Viscoelastic Synergy and Microstructure Formation in Aqueous Mixtures of Nonionic Hydrophilic Polymer and Charged Wormlike Surfactant Micelles

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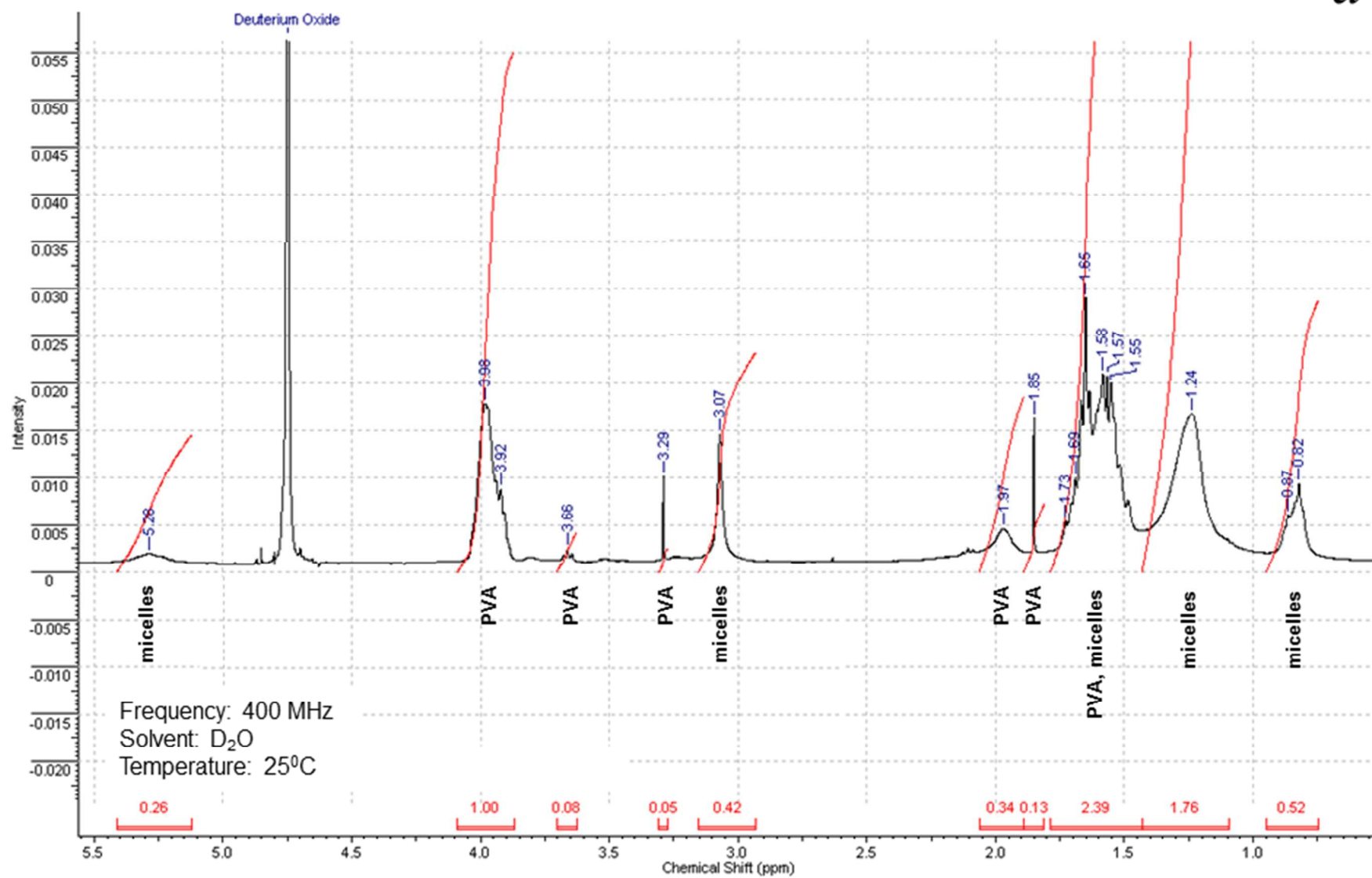[b] *Joint Institute for Nuclear Research, 141980 Dubna, Russia,*

