

Micelles and Aggregates of Oxyethylated Isononylphenols and Their Extraction Properties near Cloud Point

Victor P. Arkhipov,[†] Zhamil Sh. Idiyattullin,[†] Elisaveta F. Potapova,[‡] Oleg N. Antzutkin,^{§,||} and Andrey V. Filippov^{*,§,⊥}

[†]Kazan National Research Technological University, 420015 Kazan, Russia

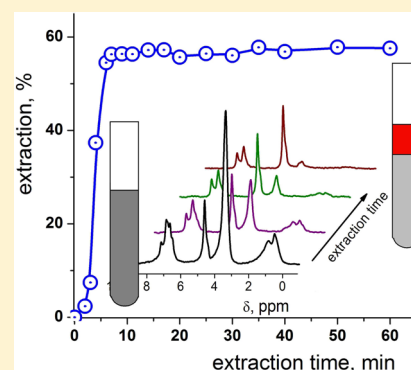
[‡]Chemical Technology, Luleå University of Technology, SE-91187 Luleå, Sweden

[§]Chemistry of Interfaces, Luleå University of Technology, SE-91187 Luleå, Sweden

^{||}Department of Physics, Warwick University, CV4 7AL, Coventry, U.K.

[⊥]Kazan Federal University, 420008 Kazan, Russia

ABSTRACT: We used nuclear magnetic resonance (NMR) spectroscopy and dynamic light scattering (DLS) techniques to study the structural and dynamic properties of micellar solutions of nonionic surfactants of a homologous series of oxyethylated isononylphenols— $C_9H_{19}C_6H_4O(C_2H_4O)_nH$, where $n = 6, 8, 9, 10$, or 12 —in a wide range of temperatures, including cloud points. The radii of the micelles and aggregates, as well as their compositions at different concentrations of surfactant, were determined. Using aqueous phenol solutions as a model, we studied the process of cloud point extraction with oxyethylated isononylphenols.



INTRODUCTION

One of the modern applications of surfactants is in micellar catalysis, based on the ability of the micelles to concentrate and orient reagent molecules.^{1–4} Ionic surfactants have this ability due to the creation of a double electric layer near the micelle surface^{5,6} and the interaction of electric dipolar moments with the electric field of this double layer. Molecules of nonionic surfactants do not have polar groups, and their surface activity is determined by hydrophilic properties of the oxyethylene chains.⁷ The catalytic activity of micelles prepared from nonionic surfactants can be explained by the steric hindrance of the reagent molecules on the branched surface of the micelle, formed by the oxyethylene chains.⁴ In the micellar state, the micelles contain water, which is bound through hydrogen bonding with oxygens of the oxyethylene groups.

In aqueous solutions of nonionic surfactants, there is one more mechanism to concentrate molecules of reagents that appears at the transition from a homogeneous micellar solution to a two-phase solution, which contains both surfactant-enriched and -depleted phases.⁷ Phase separation occurs after heating the micellar solution to temperatures higher than cloud point, t_c . The concentration of surfactant in the surfactant-depleted phase is close to the value of the critical micellization concentration (CMC). In the phase enriched with surfactant, micelles form agglomerates or clusters^{8–14} that are able to concentrate the hydrophobic components of the system. Cloud point extraction (CPE) is an extraction method based entirely on this property of nonionic surfactants.¹⁵

The phenomenon of clouding is related to increasing micelle size with increasing temperature due to dehydration of the oxyethylene chains,^{7,10,16} and due to increasing density fluctuations^{13,17–21} at temperatures approaching the cloud point. It was noted that the micelle size remains nearly unchanged,^{10,11,16,20,22} while the degree of oxyethylene group hydration remains high²³ until the cloud point is reached. Dehydration, like many other micellar properties of nonionic surfactants, is determined mainly by the length of the oxyethylene chain.^{16,24,25} The shape of the micelles changes from spherical to rod-like as the concentration of surfactant increases,^{25–30} with formation of clusters from rod-like micelles at the cloud point and liquid crystalline structures at higher surfactant concentrations.^{7,31} In contrast to ionic surfactants, solutions of nonionic surfactants are more polydisperse.^{9,20,22}

Properties of aqueous solutions of nonionic surfactants near their cloud points were studied by different methods: visual observation^{18,24,32} of clouding, determination of the cloud point ultrasound studies,³³ and viscosity and surface tension measurements.^{13,18,27,34,35} Phase transitions of nonionic surfactant solutions were studied by differential scanning calorimetry.²⁶ Fluorescence bleaching methods were used to determine aggregation numbers and the volume of micelles.^{9,10,36,37} The sizes and shapes of micelles were

Received: March 9, 2014

Revised: May 2, 2014

Published: May 2, 2014

Table 1. Physical–Chemical Characteristics of Studied Oxyethylated Isononylphenols

	neonol				
	AF9-6	AF9-8	AF9-9	AF9-10	AF9-12
density, kg/m ^{3,50}	1027 ± 3 at 40 °C	1062 ± 3 at 20 °C	1045 ± 3 at 40 °C	1040 ± 3 at 50 °C	1046 ± 3 at 50 °C
cloud point, °C, of aqueous nonionic surfactant solution at a concentration of 10 g/dm ^{3,50}		32 ± 3	54 ± 3	66 ± 3	86 ± 3
CMC, mM	0.0449 ⁵²	0.0794 ⁵²	NA	0.082 ^{52,53}	0.100 ⁵²

determined by static and dynamic light scattering (DLS),^{8,9,13,17,18,22,27,34,38–43} small angle neutron scattering,^{13,19,25,27,44} photon correlation spectroscopy,⁴⁴ and small-angle X-ray scattering.²⁴

NMR is a powerful method for studying structural and dynamic properties of micellar solutions. Changes in chemical shifts in NMR spectra^{31,45} and the widths^{11,12,16,23} and intensities of spectral lines can be analyzed to determine micelle shape and structure, degree of binding with water molecules, and the distribution of surfactant between micellar and free states. Measurements of dynamic parameters such as spin–lattice relaxation times²³ and self-diffusion coefficients^{9,11,12,16,22–24,31,35,41–48} enable one to estimate the sizes of micelles and to describe molecular motion in micellar systems and liquid-crystalline phases⁴⁹ formed by nonionic surfactants.

In this work, we studied the characteristics of micelles and aggregates in aqueous solutions of oxyethylated isononylphenols (neonols) near their cloud points and the possible application of neonols to extract organic pollutants from aqueous solutions.

