Experimental report

24/10/2024

Proposal:	**9-11-2009**	**Council:**	4/2020

Title: Microphase separation in double networks comprised of polymer and micellar chains

Research area: Chemistry

This proposal is a resubmission of 9-11-1962

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Samples: $(C_{18}H_{30}O_{15})_n + C_{18}H_{33}OK + C_{11}H_{26}NBr$

Instrument	Requested days	Allocated days	From	To
D11	3	2	02/06/2021	04/06/2021

Abstract:

Aim of the experiment is to investigate the structure of the novel systems - double interpenetrating networks of polymer chains and wormlike surfactant micelles. Surfactant molecules can self-assemble and form long wormlike micelles. They can form an entangled network what imparts viscoelastic properties to solutions. These properties can be greatly enhanced if polymer chains are introduced. Polymer molecules can be cross-linked by dynamic bonds and form a second independent network, inside of which a first network of wormlike micelles remains. Such systems combine high mechanical properties superior to the properties of the components, and high responsiveness to external factors (e.g., addition of oil or change of pH) due to labile character of bonds in all two networks. The project is aimed at studying microphase separated structure of double polymer-micellar networks, consisting in the formation of micellar-rich or polymer-rich domains of several hundreds of nanometers. Size and shape of such domains can be elucidated only by ultra-low q SANS, accessible at the D11 instrument.

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Aim. The aim of the performed experiment was to investigate the nano- and microstructure of the double dynamic hydrogels formed by wormlike surfactant micelles and polymer chains, and to correlate the structure in a wide spacial range with the practically important mechanical properties of the hydrogels, by employing ultra-small angle neutron scattering (USANS).

Samples. The study was performed on an example of mixed wormlike surfactant micelles formed by a long-chain anionic surfactant (potassium oleate) and a short-chain cationic surfactant (n-octyltrimethylammonium bromide, C8TAB). These two surfactants form viscoelastic solutions with long wormlike micelles at the conditions of the experiment (at 1.5 to 5 wt% potassium oleate and the molar ratios of C8TAB to oleate in the range of 0.3 – 0.6). Two polymers were employed - synthetic (polyvinyl alcohol, PVA, M.W. = 27000) or natural (hydroxypropyl guar, HPG, M.W. = 1600000). PVA was cross-linked into a network by dynamic covalent bonds formed by borate ions. HPG was not additionally cross-linked and formed an entangled network. Hydrogels were prepared by dissolving surfactants and polymers in D_2O, mixing the stock solutions in appropriate ratios, and then adding the cross-linker in the case of PVA.

Measurements. The structure was investigated in a wide q-range of 7.63×10^{-4} to 0.65 $Å^{-1}$ by using the D11 instrument at ILL with the sample-to-detector distances of 1.7 m, 16 m and 38 m. The wavelengths used were 4.6 Å at 1.7 m and 16 m; and 13 Å at 38 m, with a full width-half maximum (FWHM) wavelength spread of 9%. Calibration to absolute scale was performed using H_2O. Raw data were corrected for transmission and background scattering.

Results on PVA/surfactant mixtures. Fig. 1a shows the USANS scattering curves of the samples without polymer and with different concentrations of the cross-linked PVA. In the absence of polymer, the scattering curve is typical for the strongly charged WLMs with a wide structural peak at q around 0.05 $Å^{-1}$ arising from electrostatic interactions between the micelles. Indeed, the micelles were prepared in the absence of low molecular weight salt and at the excess of the anionic surfactant, which results in a strong electrostatic contribution to scattering at low q and the absence of the $I \sim q^{-1}$ dependence characteristic of cylinders. When the polymer is added, a strong upturn of intensity is observed at ultra-low q values. Since the scattering of micelles in the mixed system is much (by a factor of 10-100) stronger than of the polymer, this upturn is attributed to the change in the structure of the micellar network. In particular, as evidenced by cryo-transmission microscopy (cryo-TEM) micrographs, microphase separation occurs in the mixed polymer/surfactant system, and surfactant-rich and polymer-rich microdomains are formed. The upturn of intensity is a signature of the formation of these domains enriched by surfactants. Since the size of the domains is more than 100 nm, USANS is a unique method which allowed obtaining the proof of the microphase separated structure, which is not possible by conventional SANS.

