of their spherical shape, is related to the effective density of neonols contained in the micelle, \( \rho^* \), and the volume of the micelle

\[ M = \rho^* \times V_{mic} = \rho^* \times \frac{4}{3} \pi R_{mic}^3 \]  (4)

The effective mass of molecules and the effective density of micelles can be determined taking into account the composition of micelles.
where $m_i$, $\rho$, and $C_i$ are the mass of the molecule, density, and the relative concentration of the $i$-th neonol in the mixture, respectively. Since the total weight concentration of neonols, equal to 1 wt %, significantly exceeds the CMC of neonols, as shown in Table 1, we will assume the relative concentration of neonols in mixed micelles to be equal to the relative concentration of neonols in the mixture. The results of calculating the aggregation numbers in mixtures of neonols AF9-9, AF9-10, and AF9-12 with neonol AF9-6 depending on the relative concentration of neonol AF9-6 are shown in Figure 7.

A sharp increase in the total numbers of aggregation of neonols is observed when the composition of the mixture approaches turbidity conditions corresponding to the formation of aggregates with sizes of $\sim35$ nm. The decrease in the water solubility of such aggregates and its complete loss when the turbidity conditions are reached is associated with the presence of a short-chain, water-insoluble, neonol AF9-6 in their composition.

### Neonol Micelle Sizes and Hydrophilic–Lipophilic Balance

The sizes of micelles and the cloud points of aqueous solutions of oxyethylated nonionic surfactants depend on the structure of the aliphatic part of the nonionic surfactant molecules and on the number of oxyethylene groups, $n$, in their molecules. With increasing $n$, the micelle sizes decrease, and the value of the cloud point increases. The number of the hydrophilic–lipophilic balance ($N_{HLB}$) is a numerical characteristic that determines the ratio of hydrophilic and lipophilic properties of nonionic surfactant molecules.\(^7\)

$$N = \frac{1}{5}c_e$$

where $c_e$ is the content of oxyethylene groups in the nonionic surfactant molecule.

### HLB and Sizes of Neonol Micelles in the Presence of Electrolytes

HLB is determined not only by the structure of nonionic surfactant molecules but also depends on the temperature and the presence of electrolytes and organic additives in the solution.\(^{34-37}\) With an increase in the temperature up to the cloud point, with the introduction of electrolytes with salting-out properties, a decrease in the solubility of nonionic surfactants is observed both due to the processes of dehydration of nonionic surfactant molecules and the competing action of electrolyte ions. The HLB numbers...
determined for aqueous solutions need to be adjusted, taking these factors into account.

\( N_{\text{HLB}} \) in the presence of electrolytes can be calculated using the relationship of \( N_{\text{HLB}} \) with other parameters characterizing the physicochemical properties of nonionic surfactant solutions, for example, phase inversion temperature or the cloud point. Electrolytes (salting-out) lower the cloud point and the value of the effective \( N_{\text{HLB}} \) of nonionic surfactants. The cloud points of aqueous solutions of neonols, as shown Figure 8, decrease with the addition of sodium chloride exponentially

\[
t_{\text{cp}} = t_{\text{cp}}^0 \exp(-kC)
\]

where \( t_{\text{cp}} \) and \( t_{\text{cp}}^0 \) are cloud points of aqueous solutions of neonols in the presence and absence of salt, respectively, and \( C \) is the concentration of salt in the solution.

We assume that the dependence of the effective HLB on salt concentration also has an exponential form, and we write a similar expression

\[
N = N_0 \exp(-k^*C)
\]

where \( N \) and \( N_0 \) are HLB numbers in the presence and absence of salt, respectively.

We find the coefficients \( k^* \) from the boundary conditions for the HLB numbers: the values of \( N_0 \) at \( C_{\text{NaCl}} = 0 \) are given in Table 1; we will assume \( N \approx 12 \) at a salt concentration, leading to a cloudy solution. As can be seen from Figure 8, aqueous solutions of neonols AF9-9, AF9-10, and AF9-12, at a temperature of 25 °C, become cloudy at sodium chloride concentrations of 1.8, 3.2, and 5.9 mol/L, respectively. Calculated from these data, the values of the coefficients \( k^* \) are 0.0358, 0.0321, and 0.0273 L/mol for neonols AF9-9, AF9-10, and AF9-12, respectively. The hydrodynamic radii of neonol micelles depending on the \( N_{\text{HLB}} \) values calculated in accordance with formula (eq 9) in solutions in the presence of sodium chloride are shown in Figure 9.

