Properties of aqueous solutions of nonionic surfactants, Triton X-114 and Tween 80, at temperatures from 293 to 318 K: Spectroscopic and ultrasonic studies

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ABSTRACT

The speed of sound, density and refractive index of aqueous solutions of the nonionic surfactants, p-(1,1,3,3-tetramethylbutyl) phenoxypoly(ethyleneglycol) Triton X-114 (TX114) and polysorbate 80, Tween 80, have been measured over the entire range of concentration at 293, 298, 303, 308, 313 and 318 K under atmospheric pressure. Steady state fluorescence measurements have been also made using pyrene as a probe. From the experimental data the quantities such as critical micelle concentration (CMC), apparent dielectric constant, hydration number, isentropic compressibility, apparent specific adiabatic compressibility of a solute, intermolecular free length, acoustic impedance and molar sound number were determined. The variation of these parameters with concentration and temperature was discussed in terms of intermolecular interactions in the solution of a given surfactant.

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1. Introduction

One of the key properties of surfactants responsible for their wide application in modern technologies [1–3] is their ability to form aggregates in solution above the critical micelle concentration (CMC) [4]. In aqueous media, the so-called direct micelles are formed due to a hydrophobic effect, with nonpolar fragments of surfactant molecules isolated within the micellar interior and polar head groups facing towards bulk water. Micelles are thermodynamically stable aggregates. Their size, shape and charge (for ionic surfactant) can be modulated by other components and/or by varying the surfactant concentration, temperature, pressure, and so on. Temperature has a significant effect on the supramolecular arrangement of surfactants in aqueous solution, especially nonionic ones, whose compatibility with water depends on the extent of hydration of the hydrophilic parts of molecules, which are particularly sensitive to temperature changes [4,5].

The nonionic surfactants belonging to the Tween series (polysorbates), find their application in food, bio-technical, pharmaceutical, industrial, domestic, chemical and bio-chemical areas [6–8]. Commercially available Tweens have predominantly 20

ethylene oxide groups attached to the sorbitan headgroup, with different long-chain saturated carboxylic acids, from lauric to stearic, and unsaturated oleic acid. Tweens are clear and non-odorous liquids at room temperature. Their low toxicity and acceptable degree of bio-degradability are responsible for their extensive utility [9]. All these utilities of polysorbates in various walks of life have encouraged us to study less explored properties of aqueous solutions of one of these compounds, Tween 80, with an intention to gather information on the nature of interactions between its molecules and water at different temperatures. It was also interesting to compare the obtained results with those of Triton X-114, one of the most explored surfactants in the separation methods based on the cloud point extraction [10–12]. For this purpose measurements of speed of sound, density and refractive index of aqueous solutions of p-(1,1,3,3-tetramethylbutyl) phenoxypoly (ethyleneglycol) Triton X-114 (TX114) and polysorbate 80, Tween 80, were performed over wide temperature and concentration ranges. Moreover, properties of the solutions were studied by means of steady state fluorescence measurements. On the basis of the obtained results the nature of molecular interactions in solutions at different concentrations and temperatures depending on the kind of medium, extent of solvation in solution, structure and size of the surfactant molecule were discussed.

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2. Experimental

Aqueous solutions of Triton X-114 (TX114) and Tween 80 (Sigma-Aldrich) were prepared in the concentration range from 10^{-6} to 10^{-2} M using doubly distilled and deionized water obtained from a Destamat Bi18E distiller.

The speed of sound as well as densities of aqueous solutions of studied surfactants at the temperatures 293, 298, 303, 308, 313 and 318 K were simultaneously and automatically measured using a digital vibrating tube densitometer and the speed of sound analyzer (Anton Paar DSA 5000 M) provided with automatic viscosity correction and two integrated Pt 100 thermometers. Both the speed of sound and density are extremely sensitive to temperature so it was kept constant within 0.001 K using a proportional temperature controller. The apparatus was first calibrated with triply-distilled water and dry air. The standard uncertainties in density measurements were estimated to be $\pm 2 \times 10^{-3}$ kg·m^{-3} but for the speed of sound ± 0.1 m·s^{-1}.

