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Dynamic and structural properties of oxyethylated isononylphenols

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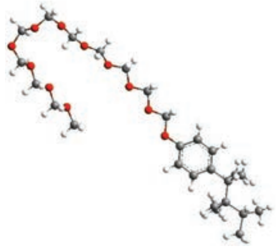
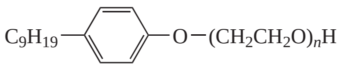
Diffusion coefficients, dielectric relaxation times and refraction coefficients were measured, and activation energies of translational and rotational mobilities were determined for a series of oxyethylated phenols (neonols AF9-*n*) *p*-$C_9H_{19}C_6H_4$-$O(CH_2CH_2O)_nH$, *n* = 4, 6, 8, 9, 10, 12, at different temperatures. The results demonstrated the existence of contraction and transition phenomena that changed the structure of neonol molecules at *n* ~ 9 from a zigzag to a meander form.



Oxyethylated isononylphenols (neonols AF9-*n*) *p*-$C_9H_{19}C_6H_4$-$O(C_2H_4O)_nH$ are effective nonionic surfactants (NSA).[1,2] An alkyl radical isononyl, C_9H_{19}, is attached to phenol principally in the *para* position relative to the hydroxyl group; *n* is the degree of oxyethylation. The hydrophilic properties of polyoxyethylene chains enable the solubility of neonols in water and polar solvents. Therefore, at *n* higher than 7, neonols are soluble in water and their solubility grows as the number of oxyethylene groups increases.[3]



It is known that lengthening the oxyethylene chain leads to a change in molecular conformation. At small *n*, the chains maintain their zigzag conformation. However, as the chain grows, it starts to fold, taking on the form of a meander. The so-called contraction of the chains occurs[4,5] due to the mutual attraction of oxygen atoms of the chain. For short chains, these forces are not sufficiently strong to cause contraction and the chain remains in the zigzag form. Thermodynamic calculations[5] showed that chain contraction should occur at $n \geqslant 9$. Experimental studies of NSA molecules prepared based on ethylene oxide have been performed by Raman and NMR spectroscopy.[6,7]

The influence on interface phenomena of oxyethylated isononylphenols with different degrees of oxyethylation and the colloidal chemical properties of oligomers and polymers has been discussed in detail earlier.[8] It has been shown that adsorption on interface borders, time of spreading, free surface energy, wetting ability and adhesion depend non-linearly on the length of the oxyethylene chain, reaching maximum value of *n* ~ 8, 9. Physical-chemical properties of oxyethylated surfactants, such as index of refraction, density, surface tension and viscosity also change non-linearly as *n* increases. The presence of extremes and change in the dependence of colloidal-chemical and physical-chemical properties of oxyethylated NSA molecules on the length of the oxyethylated chain may be evidence of contraction. Furthermore, in the absence of contraction, one can expect a change in the properties of NSA molecules (neonols) and their solutions as the number of oxyethylated groups increases in a molecule. In previous works we studied dynamic and structural properties of neonols in aqueous solutions.[9–11] In the present work properties of neonols were examined in neat substances (without solvent) to reveal contraction on growing the number of oxyethylene groups. Main attention was paid to dynamic properties, translational and rotational motion of neonol molecules. Techniques of NMR diffusometry, dielcometry and refractometry were used.[†]

Figure 1(*a*) shows the results of diffusion coefficient measurements of neonols at different temperatures. All curves contain a break near *n* = 9. If the chains of the neonol molecules maintain

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[†] The self-diffusion coefficients *D* of the neonols were measured by NMR spin-echo[12] on a Tesla BS567A NMR spectrometer (100 MHz for ^{1}H) equipped with a pulsed field gradient unit.[13] The maximum value of the pulsed field gradient *G* was 0.5 T m^{-1}. Spectra were recorded without accumulation, NS = 1, but measurements were repeated several times at different diffusion times. All diffusion decays were single-exponential. *D* measurement error did not exceed 3%. Measurements were performed in the temperature range 30–90 °C with an error in the temperature stabilization not higher than 0.5 °C.

Dielectric measurements were performed in the frequency range of 10^6–10^9 Hz and in the temperature range of 0–25 °C on a BDS Concept-80 (Novocontrol) dielectric spectrometer with an automatic temperature control, cryosystem QUATRO with precision ±0.5 °C. The cell was in the form of a plate-parallel capacitor with 10-mm diameter electrodes and a 0.5-mm gap between the electrodes. Precision in the measurements of complex dielectric permittivity was ±3%. Dielectric spectra were fitted by the Havriliak–Negami function.[14] Dielectric relaxation times were calculated using WinFIT software.[15]

Refraction indices of pure neonols were measured on an RPL-3 refractometer with absolute error not larger than 0.0002. Measurements were performed at ~23 °C. Calibration was carried out on distilled water with a refraction index of 1.333.

Neonols AF9-4, AF9-6, AF9-8, AF9-9, AF9-10 and AF9-12 were produced in Nizhnekamskneftekhim chemical plant[1] and used as purchased. Figure S1 (see Online Supplementary Materials) shows the NMR spectrum of neonol AF9-6 solution in $CDCl_3$ at room temperature. Some physical properties of neonols are presented in Figure S2.

an elongated zigzag regardless of the number of oxyethylene groups, the length and effective diameter of the molecules should change. Consequently, decrease in the D of neonol molecules also should be plane. The presence of these breaks proves a change in the mode of translational motion of the neonol molecules as the polyoxyethylene chain length increases. It can be suggested that near $n = 9$ a transition occurs from zigzag to coiled (a type of meander) form of the polyoxyethylene chain. At the same time, the effective size of the molecule increases with n, while the degree of this dependence changes as well as the diffusion coefficient. Thus, the presence of breaks in the dependence of D of neonols on the number of oxyethylene groups near $n = 9$ may be evidence of contraction.