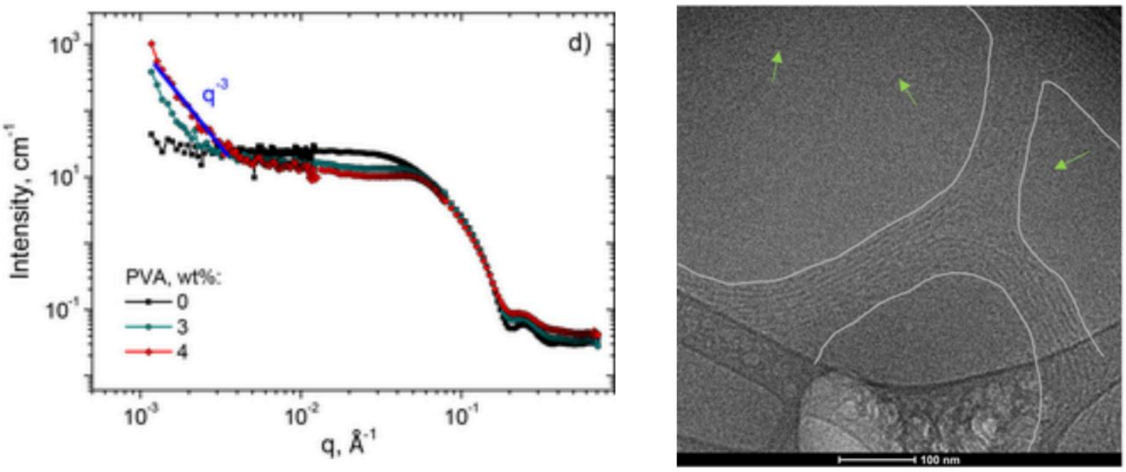

Fig. 1. a) USANS curves for cross-linked #PVA/potassium oleate/C8TAB system in D2O in the presence of increasing amounts of PVA: 0 wt% (squares), 3 wt% (circles), 4 wt% (diamonds) at 20 °C. Concentrations: 2.5 wt% potassium oleate, 0.8 wt% C8TAB, molar fraction of potassium borate with respect to PVA repeat units − 0.02.
b) Cryo-TEM pictures of cross-linked PVA/potassium oleate/C8TAB systems with 4 wt% PVA, molar fraction of potassium borate with respect to PVA repeat units − 0.02, 1.25 wt% oleate, 0.4 wt% C8TAB. The boundaries of some surfactant-rich microdomains are marked by white lines, short rods are indicated by arrows.

Results on HPG/surfactant mixtures. Fig. 2a shows the USANS scattering curves of the samples without and with different concentrations of HPG. In the absence of polymer, the scattering curve is the same presented in Fig. 1a. In the presence of HPG, a strong upturn is seen, which is due to the same effect as for PVA – microphase separation between polymer and micellar chains. This is proven by the scattering curves in the Holtzer representation (Fig. 2b).

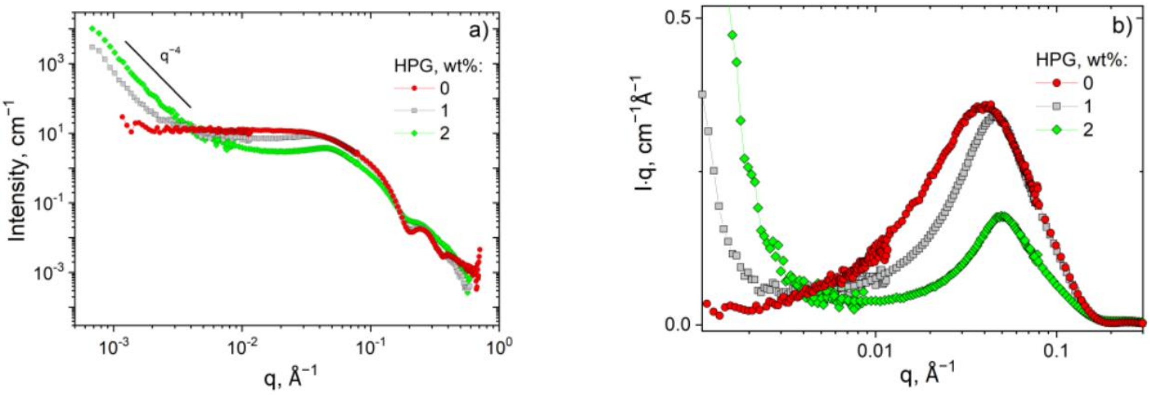

Fig. 2. USANS curves in (a) I vs. q and (b) I·q vs. q (Holtzer plot) representations for HPG/potassium oleate/C8TAB systems in D_2O containing 2.5 wt% potassium oleate, 0.8 wt% C8TAB and different concentrations of the HPG: 0 (red circles), 1 (grey squares), and 2 wt% (green diamonds)

When the scattering curves are plotted in this representation, a structural peak is well seen, which arises due to electrostatic repulsions between the micelles. The position of the peak is inversely proportional to the mean distance between the micelles. When HPG is added, the peak shifts to higher q values, meaning that the distance between the micelles decreases. This supports the hypothesis that wormlike micelles are expelled to their microphase domains, which results in the increase of the local concentration of the micelles.

Publications as a result of the experiment:

[1]A.V. Shibaev, A.I. Kuklin, V.N. Torocheshnikov, A.S. Orekhov, S.Roland, G. Miquelard-Garnier, O. Matsarskaia, I. Iliopoulos, O.E. Philippova. Double dynamic hydrogels formed by wormlike surfactant micelles and cross-linked polymer. **J. Colloid Interface Sci.** (2022) 611, 46, https://doi.org/10.1016/j.jcis.2021.11.198

[2] S. Roland, G. Miquelard-Garnier, A.V. Shibaev, A.L. Aleshina, A. Chennevière, O. Matsarskaia, C. Sollogoub, O.E. Philippova, I. Iliopoulos. Dual transient networks of polymer and micellar chains: Structure and viscoelastic synergy. **Polymers** (2021) 13, 4255, https://doi.org/10.3390/polym13234255

[3] The experimental data are available at: https://doi.org/10.5291/ILL-DATA.9-11-2009