**HLB and Micelle Sizes in Binary Mixtures of Neonols.** In mixtures of nonionic surfactants, the resulting hydrophilic–lipophilic balance can vary over a wide range depending on the ratio of components. In binary mixtures of neonols, the resulting \( N_{\text{HLB}} \) can be calculated under the assumption of additivity of the properties of neonols having a similar molecular structure according to the ratio

\[
N = x_1N_1 + x_2N_2
\]

where \( x_1 \) and \( x_2 \) and \( N_1 \) and \( N_2 \) are relative concentrations and numbers of HLB of neonol solutions and, in particular, the diffusion coefficients and sizes of micelles formed both in solutions of individual neonols and in their mixtures. Figure 10 shows the radii of neonol micelles depending on the resulting HLB in binary mixtures of neonols AF9-12.10.9 with neonol AF9-6. The HLB numbers were calculated by eqs 7 and 11.

In binary mixtures of neonols, as well as in solutions of individual neonols, the phenomenon of turbidity is observed with increasing temperature. In neonol mixtures, the cloud point temperature depends on properties of neonols and their mutual ratio. Accordingly, at a given value of the cloud point, it is possible to determine the composition of the mixture using results of a work devoted to the phenomenon of turbidity in binary mixtures of neonols. Finally, the HLB number at the cloud point can be calculated using the composition of the mixture and eqs 7 and 11. Our calculations showed that the HLB numbers in binary mixtures of neonols AF9-9, AF9-10, and AF9-12 with neonol AF9-6 at the cloud point are equal to 12.2 at 25 °C. At the cloud point, the aggregate radii are 35 nm; in Figure 10, the corresponding point is indicated by an asterisk.

[Figure 8. Cloud points of aqueous 1 wt % solutions of neonols: (1) AF9-9, (2) AF9-10, and (3) AF9-12 in the presence of sodium chloride.]

[Figure 9. Hydrodynamic radii of micelles in aqueous (D2O) solutions of neonols: (1) AF9-9, (2) AF9-10, and (3) AF9-12 in the presence of sodium chloride depending on \( N_{\text{HLB}} \). The concentration of neonols C = 1 wt %, \( t = 25^\circ C \).]
CONCLUSIONS

The NMR method was used to measure the self-diffusion coefficients of oxyethylated isononylphenol micelles in aqueous solutions in the presence of sodium chloride, as well as in their binary mutual mixtures. Using the Stokes−Einstein relation and adjusting for the interaction of micelles with each other, the effective hydrodynamic radii of the micelles were calculated. It was shown that when approaching cloudy conditions due to an increase in temperature, or a change in the concentration of electrolyte in the solution, or when the mutual ratio of neonols in their binary mixtures changes, the radii of micelles increase and reach values of the order of 35 nm. We have established a correlation between the neonol micelle radii with the hydrophilic−lipophilic balance, which is both the characteristics of the nonionic surfactant molecules themselves and the properties of the solvent. The effective hydrodynamic radius of mixed micelles in binary mixtures of neonols is determined by the resulting weighted average HLB calculated on the basis of the composition of the mixture and the HLB of individual nonionic surfactants.

EXPERIMENTAL SECTION

Materials. In this work, nonionic surfactants, oxyethylated monoalkylphenols (neonols) AF9-6, AF9-8, AF9-9, AF9-10, and AF9-12, produced by “Nizhnekamskneftekhim Ltd.” were used. The neonols are a mixture of polyethylene glycol ethers of monoalkylphenols C9H19C6H4O(C2H4O)nH, where C9H19 is the alkyl isononyl radical attached to phenol, predominantly in the para position to the hydroxyl group; n is the average number of moles of ethylene oxide attached to 1 mol of alkylphenols. Neonols at n ≤ 6 are not soluble in water, AF9-8 has limited solubility, and AF9-9,10,12 are water soluble. The main physicochemical characteristics of individual neonols are shown in Table 1. In this work, we used neonols AF9-6, AF9-8, AF9-10, and AF9-12 without extra purification or rectification. Correspondence of the degree of hydroxyethylation to the factory characteristics was monitored by the ratios of the integrated line intensities in the 1H NMR spectra of individual neonols.24

For the preparation of solutions, we used distilled and additionally deionized water H2O, deuterated water D2O (degree of substitution 99.9%), and sodium chloride. The weight concentration of individual neonols and their total concentration in mutual binary mixtures in solutions were kept constant at C = 1 wt %.