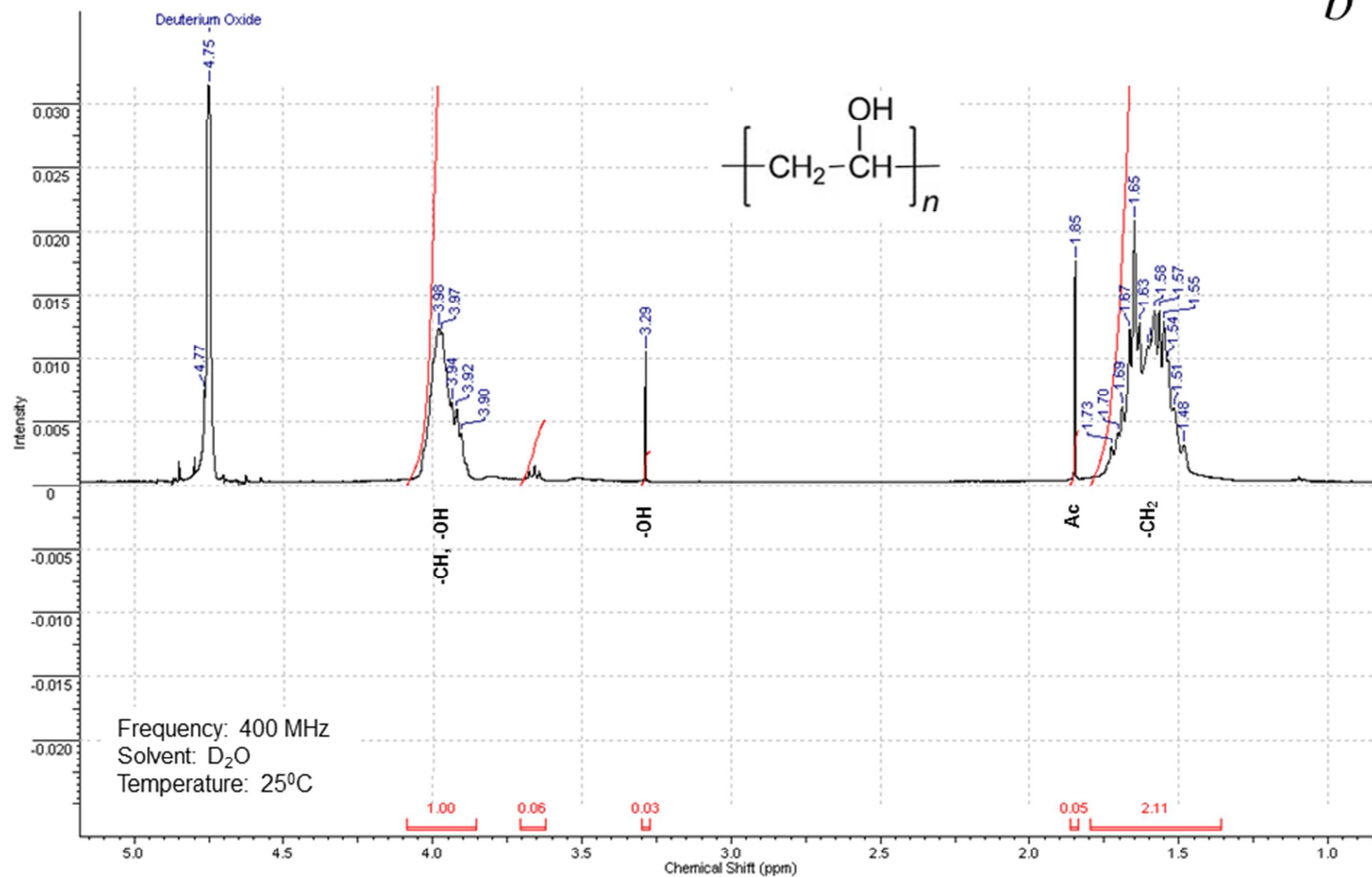[c] *National Research Centre "Kurchatov Institute", 123182 Moscow, Russia*

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SUPPORTING INFORMATION

A. NMR Data. NMR-measurements were carried out at Agilent 400 MR spectrometer. The spectra were recorded at 25^0C and accumulated from 8 scans.