Oxyethylated monoalkyl phenols (neonols) produced by Nizhnekamskneftekhim, Inc. (Russia)⁵⁰ are mixtures of poly(ethylene glycol) ethers of monoalkyl phenols of the composition C₉H₁₉C₆H₄O(C₂H₄O)_nH, where C₉H₁₉ is the isononyl group, chemically bound to the phenol hydroxyl group, predominantly in the para-position, and *n* is the average number of moles of ethylene oxide bound to one mole of alkyl phenols. The company produces neonols with different extents of oxyethylation: AF9-4, AF9-6, AF9-8, AF9-9, AF9-10, and AF9-12. In this notation, the first “9” is the number of carbon atoms in the alkyl group. In practice, the lengths of the oxyethylene chains bound to isononyl-phenolhydroxyl molecular moiety are not equal; therefore, each sample presents a mixture of molecules with varying oxyethylene chain lengths. Therefore, in this notation, the average degrees of oxyethylation of neonols AF9-4, AF9-6, AF9-8, AF9-9, AF9-10 and AF9-12 are equal to 4, 6, 8, 9, 10, and 12, respectively.

Neonols are representative of nonionic surfactants of the polyoxyethylene series, and their hydrophilic properties are due to the formation of hydrogen bonds between the oxygen atom of the polyethylene chain and water molecules, while the solubility of neonols in water and organic solvents depends on the length of the oxyethylene chain and decreases with increasing temperature. In this regard, the purpose of this work was to study the structural, dynamic, and extraction properties of water-soluble neonols of the series AF9-6, AF9-8, AF9-9, AF9-10, and AF9-12. In previous studies, we determined the sizes of micelles and the degree of binding of water molecules by neonols.⁵¹

We applied methods of NMR diffusometry, NMR spectroscopy, and DLS at constant concentrations of neonols in solution, 10 g/L (ca. 1 wt %), and temperatures in the range of

30–90 °C. This temperature range spans the temperatures necessary for formation of a micellar solution, the transition range near the cloud point, and the two-phase range, which contains aggregates of the nonionic surfactant.

EXPERIMENTAL METHODS

Materials. Oxyethylated alkylphenols AF9-6, AF9-8, AF9-9, AF9-10, and AF9-12 were produced by Nishnekamskneftekhim, Inc. (Russia)⁵⁰ and used without further purification or rectification. Characteristics of the different neonols are presented in Table 1. Deionized water and deuterated water (99% of D, “Sigma”) were used to prepare solutions. Samples were carefully mixed and allowed to equilibrate for 2 days. Neonol solutions were transparent at temperatures below the corresponding cloud points and white-bluish at higher temperatures. On the basis of the colors of the solutions, we propose that, in the micellar temperature range, the sizes of micelles do not exceed 50 nm, while clusters or aggregates at temperatures higher than cloud point are 100–1000 nm.

NMR Spectroscopy. ¹H NMR spectra were recorded using NMR spectrometers Tesla-BSS67A (¹H, 100 MHz) and Agilent/Varian/Chemagnetic CMX-360 InfinityPlus (Fort Collins, CO) (¹H, 359.92 MHz). The integral intensities of spectral lines are proportional to the numbers of molecules containing protons with a specified chemical shift, which enables investigation of, for example, chemical reaction kinetics. We measured the integral intensities of protons of water and phenyl, oxyethylene, and alkyl groups of the surfactant to elucidate changes that occur in micelle compositions when the temperature increases and approaches the cloud point. Also, the efficiency of phenol extraction performed at different temperatures was determined through examining changes in the integral intensities of phenol lines in NMR spectra of aqueous neonol solutions.

Each ¹H NMR spectrum was a sum of 16 signal transients with a pulse delay of 10 s (ca. 10T₁ for protons of phenol and neonol, where T₁ is the spin–lattice relaxation time of protons). To minimize errors in integration near the spectral lines of water and oxyethylene protons of surfactants, two series of solutions were prepared (one with H₂O and one with deuterated water), and two series of experiments were performed, respectively.

In the first series (H₂O solutions), the integral intensity values of the water lines were measured because the contribution of neonol protons was negligibly small due to the small neonol concentrations. In these experiments, we were able to avoid problems related to the long T₁ relaxation times, around 10–60 s, of residual D₂O protons. In the second series (D₂O solutions), the integral line intensities of protons of nonionic surfactant and phenol were measured; the contribution of residual protons of water was negligibly small.

We compared integral spectra at different temperatures, taking into account solution density and temperature dependence on magnetic susceptibility (Curie's law).

NMR Diffusometry. Selective measurements of self-diffusion coefficients (SDCs) of water and neonol molecules were performed by ^1H NMR with a pulsed field gradient (PFG). Measurements were taken on an NMR spectrometer Tesla-BSS67A (^1H , 100 MHz) equipped with a pulsed field gradient unit. The maximal amplitude of the pulsed field gradient was 0.5 T/m. Fourier-transformation of a half-echo signal enables one to measure the SDCs of different molecules if their isotropic chemical shifts (δ) differ.⁵⁴ The SDCs of neonol molecules were determined from diffusion decays of spectral lines of oxyethylene protons ($\delta = 4.0$ ppm), while the SDCs of water molecules were determined from diffusion decays of lines corresponding to hydroxyl protons ($\delta = 4.9$ ppm). Measurement errors did not exceed 3%. SDCs were used to calculate micelle diameters.

Dynamic Light Scattering. The sizes of micelles in aqueous solutions of neonols were also measured by 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 quartz cuvettes, which were heated to the desired temperatures in situ. At each temperature, the sample was equilibrated for 30 min prior to measurement. Thereafter, three consecutive measurements were performed at a 1 min interval to ensure that the system had reached the steady state. The DLS data was analyzed by the cumulant method. The values of the Z-average mean diameter presented in the results are the average of three replicates.

Model of Two States and Sizes of Micelles. The hydrodynamic radius of the micelles was determined by NMR diffusometry and by DLS. Calculations were performed with the assumption that the micelles were spherical, which is permissible at low surfactant concentration. Both methods are based on the hydrodynamic Stokes–Einstein equation:

$$D = \frac{k_B T}{6\pi\eta R} \quad (1)$$

where k_B is the Boltzmann constant, T is the temperature, η is the viscosity of solvent, R is the radius, and D is the SDC of the micelle or aggregate, respectively.