The refractive index of studied solutions was measured by Abbemat 550 Performance Plus (Anton Paar). The apparatus was first calibrated with triply-distilled water. The precision of the refractive index and temperature measurements given by the manufacturer are ± 0.00002 and ± 0.03 K, respectively.

All speed of sound/density and refractive index measurements were made for 3 samples of two set measurements. Next for a given concentration of surfactant and temperature, the average value of speed of sound, density and refractive index was calculated and used for other calculations and discussion.

Steady state fluorescence measurements at different temperatures were made using a Hitachi F-2700 Fluorescence Spectrometer with a pyrene ($C = 2 \times 10^{-6}$ M) as a luminescence probe. Fluorescence excitation was done for pyrene at 335 nm, and the emission spectra were recorded in the range of 350–600 nm at a scan speed of 300 nm/min. The excitation and emission slit widths were 2.5 nm.

3. Results and discussion

Pyrene is a typical bioprobe for evaluating the interactions between various biomolecules because its emission property distinctly depends on the distance between two pyrene rings. The ratio of intensity of the first (I_1) and third (I_3) vibronic peaks, i.e., I_1/I_3, of the pyrene fluorescence emission spectrum is known as the "Py scale" [13]. In the presence of surfactants this ratio is considered to be the index of micropolarity of the system; i.e., it gives an idea of the microenvironment in the micelle [14,15]. A low value of this ratio (<1) is generally taken as pyrene having nonpolar surrounding, whereas a higher value (>1) is taken as the pyrene with the polar surrounding [16]. As follows from Figs 1 and 2 for the studied solutions of TX114 and Tween 80 at all concentrations the ratio proves to be greater than 1 and initially decreases very slowly because the surfactant molecules adsorption at the air-water interface indicates a small change in polarity in the bulk. A decrease in the I_1/I_3 ratio with the increase in TX114 and Tween 80 concentrations at a given temperature indicates the presence of pyrene in the nonpolar region in the bulk due to the aggregation of surfactant monomers in the bulk. Taking into account the values of I_1/I_3 for TX114 and Tween 80, it is possible to determine their CMC using the procedure proposed by Zana et al. [17,18]. According to this method the CMC values can be obtained from the interception of extrapolation of a rapidly varying part of the plot and the nearly horizontal part at a high surfactant concentration. Because the $I_1/I_3 = f(C)$ curves (C – concentration of the surfactant in the bulk phase) for the studied surfactants are sigmoid in nature, the values of CMC can be also calculated using the Sigmoid – Boltz-
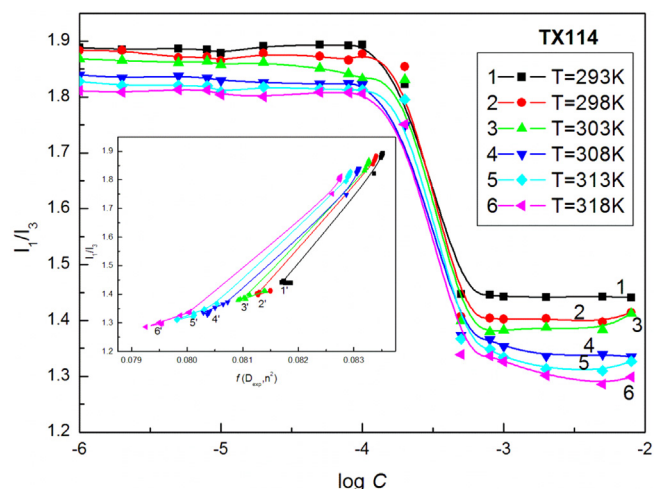