^{1}H NMR spectra of solution of poly(vinyl alcohol) (PVA) - potassium oleate/n-octyltrimethylammonium bromide (C_8TAB) in D_2O and of its constituents (polymer and surfactants solutions separately) are presented on Figure 1S. The peak assignments are indicated on the spectra.
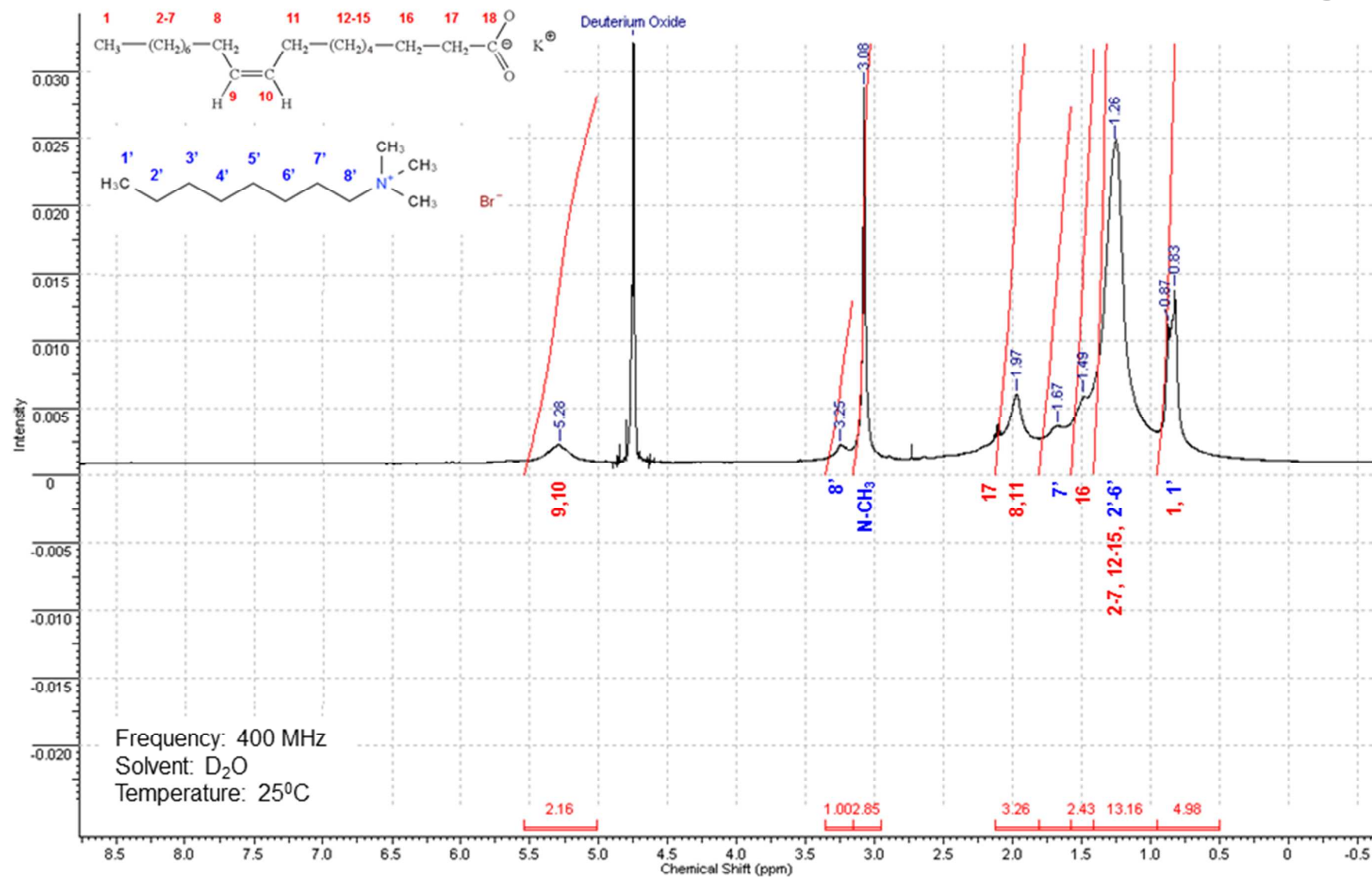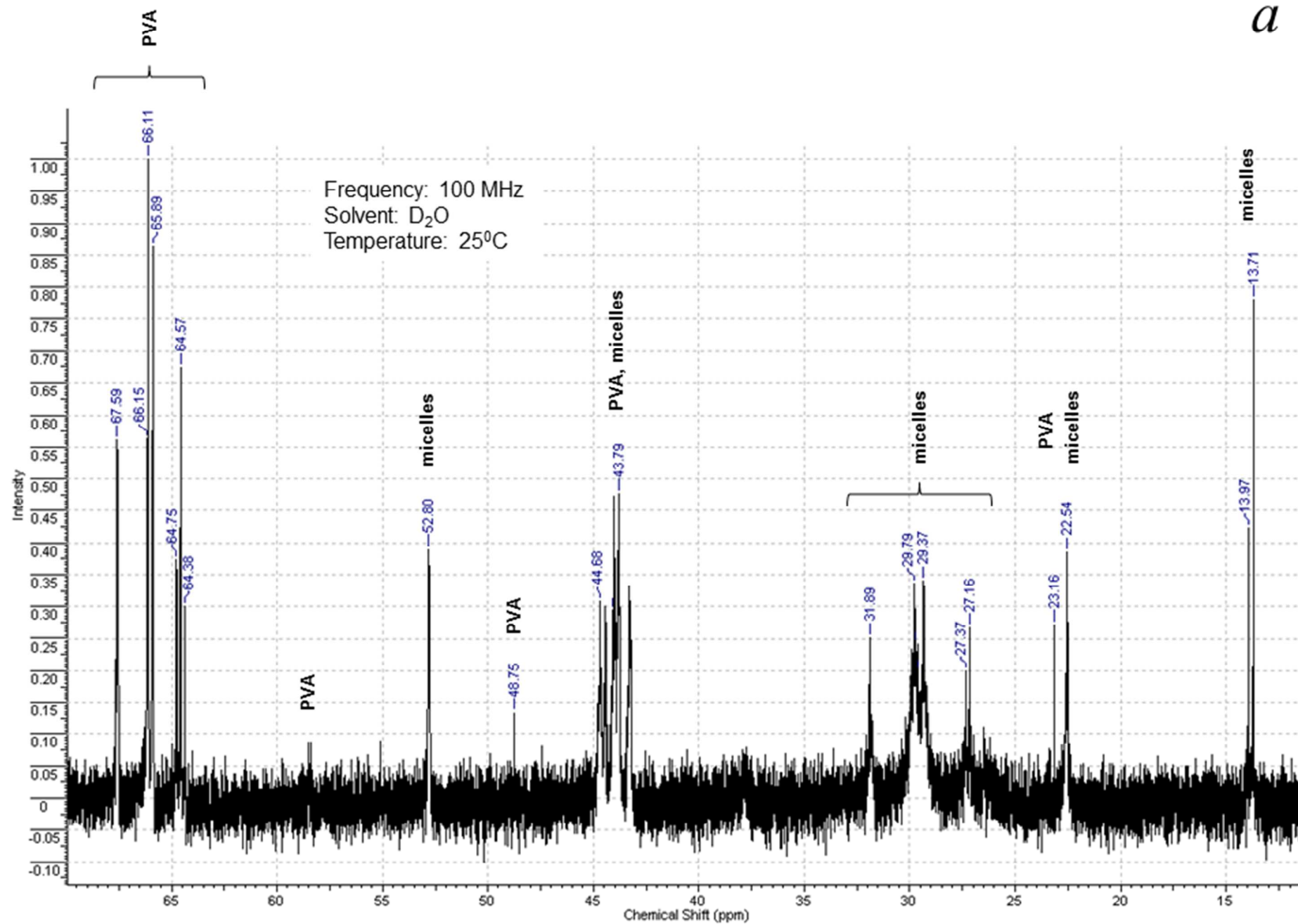
a

Deuterium Oxide

micelles PVA PVA PVA micelles PVA PVA PVA, micelles micelles micelles

Frequency: 400 MHz
Solvent: D_2O
Temperature: 25^0C

5.28 3.98 3.92 3.66 3.29 3.07 1.97 1.85 1.73 1.69 1.65 1.58 1.57 1.55 1.24 0.87 0.82