NMR enables measurement of an effective SDC of surfactant's D_S , which represents a mean-weight value of the SDC of the surfactant molecules over all surfactant states in the solution. In the model of two states,⁵⁵ only monomolecular and micellar states are presented and the mean SDC is

$$D_S = \frac{C - \text{CMC}}{C} \cdot D_S^{\text{bound}} + \frac{\text{CMC}}{C} \cdot D_S^{\text{free}} \quad (2)$$

where D_S^{free} and D_S^{bound} are SDCs of molecules and micelles of surfactant, respectively, C is the concentration of surfactant in solution, and CMC is the critical micellization concentration. The concentration of surfactant in monomolecular form at $C > \text{CMC}$ has been suggested to be equal to the CMC.^{5,55} D_S^{free} was calculated from D_S at $C = \text{CMC}$, taking into account the hindered influence of micelles:

$$D_S^{\text{free}} = \frac{D_S^{\text{CMC}}}{1 + \phi/2} \quad (3)$$

where ϕ is the volume content of micelles, which can be estimated from the known molecular masses, μ , and densities, ρ , of the surfactants (Table 1).

$$\phi = \frac{(C - \text{CMC}) \cdot \mu}{\rho} \quad (4)$$

The SDCs and radii of the micelles were calculated using eqs 2–4 and eq 1, respectively.

Applying the DLS method, by analysis of the time correlation function of the correlation of fluctuations in frequency, intensity, and direction of scattered light, we estimated the mobility of the micelles or aggregates, and their sizes were automatically calculated using eq 1. Z-average (cumulant mean) sizes were determined. Measurements were repeated three times, showing a discrepancy between the results of not more than 1%.

RESULTS AND DISCUSSION

Integral Intensities of Lines, Micelles Composition, and Surfactant-Enriched and -Depleted Phases. All the aqueous solutions of surfactants (AF9-8, -9, -10, and -12) in this study demonstrate similar changes as the temperature increases: (a) below cloud point, they remain transparent; (b) at cloud point and at higher temperatures, solutions become cloudy and then phase separation occurs. The potential for spatial separation into phases is determined by the ratio of the densities of water and neonol; it is different for solutions prepared from standard and deuterated water. The density of deuterated water ($\rho = 1100$ kg/m³) is higher than the density of the neonols studied here, while the density of standard water ($\rho = 997$ kg/m³) is lower. Therefore, it is reasonable to propose that in solutions of D₂O the surfactant-enriched phase will collect in the upper part of the sample tube. Thus, by positioning the sensitive part of the NMR probe at the bottom of the NMR sample tube, we can study differences in the composition, sizes, and concentrations of micelles in the surfactant-depleted phase through changes in SDCs and the integral intensities of NMR spectral lines of water and surfactants in the solution.

All samples exhibited similar behaviors regarding changes in integral intensities of spectral lines with changing temperature. The sample exposure time at each successive temperature was 20 min. During this time, molecules were distributed between phases characteristic for the specified temperature, and no further changes in integral intensities occurred. Integral intensities of lines corresponding to protons of water do not show marked changes with temperature (below, near, and above the cloud point). Integral intensity widths of spectral lines of surfactant in all samples remain unchanged only below their cloud points and then sharply decrease, almost 10-fold, above the cloud point. Figure 1 shows normalized values of integral intensities of lines corresponding to water protons (as an example, results for AF9-10 are shown) and oxyethylated protons in the spectra of 1% aqueous solutions of neonols AF9-8, -9, -10, and -12 as a function of temperature.

All integral intensities of the NMR lines of discussed surfactants decreased sharply at specific temperatures for two reasons. First, the oxyethylene groups of the surfactant dehydrate, and these dehydrated molecules form large enough aggregates. This phenomenon itself does not lead immediately to a change in integral intensities. However, the rates of exchange of surfactant molecules between their different states

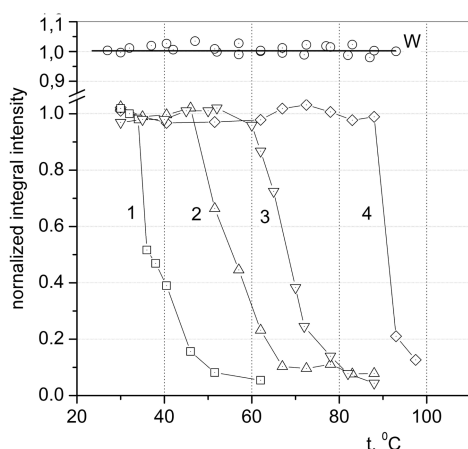


Figure 1. Normalized integral intensities of NMR peaks of water (w); curves 1, 2, 3, and 4 correspond to neonols AF9-8, AF9-9, AF9-10, and AF9-12, respectively, in aqueous 1 wt % solutions.

(free, bound in micelles, and bound in aggregates) are rather high on the NMR time scale. Therefore, we can expect broadening of the NMR spectra lines while the integral intensities of these lines should not be changed. The second reason is due to sedimentation of the aggregates as they form from dehydrated surfactant molecules. A decrease in hydrogen bonding of the surfactant molecules with water molecules leads to a decrease in the solubility of the surfactant in water, and as a result, sedimentation causes spatial separation of the surfactant-rich and surfactant-depleted phases. In D_2O neonol solutions, the lighter phase enriched with surfactant collects in the upper part of the sample, which is located far from the sensitive part of the NMR sample probe. Consequently, the signal observed contains only those of surfactant protons from the surfactant-depleted phase.

Thus, the micellar character of neonol solutions persists below the cloud point. Dehydration of oxyethylene chains occurring as the temperature increases leads to formation of aggregates from partly or completely dehydrated surfactant molecules. This system is not stable, and as a result of sedimentation, separation into two phases (enriched and depleted with surfactant) occurs. The rest of the NMR line, corresponding to oxyethylene protons of surfactant at temperatures higher than cloud point in the phase depleted of surfactant, is due to the presence of separate molecules of surfactant in the solution. The calculated concentration of surfactant in the depleted phase is close to the CMC.

Self-Diffusion Coefficients and Sizes of Molecules.

Figure 2 shows the temperature dependence of the SDCs of water and surfactant in neonol solutions of AF9-8, -9, -10, and -12. The SDCs of water and surfactant differ by two orders of magnitude, which allows separate diffusion decays of water and surfactant using different pulsed field gradient durations.

