Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2016, **26**, 355–357
Mendeleev Communications

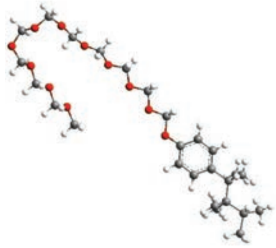
Dynamic and structural properties of oxyethylated isononylphenols

Victor P. Arkhipov,[a] Svetlana A. Bogdanova,[a] Zamil Sh. Idiyatullin,[a]
Ivan V. Lunev[b] and Andrei V. Filippov*[b,c]

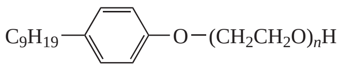
[a] *Kazan National Research Technological University, 420015 Kazan, Russian Federation*
[b] *Institute of Physics, Kazan (Volga Region) Federal University, 420008 Kazan, Russian Federation.*
Fax: +7 843 231 5189; e-mail: Andrey.Filippov@kpfu.ru
[c] *Chemistry of Interfaces, Luleå University of Technology, SE-97187 Luleå, Sweden*

DOI: 10.1016/j.mencom.2016.07.030

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

---

[†] The self-diffusion coefficients *D* of the neonols were measured by NMR spin-echo[12] on a Tesla BS567A NMR spectrometer (100 MHz for ^1H) 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.