0.26 1.00 0.08 0.05 0.42 0.34 0.13 2.39 1.76 0.52

Chemical Shift (ppm)
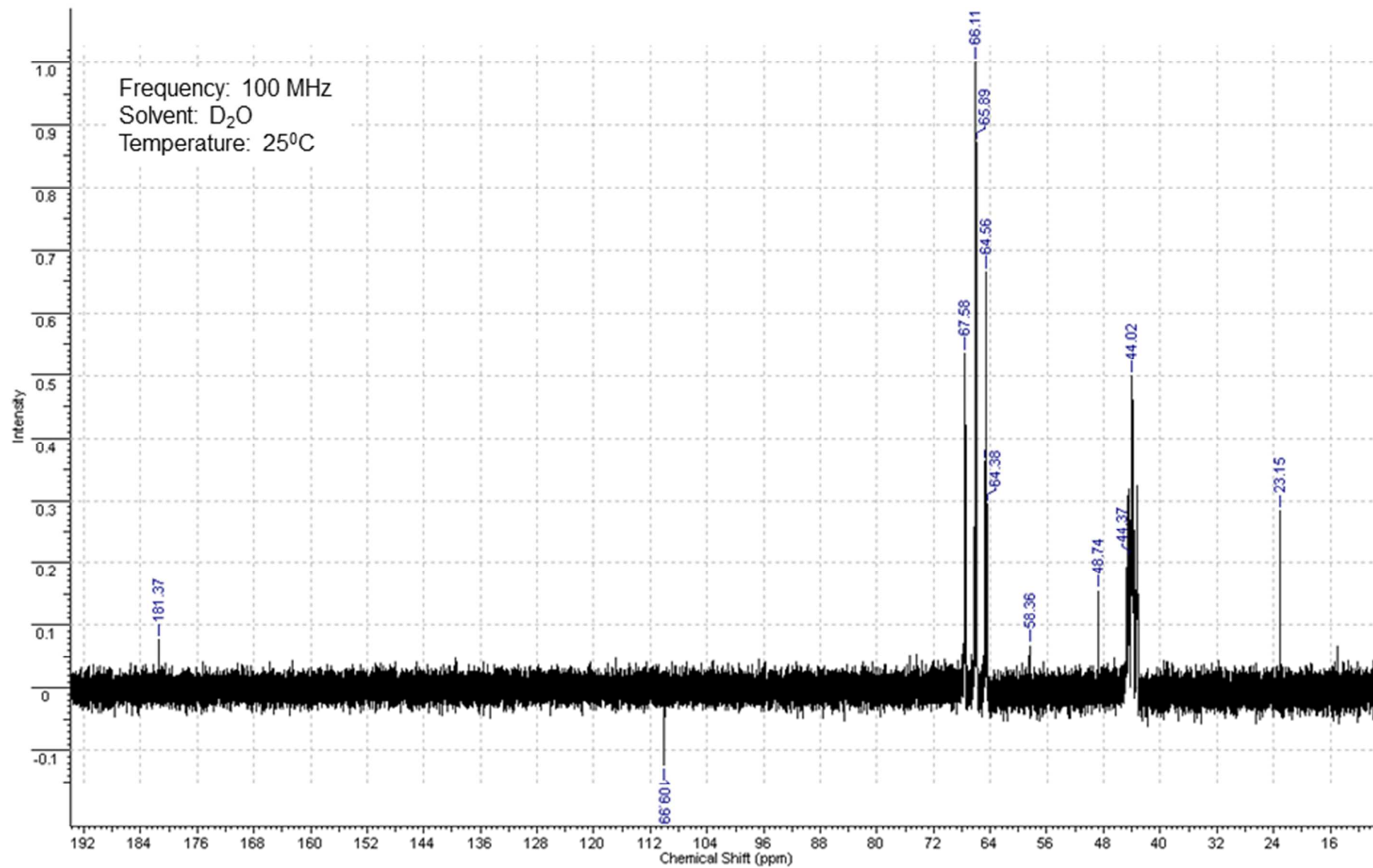
2

Frequency: 400 MHz
Solvent: D$_2$O
Temperature: 25^{0}C

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Figure 1S. ^{1}H NMR spectra of (a) solution containing 2 wt % PVA and 1.6 wt % potassium oleate/C_8TAB (molar ratio [potassium oleate]/[C_8TAB] = 2.5) in D_2O, (b) 2 wt % solution of PVA in D_2O, and (c) 1.6 wt % solution of potassium oleate/C_8TAB (molar ratio [potassium oleate]/[C_8TAB] = 2.5) in D_2O at 20^0C. The assignment of different peaks in PVA spectrum were done by using the results of Petit and Zhu [Petit, J.-M.; Zhu, X. X. ^{1}H and ^{13}C NMR Study on Local Dynamics of Poly(vinyl alcohol) in Aqueous Solutions. *Macromolecules* **1996**, *29*, 2075-2081], whereas the assignments of peaks in potassium oleate/C_8TAB spectrum were made on the basis of the data presented on www.chemicalbook.com (SpectrumEN_143-18-0_1HNMR and SpectrumEN_2083-68-3_1HNMR, respectively).

From Figure 1S it is seen that the chemical shifts in the spectrum of polymer-surfactants mixture do not differ from those in the spectra of polymer and surfactants taken separately.