The dependence of the SDCs of water on temperature for all solutions is linear (in an Arrhenius plot), which enables one to estimate its activation energy for diffusion, $\Delta E = 15.3$ kJ/mol. The SDC values of water in 1 wt % aqueous solutions of these surfactants are less than those of H_2O molecules in pure water because of the restrictive effect of micelles and surfactant hydration.^{12,23,23,47,56}

Measurements of the SDCs of surfactants were performed up to the corresponding cloud points. However, values measured at temperatures higher than the cloud points have high errors

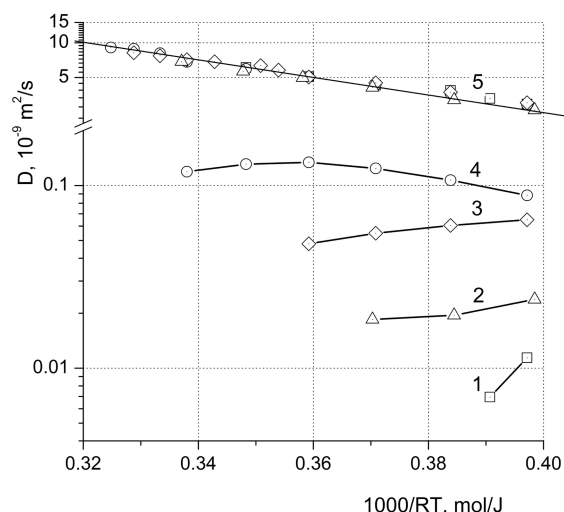


Figure 2. Self-diffusion coefficients of surfactants and water: AF9-8 (1), AF9-9 (2), AF9-10 (3), AF9-12 (4), and water (5) in 1 wt % aqueous solutions.

because of the low concentration of surfactant remaining in the depleted phase. The temperature dependence of the SDCs of different neonol molecules in aqueous solutions demonstrated different characteristics dependent on the solubility of neonols in water and, hence, on the oxyethylene chain lengths of the surfactant molecules (Figure 2). Apparent activation energies of diffusion, ΔE , have negative values in solutions of neonols AF9-8, -9, and -10 and are equal to -76 , -15.5 , and -9.8 kJ/mol, respectively. Negative values of apparent activation energies indicate structural changes occurring in surfactant solutions, namely, temperature increase leads to intensified molecular motion and increase in micelle size.⁵⁷ A combination of these two factors leads to a decrease in the SDCs at increased temperature instead of a decrease in the SDCs when micelle size does not change.

In aqueous solutions of neonol AF9-12, the SDCs of the surfactant increase with rising temperature in the range of 30–60 °C and energy activation of surfactant diffusion is close to the ΔE of water. It can be assumed that micelles of AF9-12 retain their size in this temperature range. A further increase in temperature higher than 60 °C leads to a decrease in the SDCs of AF9-12 and the apparent activation energy, ΔE , becoming -7.9 kJ/mol. This demonstrates increasing of the micelle size, similar to AF9-8, AF9-9, and AF9-10.

Using the experimental values of the SDCs of water and surfactants in eqs 1–4, we estimated the diameters of surfactant micelles (Figure 3). Data obtained by DLS is also shown in Figure 3. It should be noted that the results obtained by these two methods in the micellar temperature region below the cloud point are in a qualitative agreement. However, sizes of micelles estimated by DLS exceed sizes obtained from NMR. We suggest that sizes of micelles estimated by DLS include their hydration shells. In NMR diffusion time scale, the solvent is in the so-called “fast exchange” conditions; therefore, it gives no contribution in the micelle size. Thus, the DLS method essentially complements the NMR method at temperatures higher than the cloud point. Dotted lines in Figure 3 show cloud points in surfactant solutions; as seen from the figure, the diameters of micelles at these temperatures increase up to ca. 80 nm. At the same time, the size of the micelles increases gradually without any jumps. Hence, the size of the micelles

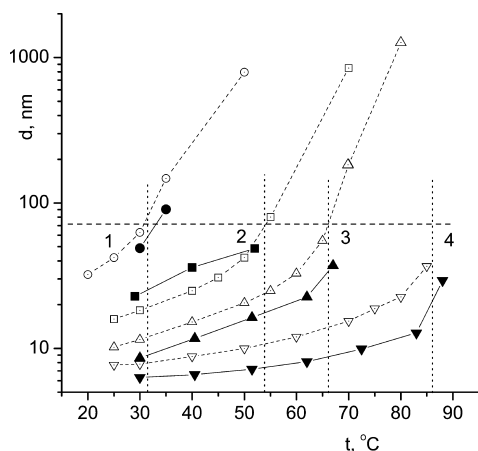


Figure 3. Z-average mean diameters of micelles and aggregates of surfactants in aqueous 1 wt % solutions: filled symbols and solid lines are the results of NMR diffusometry; open symbols and dashed lines represent data obtained by dynamic light scattering; AF9-8 (1), AF9-9 (2), AF9-10 (3), and AF9-12 (4).

gradually increases with increasing temperature in all the studied surfactant solutions, and the phenomenon of cloudiness itself has no sharp or clear-cut phase transition.

Extraction Properties of Neonols. The phase enriched with surfactant, formed in aqueous solutions at temperatures higher than cloud point, is able to concentrate inside organic and other deleterious impurities contained in the solution. Cloud point extraction (CPE) can be used, for example, to extract hydrophobic organic compounds, phenols, and polycyclic aromatic hydrocarbons; to determine the concentration of pesticides in soil; and to extract metal ions.^{58–66}

Below, the possibility of using the neonols AF9-6, -8, -9, -10, and -12 in CPE is discussed using extraction of phenol from an aqueous solution as an example. As phenol is a dangerous environmental pollutant, developing a method for efficient extraction is of high importance.

We estimated the efficiency and dynamics of the extraction process on the basis of the integral intensities of NMR spectral lines corresponding to phenol (Figure 4). In a two-part process,

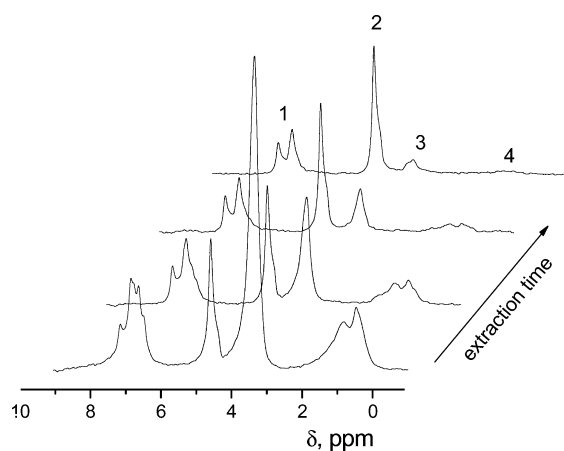


Figure 4. Integral intensities of lines in the ^1H NMR spectra of aqueous solutions of neonol AF9-6 during the process of extraction: overlapping lines of phenol and phenyl groups of surfactant (1), protons of residual water (2), and oxyethylene and alkyl protons of surfactant (3 and 4). $t = 40\text{ }^\circ\text{C}$.

phenol concentrates in the surfactant-enriched phase, and this phase separates along with phenol in the upper part of the NMR sample tube; therefore, the bottom part of the sample contains the surfactant-depleted phase and the remaining phenol. By measuring the concentration of phenol in the bottom of the sample tube compared with its initial concentration, we can determine the dynamics and efficiency of the extraction process.