Fig. 1. A plot of the values of I_1/I_3 of aqueous solutions of TX114 vs. log C (curves 1–6) and vs. $f(D_{exp}, n^2)$ (curves 1′–6′) at T = 293 K (curves 1 and 1′), 298 K (curves 2 and 2′), 303 K (curves 3 and 3′), 308 K (curves 4 and 4′), 313 K (curves 5 and 5′) and 318 K (curves 6 and 6′).
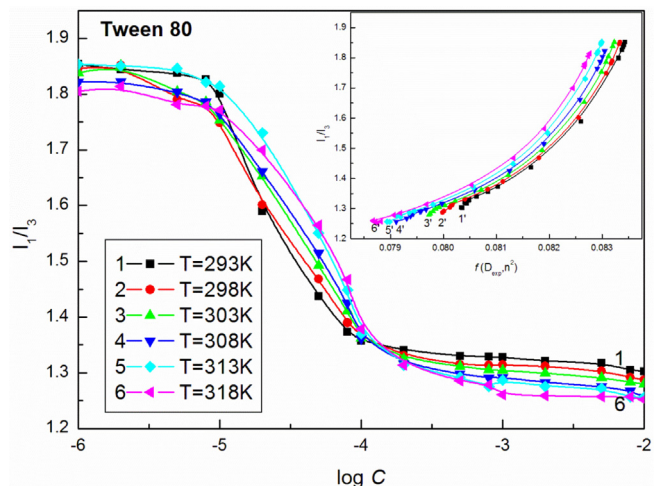

Fig. 2. A plot of the values of I_1/I_3 of aqueous solutions of Tween 80 vs. log C (curves 1–6) and vs. $f(D_{exp}, n^2)$ (curves 1′–6′) at T = 293 K (curves 1 and 1′), 298 K (curves 2 and 2′), 303 K (curves 3 and 3′), 308 K (curves 4 and 4′), 313 K (curves 5 and 5′) and 318 K (curves 6 and 6′).

man equation (SBE) [19,20]. Table 1 presents the values of CMC of TX114 and Tween 80 determined from the intersection points on the $I_1/I_3 = f(C)$ curves as well as those of CMC$_1$ and CMC$_2$ from the SBE equation according to the procedure of Aguiar et al. [21]. This Table shows that the obtained values of CMC and CMC$_1$ for TX114 are close to the literature data [7,22], but in the case of Tween 80 only those of CMC$_1$ are comparable because the others are much higher [23–26]. In addition, for Tween 80 both CMC, CMC$_1$ and CMC$_2$ values increase with the increasing temperature (T), which is in contrast with the literature data [23,24]. In the case of TX114 the values of CMC increase up to T = 298 K and then decrease but those of CMC$_1$ and CMC$_2$ increase with T. Generally, the CMC of nonionic detergents decreases with the increasing temperature [4]. It should be remembered that the effect of temperature on the CMC values of surfactants in aqueous solution is found to be quite complex. Hydrophobic interactions are considered to be responsible for micelle formation. The temperature increase disrupts hydration of hydrophilic groups of the surfactant favouring micellization and breaks down the structured water

Table 1
Values of CMC, CMC_1 and CMC_2 (M) of TX114 and Tween 80 determined at different temperatures from the pyrene emission spectra.

		293 K	298 K	303 K	308 K	313 K	318 K
TX114	CMC_1	2.57×10^{-4}	2.85×10^{-4}	2.96×10^{-4}	2.83×10^{-4}	3.35×10^{-4}	3.00×10^{-4}
	CMC_2	3.40×10^{-4}	3.57×10^{-4}	3.89×10^{-4}	4.39×10^{-4}	4.74×10^{-4}	4.48×10^{-4}
	CMC	5.92×10^{-4}	6.11×10^{-4}	6.09×10^{-4}	5.86×10^{-4}	5.75×10^{-4}	5.69×10^{-4}
Tween 80	CMC_1	2.28×10^{-5}	2.49×10^{-5}	3.11×10^{-5}	3.84×10^{-5}	4.59×10^{-5}	5.43×10^{-5}
	CMC_2	9.90×10^{-5}	9.96×10^{-5}	1.27×10^{-4}	1.50×10^{-4}	1.51×10^{-4}	1.91×10^{-4}
	CMC	9.31×10^{-5}	1.07×10^{-4}	1.19×10^{-4}	1.23×10^{-4}	1.25×10^{-4}	1.27×10^{-4}