^{13}C NMR spectra of solution of PVA - potassium oleate/C_8TAB in D_2O as well as of PVA and surfactants solutions individually are presented on Figure 2S. Similar to the case of ^{1}H NMR spectra, it is seen that the chemical shifts in the spectrum of polymer-surfactants mixture do not differ from those in the spectra of polymer and surfactant taken separately. The absence of any chemical shift changes upon mixing of polymer and surfactant indicates that there is no strong attraction between them.
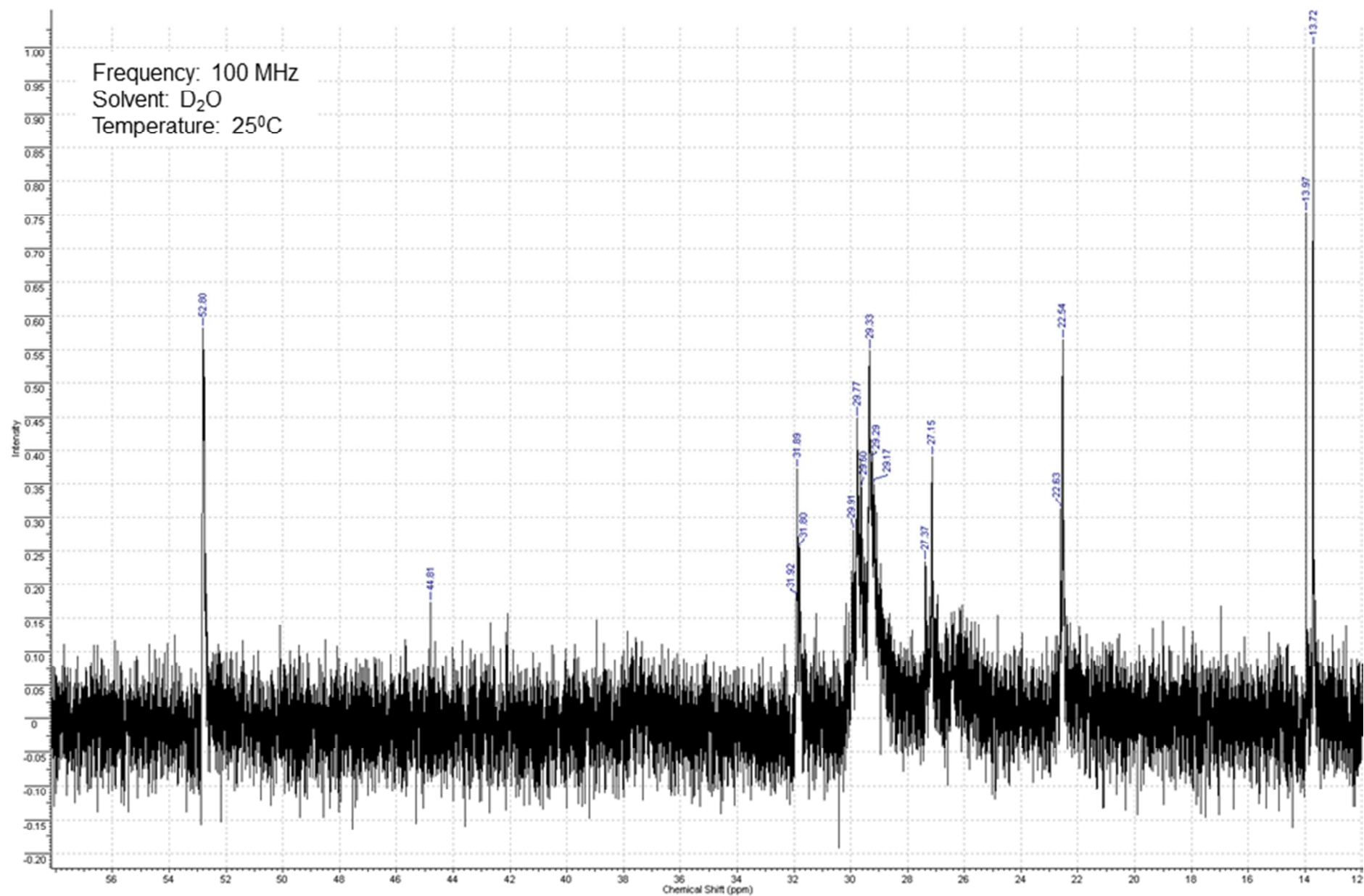
a

Frequency: 100 MHz
Solvent: D_2O
Temperature: 25^0C

b

Frequency: 100 MHz
Solvent: D$_2$O
Temperature: 25^{0}C

c

Frequency: 100 MHz
Solvent: D₂O
Temperature: 25⁰C

Figure 2S. ^{13}C NMR spectra of (a) solution containing 2 wt % PVA and 1.6 wt % potassium oleate/C$_8$TAB (molar ratio [potassium oleate]/[C$_8$TAB] = 2.5) in D$_2$O, (b) 2 wt % solution of PVA in D$_2$O, and (c) 1.6 wt % solution of potassium oleate/C$_8$TAB (molar ratio [potassium oleate]/[C$_8$TAB] = 2.5) in D$_2$O at 20^{0}C.

B. Determination of Critical Micelle Concentration (cmc). The effect of PVA on cmc value in the mixture of anionic surfactant potassium oleate and cationic surfactant C$_8$TAB (at molar ratio [potassium oleate]/[C$_8$TAB] = 2.5) was studied by fluorescence spectroscopy with pyrene as a probe. The fluorescence spectroscopy measurements were performed with the Perkin Elmer LS-55 spectrofluorimeter using 5 and 1.5 nm bandpass settings for excitation and emission, respectively. The excitation wavelength was 338 nm. Pyrene obtained from Fluka was recrystallized three times from absolute ethanol. Solutions for fluorescence measurements were prepared by first pipetting 0.012 ml of pyrene stock solutions (2×10^{-4} mol/l in ethanol). Then, 3 ml of polymer solution of a given concentration was added to the flask and stirred for 1 day before the fluorescence measurements were made.