Because the spectral lines of protons of phenol and phenyl groups of surfactant are overlapping, the integral intensity of the lines of phenol I_{ph} can be estimated using the integral intensities of alkyl I_{alk} and oxyethylene I_{eth} protons of surfactant:

$$I_{\text{ph}} = I_{\Sigma} - 2(I_{\text{alk}}/19 + I_{\text{eth}}/4n) \quad (5)$$

where I_{Σ} is the total intensity of the lines of phenol and surfactant in the aromatic region of the NMR spectrum, n is the number of oxyethylene groups in the neonol molecules, and the number of alkyl protons is equal to 19.

The efficiency of extraction was estimated according to a standard procedure:⁶⁵

$$E = \frac{I_{\text{ph},0} - I_{\text{ph}}}{I_{\text{ph},0}} \quad (6)$$

where $I_{\text{ph},0}$ and I_{ph} are integral intensities of the ^1H NMR resonance lines of phenol in the bottom part of the NMR sample tube initially and during extraction, respectively. Measurements were performed at constant initial concentrations (50 mM) of surfactants and phenol in solutions and at different temperatures and extraction times.

The primary parameter influencing the rate and efficiency of extraction is temperature. At temperatures below the cloud point, the extraction process occurs at a very low rate and efficiency. For example, in solutions of AF9-12 (cloud point $86\text{ }^\circ\text{C}$) the efficiency of extraction is less than 20% and 25% at temperatures of 90 and $95\text{ }^\circ\text{C}$, respectively. On the other hand, at temperatures higher than the cloud points in all systems, the efficiency of extraction is notably higher. Figures 5 and 6 show data from the extraction of phenol from aqueous solutions of neonols AF9-8 and AF9-9.

The process of extracting phenol from aqueous solutions using neonol proceeds rather quickly at temperatures near and higher than the cloud points, and is completed within 10–20

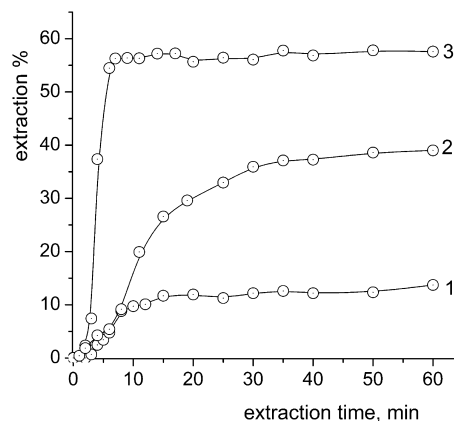


Figure 5. Efficiency of extraction of phenol in aqueous solutions of neonol AF9-8 at temperatures of $40\text{ }^\circ\text{C}$ (1), $60\text{ }^\circ\text{C}$ (2), and $70\text{ }^\circ\text{C}$ (3). Initial concentrations of neonol and phenol are 50 mM.

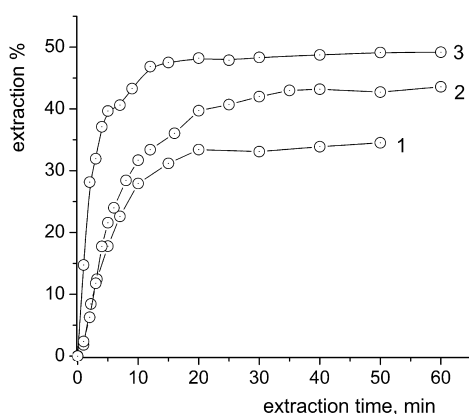


Figure 6. Efficiency of extraction of phenol in aqueous solutions of neonol AF9-9 at temperatures of 30 °C (1), 50 °C (2), and 70 °C (3). Initial concentrations of neonol and phenol are 50 mM.

min. Similar results have been reported in papers^{65–67} on the extraction of phenol from aqueous solutions by the nonionic surfactants PONPE10 and Triton X-114. The efficiency of extraction decreases with increasing of number of oxyethylene groups in the neonol molecules (Figure 7).

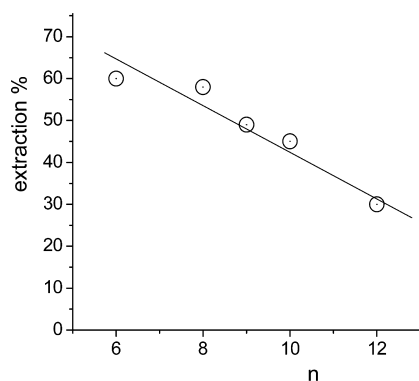


Figure 7. Maximum efficiency of extraction of phenol in aqueous solutions of neonols as a function of amount of oxyethylene groups in the surfactant molecules. Initial concentrations of neonol and phenol are 50 mM.

Table 2 shows data on the efficiency of extracting phenol from aqueous solutions at different temperatures using different

Table 2. Efficiencies of Extraction of Phenol from Aqueous Solutions Using Oxyethylated Isononylphenols at Different Temperatures^a

<i>t</i> , °C	extraction efficiency, %				
	neonol				
	AF9-6	AF9-8	AF9-9	AF9-10	AF9-12
30		7 ± 2	33 ± 3		
40	56 ± 4	14 ± 2	42 ± 3	40 ± 3	
50	57 ± 4	15 ± 2	44 ± 3	45 ± 3	
60	59 ± 4	42 ± 3	47 ± 3	44 ± 3	
70	60 ± 4	58 ± 3	49 ± 4	42 ± 3	
80				40 ± 3	21 ± 2
90					25 ± 2
95					30 ± 2

^aInitial concentrations of neonols and phenol are 50 mM.

neonols. The most effective, almost 60% extraction, is the short-chain neonol AF9-6; the same neonol has high efficiency of extraction, even at comparatively low temperatures. For example, at 40 °C the efficiency of extraction is 56%.

CONCLUSIONS

NMR spectroscopy, NMR diffusometry, and DLS were used to study processes of micellization in aqueous 1 wt % solutions of nonionic surfactants, oxyethylated isononylphenols AF9-8, -9, -10, and -12, in a wide temperature range, including cloud points.

Using integral intensities of the lines in NMR spectra, we analyzed changes in the structure of micelles at increased temperature. Integral intensities of the lines of water protons do not change markedly with temperature, while integral intensities of the lines of surfactant in all samples remain unchanged only below the cloud points and then sharply decrease in order of their initial values. We described this behavior as resulting from dehydration of the oxyethylene groups of the surfactant molecules and formation of large aggregates, whereby clusters form from the dehydrated molecules and these clusters sediment.