NMR Diffusometry. The diffusion coefficients were measured using a pulsed sequence of stimulated spin echo with a pulsed gradient magnetic field on an NMR spectrometer (Bruker-Avance, 1H - 400 MHz). The amplitude of the stimulated spin-echo signal is determined by the expression

\[ A(\tau, \tau_1, g, \delta) \propto \exp \left( -\frac{2\tau}{T_2} - \frac{\tau_1}{T_1} \right) \exp(-\gamma^2 g^2 \delta^2 D t_0) \]  

(12)
where $T_1$ and $T_2$ are times of spin–lattice and spin–spin relaxation, respectively, $t$ and $t_1$ are time intervals in the pulse sequence, $\gamma$ is the gyromagnetic ratio of protons, $g$ and $\delta$ are amplitude and duration of pulses of the gradient of the magnetic field, $D$ is the diffusion coefficient, and $t_d = (\Delta - \delta/3)$ is the measurement time, $\Delta = (\tau + t_1)$.

In the measurements, the value of the pulse gradient was varied; the remaining parameters did not change and amounted to: $t_d = 50$ ms, the number of scans $NS = 4$. The preliminarily measured spin–lattice relaxation time of oxyethylene protons of neonols was $\approx 0.5$ s; in accordance with this, the time between successive scans was set to $RT = 5$ s. Diffusion decay processing and determination of self-diffusion coefficients $D$ were performed using Bruker TopSpin 3.5 software. The self-diffusion coefficients were determined from the decays of the integrated intensities of the proton lines of solvent molecules (water); the concentration of neonols in a solution (1 wt %) were both in individual solutions and in mixtures, AF9-9 and AF9-12 with AF9-6 (in a ratio of 4:1). The concentration of neonols in all solutions and in binary mixtures was 1 wt %.

It is evident that at concentrations where $C < CMC$, $D = D_0 \alpha$, while at $C > KKM$, the diffusion coefficient $D$ decreases and is determined mainly by diffusion of micelles. It was shown that at $C > 5 \times CMC$, the difference between $D$ and $D_0$ does not exceed 5%. The aggregation numbers of ethoxylated nonionic surfactants are, on average, 60.1;32,42 The molar concentrations of neonols at $C = 1$ wt % are 13 mM (AF9-12) and 20 mM (AF9-6) and are 2 orders of magnitude higher than CMC (Table 1). Consequently, at concentrations of neonols in solutions of 1 wt %, the measured diffusion coefficient is the diffusion coefficient of micelles or aggregates.

In this work, the effective hydrodynamic radii of micelles and aggregates were calculated in the approximation (assumption) of their spherical shapes. The sizes of micelles and, moreover, aggregates are significantly higher than the sizes of solvent molecules (water); the concentration of neonols in a solution (1 wt %) is small; both in individual solutions and in mixtures, is relatively small—these two arguments made it possible to use the Stokes–Einstein ratio valid for a spherical particle in a continuous medium

$$R = \frac{kT}{\alpha \pi \eta D_0 \phi}$$

(14)

where $R$ is the radius of the diffusing particle, $k$ is the Boltzmann constant, $\eta$ is the dynamic viscosity, and $D_0 \phi$ is the diffusion coefficient of the particle under the condition of infinite dilution. Coefficient $\alpha$ depends on boundary conditions between the particle and the medium. For so-called sliding conditions, $\alpha = 4$, and for adhesion conditions, $\alpha = 6$. The hydrogen bonds of water molecules with oxygen of oxyethylene groups provide adhesion conditions; therefore, in the calculations of the radii of micelles and aggregates, we used the value $\alpha = 6$. In micellar surfactant solutions, the condition of infinite dilution is violated due to the interaction of micelles and aggregates with each other. To calculate the diffusion coefficients, $D_0 \phi$ corresponding to the condition of infinite dilution, we used the equation

$$D = D_0(1 - 2\phi)$$

(15)

where $D$ and $\phi$ are the diffusion coefficient and the volume fraction of micelles or aggregates in the solution.

**Dynamic Light Scattering.** The sizes and the PDI of micelles in aqueous solutions of neonols were measured by dynamic light scattering (DLS) using Zetasizer Nano-ZS (Malvern Instruments Ltd., Malvern, U.K.). A He–Ne laser with $\lambda = 632.8$ nm was used. Solutions for DLS measurements were subjected to fine filtration to remove microscopic impurities. The measurements were performed in disposable polystyrene cuvettes of a standard volume. The DLS data were analyzed by the cumulant method. The values of the Z-average mean diameter and the PDI presented in the results are the average of three replicates.

**Cloud Point.** The cloud points of aqueous solutions of neonols were determined visually. Samples were slowly heated (5 °C/min) until turbidity appeared and then cooled (0,5 °C/min). The temperature at which the slowly cooled solutions became transparent (the disappearance of turbidity) was taken as the cloud point. To increase the reliability, the process was repeated at least three times.

![Figure 12](https://dx.doi.org/10.1021/acsomega.0c04041)
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