The ratio of the first (371 nm) to the third (383 nm) vibronic peaks in fluorescence spectra of pyrene I_1/I_3 is known to be quite sensitive to the polarity of its microenvironment [Kalyanasundaram, K.; Thomas, J. K. Environmental Effects on Vibronic Band Intensities in Pyrene Monomer Fluorescence and their Application in Studies of Micellar Systems. *J. Am. Chem. Soc.* **1977**, *99*, 2039-2044]. The formation of micelles and the penetration of hydrophobic pyrene molecules in their cores leads to the drop of the polarity parameter I_1/I_3, and the cmc value can be determined as an inflexion point of the curve depicting I_1/I_3 as a function of the surfactant concentration. Figure 3S shows the dependence of the polarity parameter I_1/I_3 of pyrene on the concentration of surfactants in potassium oleate/ C$_8$TAB solution (at molar ratio [potassium oleate]/[C$_8$TAB] = 2.5) in the absence and in the presence of 4 wt% PVA. It is seen that at these conditions, the polymer does not affect the inflexion point of the curve, i.e.

it does not influence the cmc value. This observation implies that there is no attractive interactions between polymer and surfactant micelles.
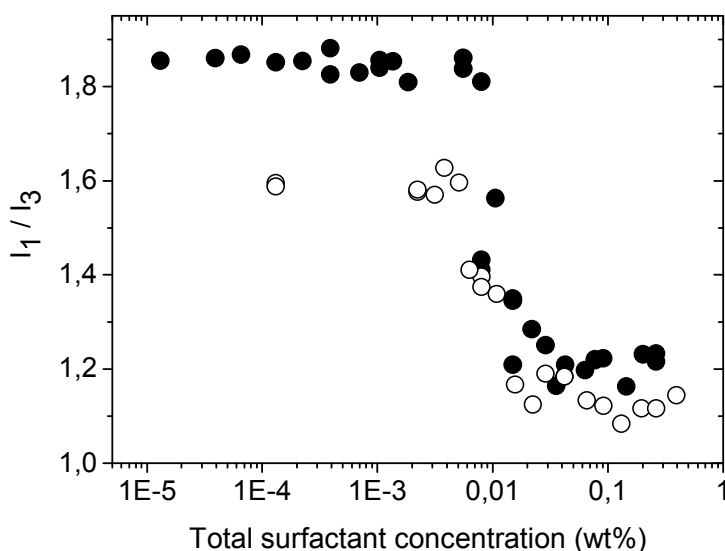

Figure 3S. Dependence of the polarity parameter of pyrene I_1/I_3 on the concentration of surfactants in potassium oleate/C_8TAB solution in the absence (filled symbols) and in the presence (open symbols) of 4 wt% PVA at 20^0C. Molar ratio [potassium oleate]/[C_8TAB] = 2.5.

C. Rheology of Surfactant Mixture. Below we present some rheological data for pure surfactant mixture (without added polymer). From Figure 4S it is seen that for potassium oleate/C_8TAB aqueous solutions at molar ratio [potassium oleate]/[C_8TAB] = 2.5 the C* concentration corresponding to the onset of sharp rise of viscosity is of ca. 2 wt%. Therefore, 3.3 wt% surfactant concentration, at which the effect of polymer on the rheological properties of surfactant solutions was studied, belongs to semi-dilute regime.
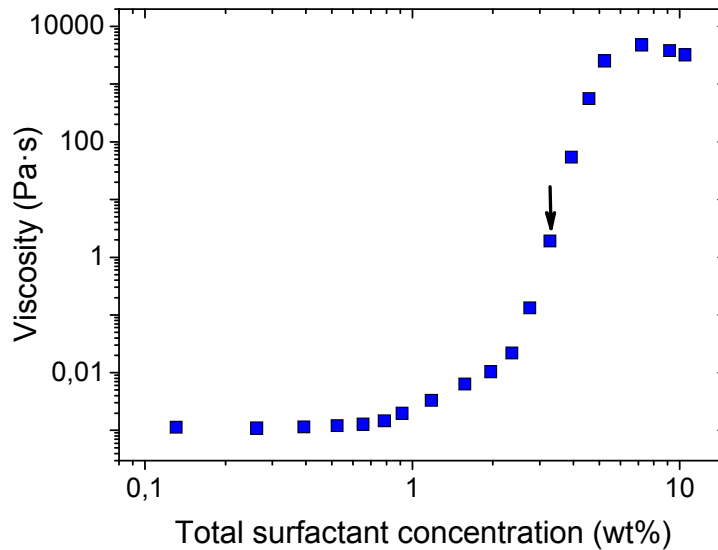
Figure 4S. Dependence of zero-shear viscosity on the total surfactant concentration for aqueous potassium oleate/C_8TAB solutions at 20^0C. Molar ratio [potassium oleate]/[C_8TAB] = 2.5. The viscosity value at 3.3 wt% surfactant concentration, at which the effect of polymer on the rheological properties of surfactant solutions was studied, is marked by arrow.