NMR diffusometry was used to measure the self-diffusion coefficients of water and surfactants in neonol solutions. The studies revealed that the apparent activation energies for diffusion in neonols AF9-8, -9, and -10 are negative because of the increase in sizes of aggregates at increasing temperature. The sizes of micelles at different temperatures were determined from NMR diffusometry and DLS data.

We studied the potential application of neonols AF9-6, -8, -9, -10, and -12 in extracting phenol from aqueous solutions by the CPE method. This process of extraction occurs rather fast near and at temperatures higher than the corresponding cloud points of neonols, and is completed within 10–20 min. The efficiency of extraction decreases when the number of oxyethylene groups of the neonol increases. The most effective (up to 60%) extraction agent was AF9-6, which also provides the most effective extraction at low temperatures. Application of short-chain neonols for cloud point extraction overcomes one of the problems posed by the need to perform extractions at rather high temperatures (above cloud point). This method might therefore be important for extraction of nonstable chemical compounds that decompose or denature at high temperatures.

AUTHOR INFORMATION

Corresponding Author

*E-mail: Andrey.Filippov@ksu.ru. Tel: +7 843 5315189.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Work was partially sponsored by the Development of Kazan State Technological University in 2010–2019 program. We are grateful to the J. C. Kempe and Seth M. Kempe Memorial Foundations for grants, with which equipment for the NMR diffusion measurements was purchased, and to the Centre of Advanced Mining and Metallurgy (CAMP) at Luleå University of Technology, Sweden.