Rotational mobility, as well as translational mobility, is sensitive to changes in the shape and size of molecules. A parameter related to rotational mobility of molecules is dielectric relaxation. The time of dielectric relaxation τ can be used to obtain more information than self-diffusion coefficients about the change in the shape of molecules. Figure 1(*b*) shows the time of dielectric relaxation of pure neonols at temperatures from 0 to 25 °C. A distinct ‘step’ on the dependences on the number of oxyethylene groups at $n = 9$ is observed for all temperatures.

The dependence of refraction index on n provides additional evidence of conformational changes occurring in neonol molecules with increasing the number of oxyethylene chains. The refraction index of a substance is determined by the polarizability of molecules and their concentration. The density of a liquid typically decreases on raising the temperature; therefore, the refraction index also decreases. The polarizability of molecules is determined by their structure. Therefore, for neonol molecules in the absence of conformational changes, it is expected that a change of refraction indices on raising n would occur. Results of measuring refraction indices of the neonols are shown in Figure 1(*c*). Similarly to previous dependences of D on the number of oxyethylene groups, there is a clear break near $n = 9$. In the absence of sufficient variations in the density of the media, such a break can be explained only by a difference in the molecular conformations.

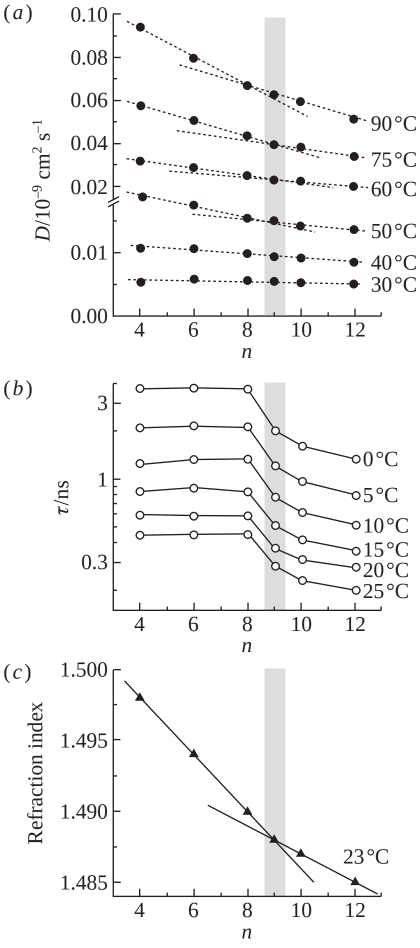

Figure 1 (*a*) Diffusion coefficients, (*b*) dielectric relaxation time and (*c*) refraction indices of neonols AF9-4, AF9-6, AF9-8, AF9-9, AF9-10 and AF9-12 *vs*. the number of oxyethylene groups n at indicated temperatures.

According to the Eyring’s theory of the absolute rates of reactions, the translational and rotational motions of molecules represent jumps through corresponding energy barriers. A characteristic parameter of the transition process from one ‘equilibrium’ state to another is the activation energy. The energy of activation for diffusion (energy of activation of translational displacement of molecules):

$$\Delta E_D = -\frac{\partial \ln D}{\partial (1/RT)}, \tag{1}$$

and energy of activation for dipolar relaxation (energy of activation of reorientation of dipolar moments of molecules):

$$\Delta E_\tau = -\frac{\partial \ln \tau}{\partial (1/RT)}. \tag{2}$$

Results of calculation of the activation energies ΔE_D and ΔE_τ depending on the number of oxyethylene groups in neonol molecules at different temperatures are shown in Figure S3 (Online Supplementary Materials). Both activation characteristics of translational and rotational motions of neonol molecules depend on temperature, which is usually observed for highly viscous liquids. The high viscosity values of pure neonols (~10^2–10^3 cP at room temperature) and their ability to associate lead to the phenomenon of temperature-dependent activation energy for pure neonols. Values of activation energies ΔE_D and ΔE_τ decrease with elongation of the polyoxyethylene chain of neonol molecules. These dependences as well as dependences of D and τ on n are not smooth but contain a break near $n = 9$. The presence of breaks in the dependences of ΔE_D and ΔE_τ on the length of the neonol molecules is also an evidence that near $n = 9$ a change in the character of the translational and rotational motion of neonol molecules occurs.

Really, neonols are not spherical molecules. However, we can estimate hydrodynamic radii of neonol molecules using experimental values of diffusion coefficients D and coefficients of dynamic viscosity[8] η from the Einstein–Stokes relation:

$$D = \frac{kT}{6\pi\eta R}, \tag{3}$$

where k is the Boltzmann constant, T is the temperature. The Einstein–Stokes model can be applied to diffusion of relatively large particles in a continuous viscous media. Our systems do not satisfy this model, anyway, we apply it as a very rough approach just for estimation. The results of calculations are presented in Figure S4. Note that near $n = 9$, the initial increase in the hydrodynamic radius is followed by its decrease, which also proves the occurrence of the contraction phenomenon in neonol molecules.

Thus, in the homologic series of oxyethylated isononylphenols (neonols AF9-n, n = 4, 6, 8, 9, 10, 12), their coefficients of diffusion and dielectric relaxation times were measured, and their hydrodynamic radii as well as energies of activation of translational and rotational motions were calculated. The results obtained provide evidence of contraction phenomena and transition from zigzag to meander shape of molecules near $n = 9$.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.07.030.

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