At the same time, at this concentration, there is no plateau on the frequency dependence of the storage modulus (Figure 5S a), which would be the signature of entanglements. Therefore, the studied surfactant concentration (3.3 wt%) corresponds to unentangled semi-dilute solution. Cole-Cole plot (Figure 5S b) with significant deviation from a semi-circle suggests that at these conditions, the length of micelles is not long enough to provide a Maxwell behavior with a single relaxation time.
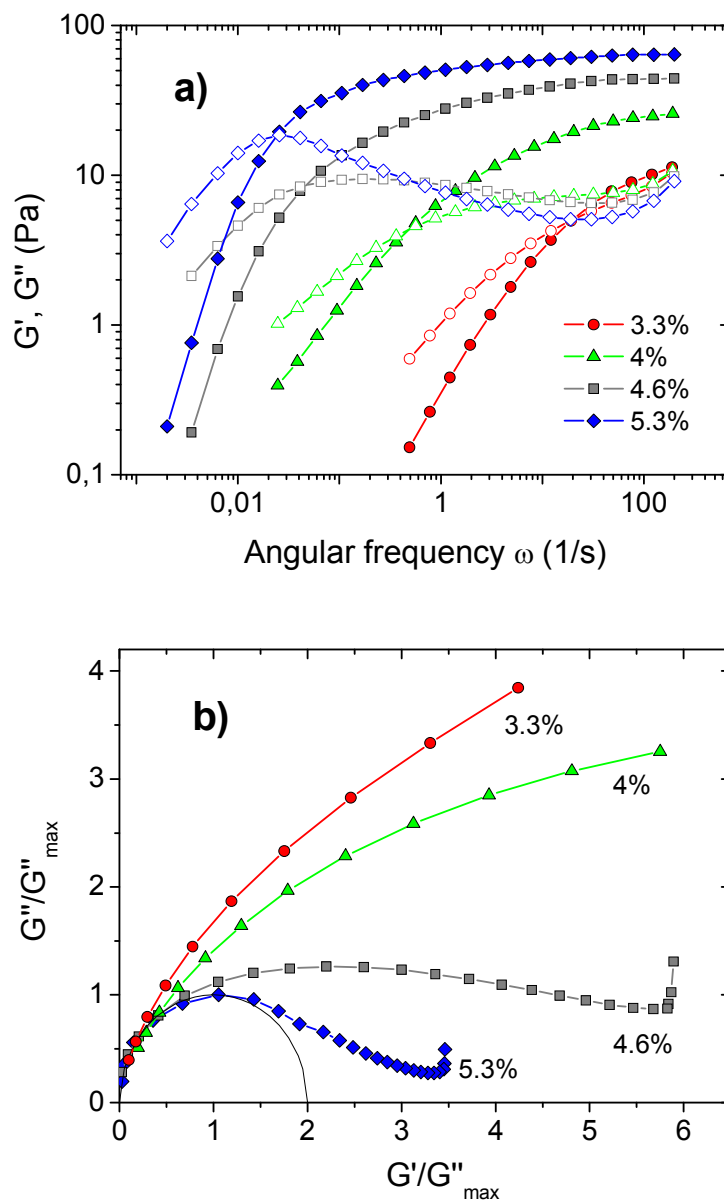
Figure 5S. (a) Frequency dependences of storage G′ (filled symbols) and loss G″ (open symbols) moduli and (b) normalized Cole-Cole plots for potassium oleate/C_8TAB aqueous solutions at different total surfactant concentrations: 3.3 wt% (circles), 4 wt% (triangles), 4.6 wt% (squares), 5.3 wt% (diamonds) at 20^0C. Molar ratio [potassium oleate]/[C_8TAB] = 2.5.

D. SANS Data. The SANS data were obtained in an absolute scale. For this aim, a vanadium standard was installed in front of each detector and it was introduced into the beam for calibration measurement

together with the sample under investigation keeping its own position. For each sample, two kinds of measurements were performed: determination of the scattered intensity for the sample alone and for the sample and vanadium exposed to the beam together. After easy treatment of the data [Ostanevich, Y. M. Time-of-Flight Small-Angle Scattering Spectrometers on Pulsed Neutron Sources. *Makromol. Chem., Macromol. Symp.* **1988**, *15*, 91-103; Kuklin, A.I.; Islamov, A. X.; Kovalev, Yu. S.; Utrobin, P. K.; Utrobin, V. I. Optimization of Two-Detector System of Small-Angle Neutron Spectrometer for Study of Nanoobjects. *Surface* **2006**, *6*, 74-83], the intensity scale is obtained in absolute units (cm^{-1}). The average error of these measurements is a few percent of the intensity value.

Figures 6S and 7S show the scattering patterns for polymer and surfactant solutions taken separately. Figure 6S represents the scattering pattern for 4 wt % PVA solution in D_2O. It shows a power-law behavior with an exponent -2 characteristic for random walk configuration of a chain in θ-solvent [Dreiss, C. A. Wormlike Micelles: where Do we Stand? Recent Developments, Linear Rheology and Scattering Techniques. *Soft Matter* **2007**, *3*, 956−970].
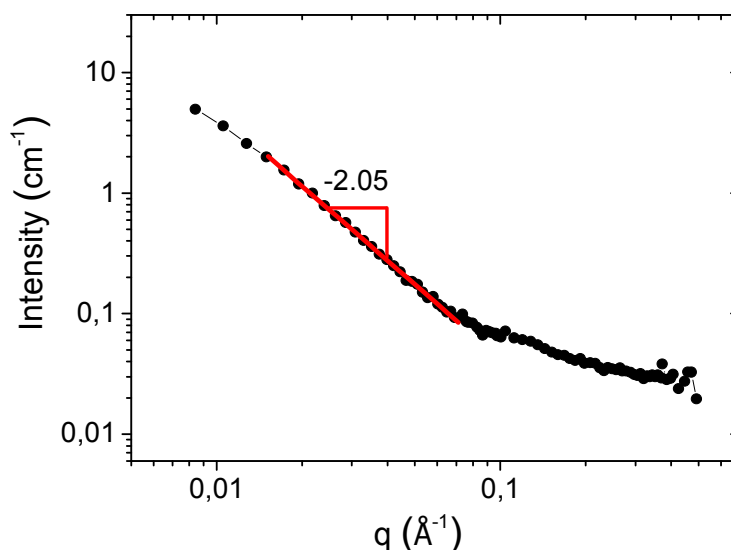