REFERENCES

- (1) Berezin, I. V.; Martinek, K.; Jarzimirsky, A. K. Physicochemical Foundations of Micellar Catalysis. *Russ. Chem. Rev.* **1973**, *42*, 787–802.
- (2) Martinek, K.; Yatsimirski, A. K.; Levashov, A. V.; Berezin, I. V. The Kinetic Theory and the Mechanisms of Micellar Effects on Chemical Reactions. In *Micellization, Solubilization and Microemulsions*; Mittal, K. M., Ed.; Plenum Press: New York, 1977; Vol. 2, pp 489–508.
- (3) Engberts, J. B. F. N. Catalysis by Surfactant Aggregates in Aqueous Solutions. *Pure Appl. Chem.* **1992**, *64*, 1653–1660.
- (4) Khan, M. N. *Micellar Catalysis*, Surfactant Science Series 133; CRC Press, Taylor & Francis Group: Boca Raton, FL, 2007.
- (5) Friedrichsberg, D. A. *A Course in Colloid Chemistry*; Khimiya: Leningrad, 1984.
- (6) Us'yarov, O. G. Charge and Potential of the Diffuse Part of the Double Layer for Sodium Dodecyl Sulfate Micelles in NaCl Solutions. *Colloid J.* **2005**, *67*, 369–374.
- (7) Holmberg, K.; Jönsson, B.; Kronberg, B.; Lindman, B. *Surfactants and Polymers in Aqueous Solution*; John Wiley & Sons, Ltd.: New York, 2003.
- (8) Imae, T. Aqueous Sodium Halide Solutions of Nonionic and Cationic Surfactants with a Consolute Phase Boundary. Light Scattering Behavior. *Langmuir* **1989**, *5*, 205–210.
- (9) Brown, W.; Rymdik, R.; van Stam, J.; Almgren, M.; Svensk, G. Static and Dynamic Properties of Nonionic Amphiphile Micelles: Triton X-100 in Aqueous Solution. *J. Phys. Chem.* **1989**, *93*, 2512–2519.
- (10) Komaromy-Hiller, G.; Calkins, N.; von Wandruszka, R. Changes in Polarity and Aggregation Number upon Clouding of a Nonionic Detergent: Effect of Ionic Surfactants and Sodium Chloride. *Langmuir* **1996**, *12*, 916–920.
- (11) Stubenrauch, C.; Nyden, M.; Findenegg, G. H.; Lindman, B. NMR Self-Diffusion Study of Aqueous Solutions of Tetraoxyethylene *n*-Octyl Ether (C_8E_4). *J. Phys. Chem.* **1996**, *100*, 17028–17033.
- (12) Stjern Dahl, M.; Lundberg, D.; Zhang, H.; Menger, F. M. NMR Studies of Aggregation and Hydration of Surfactants Containing Amide Bonds. *J. Phys. Chem. B* **2007**, *111*, 2008–2014.
- (13) Ganguly, R.; Choudhury, N.; Aswal, V. K.; Hassan, P. A. Pluronic L64 Micelles near Cloud Point: Investigating the Role of Micellar Growth and Interaction in Critical Concentration Fluctuation and Percolation. *J. Phys. Chem. B* **2009**, *113*, 668–675.
- (14) Ganguly, R.; Kadam, Y.; Choudhury, N.; Aswal, V. K.; Bahadur, P. Growth and Interaction of the Tetronic 904 Micelles in Aqueous Alkaline Solutions. *J. Phys. Chem. B* **2011**, *115*, 3425–3433.
- (15) Quina, F. H.; Hinze, W. L. Surfactant-Mediated Cloud Point Extractions: An Environmentally Benign Alternative Separation Approach. *Ind. Eng. Chem. Res.* **1999**, *38*, 4150–4168.
- (16) Nilsson, P.-G.; Wennerstrom, H.; Lindman, B. Structure of Micellar Solutions of Nonionic Surfactants. Nuclear Magnetic Resonance Self-Diffusion and Proton Relaxation Studies of Poly(ethylene oxide) Alkyl Ethers. *J. Phys. Chem.* **1983**, *87*, 1377–1385.
- (17) Corti, M.; Degiorgio, V. Micellar Properties and Critical Fluctuations in Aqueous Solutions of Nonionic Amphiphiles. *J. Phys. Chem.* **1981**, *85*, 1442–1445.
- (18) Corti, M.; Minero, C.; Degiorgio, V. Cloud Point Transition in Nonionic Micellar Solutions. *J. Phys. Chem.* **1984**, *88*, 309–311.
- (19) Triolo, R.; Magid, L. J.; Johnson, J. S., Jr.; Child, H. R. Small-Angle Neutron Scattering from Aqueous Micellar Solutions of a Nonionic Surfactant as a Function of Temperature. *J. Phys. Chem.* **1982**, *86*, 3689–3695.
- (20) Magid, L. J.; Triolo, R.; Johnson, J. S., Jr. Small-Angle Neutron Scattering Study of Critical Phenomena in Aqueous Solutions of $C_{12}E_8$, a Nonionic Amphiphile. *J. Phys. Chem.* **1984**, *88*, 5730–5134.
- (21) Martin, A.; Lesemann, M.; Belkoura, L.; Woermann, D. Slowing Down of the Mutual Diffusion Process Approaching the Liquid/Liquid Coexistence Curve of a Nonionic Surfactant/Deuterium Oxide System: Study of the System $C_{12}E_5/D_2O$. *J. Phys. Chem.* **1996**, *100*, 13760–13764.
- (22) Brown, W.; Pu, Z.; Rymden, R. Size and Shape of Nonionic Amphiphile Micelles: NMR Self-Diffusion and Static and Quasi-Elastic Light-Scattering Measurements on $C_{12}E_5$, $C_{12}E_7$, and $C_{12}E_8$ in Aqueous Solution. *J. Phys. Chem.* **1988**, *92*, 6086–6094.
- (23) Nilsson, P. G.; Lindman, B. Water Self-Diffusion in Nonionic Surfactant Solutions. Hydration and Obstruction Effects. *J. Phys. Chem.* **1983**, *87*, 4756–4761.
- (24) Shigeta, K.; Olsson, U.; Kunieda, H. Correlation between Micellar Structure and Cloud Point in Long Poly(oxyethylene) $_n$ Oleyl Ether Systems. *Langmuir* **2001**, *17*, 4717–4723.
- (25) Fitzgerald, P. A.; Davey, T. W.; Warr, G. G. Micellar Structure in Gemini Nonionic Surfactants from Small-Angle Neutron Scattering. *Langmuir* **2005**, *21*, 7121–7128.
- (26) Ilgenfritz, G.; Schneider, R.; Grell, E.; Lewitzki, E.; Ruf, H. Thermodynamic and Kinetic Study of the Sphere-to-Rod Transition in Nonionic Micelles: Aggregation and Stress Relaxation in $C_{14}E_8$ and $C_{16}E_8/H_2O$ Systems. *Langmuir* **2004**, *20*, 1620–1630.
- (27) Glatter, O.; Fritz, G.; Lindner, H.; Brunner-Popela, J.; Mittelbach, R.; Strey, R.; Egelhaaf, U. S. Nonionic Micelles near the Critical Point: Micellar Growth and Attractive Interaction. *Langmuir* **2000**, *16*, 8692–8701.
- (28) Lindman, B.; Wennerstrom, H. Nonionic Micelles Grow with Increasing Temperature. *J. Phys. Chem.* **1991**, *95*, 6053–6054.
- (29) Velinova, M.; Sengupta, D.; Tadjer, A. V.; Marrink, S.-J. Sphere-to-Rod Transitions of Nonionic Surfactant Micelles in Aqueous Solution Modeled by Molecular Dynamics Simulations. *Langmuir* **2011**, *27*, 14071–14077.
- (30) Yu, Z.-J.; Neuman, R. D. Noncritical Behavior near the Cloud Point in Perfluorinated Ionic Micellar Solutions. *Langmuir* **1994**, *10*, 377–380.
- (31) Fournial, A.-G.; Zhu, Y.; Molinier, V.; Vermeersch, G.; Aubry, J.-M.; Azaroual, N. Aqueous Phase Behavior of Tetraethylene Glycol Decanoyl Ester (C_9COE_4) and Ether ($C_{10}E_4$) Investigated by Nuclear Magnetic Resonance Spectroscopic Techniques. *Langmuir* **2007**, *23*, 11443–11450.
- (32) Marszall, L. Effect of Aromatic Hydrotropic Agents on the Cloud Point of Mixed Ionic-Nonionic Surfactant Solutions. *Langmuir* **1990**, *6*, 347–350.
- (33) Borthakur, A.; Zana, R. Ultrasonic Absorption Studies of Aqueous Solutions of Nonionic Surfactants in Relation with Critical Phenomena and Micellar Dynamics. *J. Phys. Chem.* **1987**, *91*, 5957–5960.
- (34) Attwood, D. A Light-Scattering Study of the Effect of Temperature on the Micellar Size and Shape of a Nonionic Detergent in Aqueous Solution. *J. Phys. Chem.* **1968**, *76*, 339–345.
- (35) Lesemann, M.; Martin, A.; Belkoura, L.; Fleischer, G.; Woermann, D. Study of the Viscosity of Nonionic Surfactant/Deuterium Oxide Mixtures and of the Self-Diffusion Coefficient of the Surfactant Approaching the Liquid/Liquid Coexistence Curve. *Langmuir* **1997**, *13*, 5289–5293.
- (36) Komaromy-Hiller, G.; Wandruszka, R. Clouding of Nonionic Detergents: Energy Transfer to a Solubilized Probe. *J. Phys. Chem.* **1995**, *99*, 1436–1441.
- (37) Toerne, K.; Rogers, R.; Wandruszka, R. Thermal Stability of Nonionic Surfactant Aggregates. *Langmuir* **2001**, *17*, 6119–6121.
- (38) Phillies, G. D. J.; Yambert, E. Solvent and Solute Effects on Hydration and Aggregation Numbers of Triton X-100 Micelles. *Langmuir* **1996**, *12*, 3431–3436.
- (39) Molina-Bolivar, J. A.; Aguiar, J.; Ruiz, C. C. Growth and Hydration of Triton X-100 Micelles in Monovalent Alkali Salts: A Light Scattering Study. *J. Phys. Chem. B* **2002**, *106*, 870–877.
- (40) Kato, T.; Anzai, S.; Seimiya, T. Light Scattering from Semidilute Solutions of Nonionic Surfactants ($C_{12}E_5$ and $C_{12}E_8$) and the Scaling Law. *J. Phys. Chem.* **1990**, *94*, 7255–7259.
- (41) Kato, T.; Anzai, S.; Seimiya, T. Dynamic Light Scattering in Semidilute Solutions of Nonionic Surfactants: Entanglement of Elongated Micelles. *J. Phys. Chem.* **1987**, *91*, 4655–4657.
- (42) Kato, T.; Terao, T.; Tsukada, M.; Seimiya, T. Self-Diffusion Processes in Semidilute Solutions of Nonionic Surfactant ($C_{16}E_7$)

Studied by Light Scattering and Pulsed-Gradient Spin Echo Methods. *J. Phys. Chem.* **1993**, *97*, 3910–3917.

(43) Brown, W.; Johnsen, R.; Stilbs, P.; B. Lindman, B. Size and Shape of Nonionic Amphiphile ($C_{12}E_6$) Micelles in Dilute Aqueous Solutions as Derived from Quasielastic and Intensity Light Scattering, Sedimentation, and Pulsed-Field-Gradient Nuclear Magnetic Resonance Self-Diffusion Data. *J. Phys. Chem.* **1983**, *87*, 4548–4553.

(44) Gapinski, J.; Szymanski, J.; Wilk, A.; Kohlbrecher, J.; Patkowski, A.; Holyst, R. Size and Shape of Micelles Studied by Means of SANS, PCS, and FCS. *Langmuir* **2010**, *26*, 9304–9314.