Figure 6S. Scattering pattern for 4 wt % solution of PVA in D_2O. Solid line has the slope - 2.05.
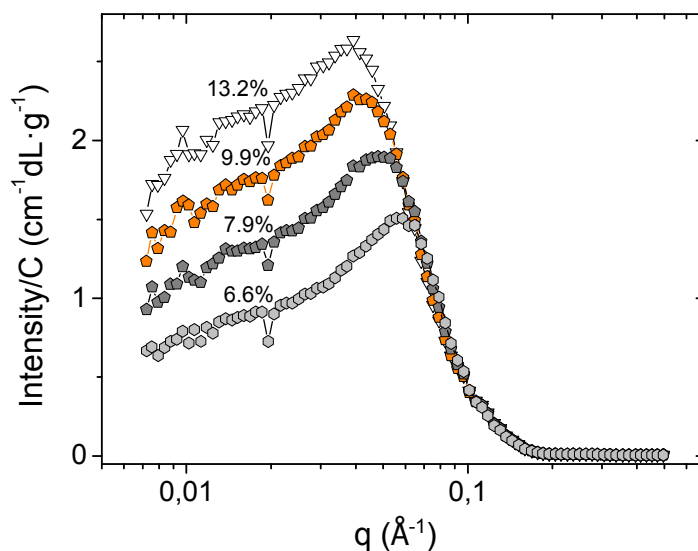
Figure 7S. Normalized scattering curves I/C in semi-logarithmic presentation for potassium oleate/C_8TAB solutions of different concentrations in D_2O: 6.6 wt % (light grey hexagons), 7.9 wt % (grey pentagons), 9.9 wt % (orange pentagons), 13.2 wt % (open reverse triangles). Molar ratio [potassium oleate]/[C_8TAB] = 2.5.

Figure 7S shows lin-log scattering curves for potassium oleate/C_8TAB solutions in D_2O. The curves are normalized with respect to surfactant concentration. It is seen that all solutions have a structure peak, which can be attributed to repulsive interactions between similarly charged micellar chains.

Figure 8S represents scattering curves of the mixed polymer-surfactant system and of its polymer and surfactant components taken separately at the same concentration as in the mixture. Also, Figure 8S shows a mathematical sum of the scattering intensities of the two components. It is seen that at low surfactant concentration (0.66 wt %) the sum curve coincides perfectly with the scattering curve of the mixed system. This indicates that there is no appreciable interactions between polymer and micellar chains. By contrast, at higher surfactant concentration (3.3 wt %) the sum diverges from the scattering curve of the mixed system especially at the intermediate wave vectors (0.015 $Å^{-1}$ < q < 0.05 $Å^{-1}$). Such behavior is indicative of repulsive interactions between the components of the mixture [Klymenko, A.;

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Nicolai, T.; Benyahia, L.; Chassenieux, C.; Colombani, O.; Nicol, E. Multiresponsive Hydrogels Formed by Interpenetrated Self-Assembled Polymer Networks. *Macromolecules* **2014**, *47*, 8386-8393].
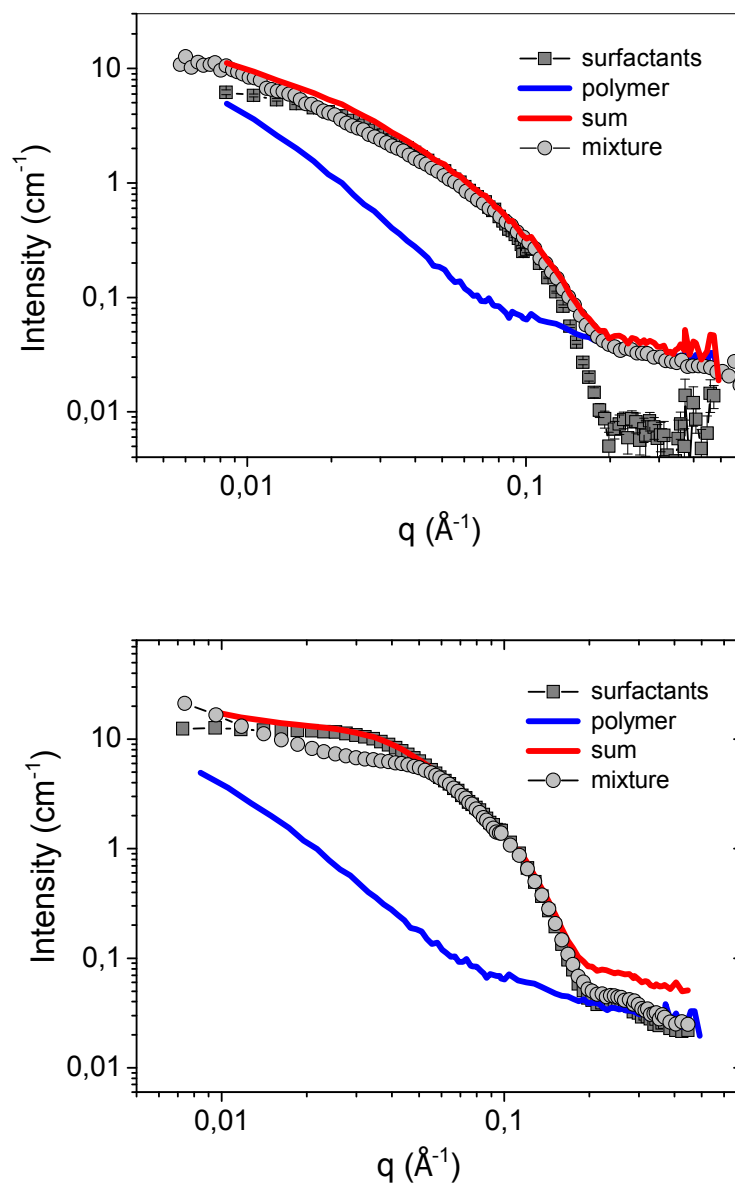
Figure 8S. Scattering curves of 0.66 wt % (a) and 3.3 wt % (b) potassium oleate/C_8TAB surfactants solution ("pure surfactant") (squares), 4 wt % PVA solution ("pure polymer") (blue line), and their mixture containing 0.66 wt % (a) and 3.3 wt % (b) potassium oleate/C_8TAB surfactants and 4 wt % PVA (circles). Molar ratio [potassium oleate]/[C_8TAB] = 2.5. Solvent: D_2O. Red line is the sum of scattering intensities of the pure surfactant and pure polymer solutions.