(45) Guerrero-Martinez, A.; Montoro, T.; Vinas, M. H.; Gonzalez-Gaitano, G.; Tardajos, G. Study of the Interaction between a Nonyl Phenyl Ether and β -Cyclodextrin: Decoupling Nonionic Surfactant Solutions by Complexation. *J. Phys. Chem. B* **2007**, *111*, 1368–1376.

(46) Henriksson, U.; Jonstromer, M.; Olsson, U.; Soderman, O.; Klose, G. 2H NMR Study of Molecular Dynamics and Organization in the System $C_{12}E_4$ –Water. *J. Phys. Chem.* **1991**, *95*, 3815–3819.

(47) Jonstromer, M.; Jonsson, B.; Lindman, B. Self-Diffusion in Nonionic Surfactant–Water Systems. *J. Phys. Chem.* **1991**, *95*, 3293–3300.

(48) Yethiraj, A.; Capitani, D.; Burlinson, N. E.; Burnell, E. E. An NMR Study of Translational Diffusion and Structural Anisotropy in Magnetically Alignable Nonionic Surfactant Mesophases. *Langmuir* **2005**, *21*, 3311–3321.

(49) Stubenrauch, C.; Kleinschmidt, F.; Schmidt, C. Structural Evolution in the Isotropic Channel of a Water-Nonionic Surfactant System that has a Disconnected Lamellar Phase: A 1H NMR Self-Diffusion Study. *Langmuir* **2012**, *28*, 9206–9210.

(50) Elarum, exports of chemical products. Neonol. <http://elarum.com/info/standards/tu-2483-077-05766801-98/>.

(51) Archipov, V. P.; Potapova, E. F.; Antzutkin, O. N.; Filippov, A. V. Micelle Structure and Molecular Self-Diffusion in Isononylphenol Ethoxylate–Water Systems. *Magn. Reson. Chem.* **2013**, *51*, 424–430.

(52) Razina, I. S. *Colloidal Properties of the Reaction Medium on the Neonols and Bromide Basis for the Hydrolysis of Esters of Phosphorus Acids*. Ph.D. Thesis, Kazan National Research Technological University, Kazan, Russia, 2009.

(53) Tihova, A.; Gluhareva, N.; Kolesnikova, E. Study of Aggregation in Aqueous Solutions of Non-Ionic Ethoxylated Surfactants by Dynamic Light Scattering. *Sci. Bull. BelSU, Ser. Natur. Sci.* **2010**, *21*, 127.

(54) James, T. L.; McDonald, G. G. Measurement of the Self-Diffusion Coefficient of each Component in a Complex System Using Pulsed-Gradient Fourier-Transform NMR. *J. Magn. Reson.* **1973**, *11*, 58–61.

(55) *Microemulsions: Structure and Dynamics*; Friberg, S. E., Bothorel, P., Eds.; CRC Press, Inc.: Boca Raton: FL, 1988.

(56) Vass, S.; Grimm, H.; Banyai, I.; Meier, G.; Gilanyi, T. Slow Water Diffusion in Micellar Solutions. *J. Phys. Chem. B* **2005**, *109*, 11870–11874.

(57) Wyn, B.; Johnsen, R.; Stilbs, P.; Lindman, B. Size and Shape of Nonionic Amphiphile ($C_{12}E_6$) Micelles in Dilute Aqueous Solutions as Derived from Quasielastic and Intensity Light Scattering, Sedimentation, and Pulsed-Field-Gradient Nuclear Magnetic Resonance Self-Diffusion Data. *J. Phys. Chem.* **1983**, *87*, 4548–4553.

(58) Materna, K.; Szymanowski, J. Separation of Phenols from Aqueous Micellar Solutions by Cloud Point Extraction. *J. Colloid Interface Sci.* **2005**, *255*, 195–201.

(59) Materna, K.; Milosz, I.; Miesiac, I.; Cote, G.; Szymanowski, J. Removal of Phenols from Aqueous Streams by the Cloud Point Extraction Technique with Oxyethylated Methyl Dodecanoates as Surfactants. *Environ. Sci. Technol.* **2001**, *35*, 2341–2346.

(60) Bai, D.; Li, J.; Chen, S. B.; Chen, B. - H. A Novel Cloud-Point Extraction Process for Preconcentrating Selected Polycyclic Aromatic Hydrocarbons in Aqueous Solution. *Environ. Sci. Technol.* **2001**, *35*, 3936–3940.

(61) Yao, B.; Yang, L. Stirring-Assisted Cloud-Point Extraction of Polycyclic Aromatic Hydrocarbons. *Ind. Eng. Chem. Res.* **2008**, *47*, 3949–3956.

(62) Zhou, Z.; Chen, J.; Zhao, D.; Yang, M. Determination of Four Carbamate Pesticides in Corn by Cloud Point Extraction and High-Performance Liquid Chromatography in the Visible Region Based on Their Derivatization Reaction. *J. Agric. Food Chem.* **2009**, *57*, 8722–8727.

(63) Shevchenko, G.; Sjodin, M. O. D.; Malmstrom, D.; Wetterhall, M.; Bergquist, J. Cloud-Point Extraction and Delipidation of Porcine Brain Proteins in Combination with Bottom-Up Mass Spectrometry Approaches for Proteome Analysis. *J. Proteome Res.* **2010**, *9*, 3903–3911.

(64) Reffas, H.; Benabdallah, T.; Youcef, M. H.; Ilikti, H. Study on the Cloud Point Extraction of Copper(II) from an Aqueous Sulfate Medium with N,N' -Bis(salicylideneaminoethyl) Amine Polydentate Schiff Base into a Nonionic Surfactant Phase. *J. Chem. Eng. Data* **2010**, *55*, 912–918.

(65) Akita, S.; Takeuchi, H. Cloud-Point Extraction of Organic Compounds from Aqueous Solutions with Nonionic Surfactant. *Sep. Sci. Technol.* **1995**, *30*, 833–846.

(66) Akita, S.; Takeuchi, H. Equilibrium Distribution of Aromatic Compounds between Aqueous Solution and Coacervate of Nonionic Surfactants. *Sep. Sci. Technol.* **1996**, *31*, 401–412.

(67) Katsoyannos, E.; Chatzilazarou, A.; Gortzi, O.; Lalas, S.; Konteles, S.; Tataridis, P. Application of Cloud Point Extraction using Surfactants in the Isolation of Physical Antioxidants (Phenols) from Olive Mill Wastewater. *Fresenius Environ. Bull.* **2006**, *15*, 1122–1125.