around the hydrophobic moieties thus inhibiting micelle formation. Therefore the combination of these two opposite effects decides whether the CMC increases or reduces over a specified range of temperature [24,27]. As for Tween 80 all the values of CMC increase with T, it means that disorder of structured water around the hydrophobic portion plays a main role and influences on the CMC value. It should be remembered that the hydrophobic parts of Tween 80 are all aliphatic but with one double bond [28]. It seems that the shift of electronic charge from C^9 to C^{10} in Tween 80 molecules develops electron deficient and electron rich sites that induce electrophilic and nucleophilic mechanisms affecting dipoles of water or its caging. Such arrangements affect Tween-water, Tween-water-Tween, and water-Tween-water interactions [29]. It is also noted that water and Tween 80 molecules can not be completely mixed in solution.

The situation is more complicated in the case of TX114 molecules which possess an aromatic ring in the hydrophobic chain [30]. Our earlier studies based on the viscosity measurements showed that in the case of TX114 aqueous solutions at C higher than 10^{-3} M, the structure making effect becomes significant at temperatures higher than 298 K [31]. In the same range of temperatures the values of CMC, much lower than 10^{-3} M, decrease with T which suggests that around the CMC values there is dehydration of hydrophilic parts of TX114 molecules and this effect exceeds the disorder near the hydrophobic parts. It is known that the oxyethylene group (EO), of which the hydrophilic part of surfactants is made, can be associated with two molecules of water [32]. Additionally, in the literature it can be found that most water molecules are mechanically trapped in the polyoxyethylene chains of nonionic surfactants, with 5.2–10.5 water molecules per oxyethylene units [33,34].

On the other hand, for TX114 the intensity ratio I_1/I_3 (Fig. 1) decreases as the temperature increases in the whole studied concentration range. This is probably due to "squeezing out" of associated water molecules as the polyoxyethylene chains tighten [35] but it can also be explained as decrease in the medium polarity with the increasing temperature, which was found for pure solvents [36]. At C = 10^{-3} M and T = 293 K the intensity ratio I_1/I_3 is higher for TX114 (1.4426) than for Tween 80 (1.3278) and close to the external surface of the hydrophobic core of the Triton micelles [35]. It should be remembered that the nonpolar hydrocarbon chains, phenyls and the first adjacent oxyethylene group form the micellar core of TX114. Some authors stated that water penetration into the micellar core is excluded [37]. Consequently, Triton micelles are molecularly non-homogeneous showing biphasic nature of two microenvironments: hydrocarbon-like core and hydrophilic polyethylene mantle. Such structure of micellar aggregates suggests that local polarity inside the micelle is lower in the core and higher close to the micellar surface. Therefore various indicators exhibit a wide range of effective dielectric constants inside Tritons micelles (15–40) [38].

Knowing the values of I_1/I_3 for a given surfactant it is possible to calculate the apparent dielectric constant (D_{exp}) of the medium that is a measure of local polarity in which the probe is located [14,39] from the expression:

$$\frac{I_1}{I_3} = 1.00461 + 0.01253 D_{exp} \tag{1}$$

From Tables 2 and 3 it results that for a given temperature and concentration the values of D_{exp} for TX114 are much higher than for Tween 80. As the emission spectra of probes like pyrene are not only related to D_{exp} but also to the refractive index (n), taking into account the measured values of n of aqueous solutions of TX114 and Tween 80 at different temperatures (Figs. 3 and 4) the values of the dielectric cross term ($f(D_{exp}, n^2)$) were calculated (Figs. 1 and 2) from the equation [40]:

$$f(D_{exp}, n^2) = [(D_{exp} - 1)/(2D_{exp} + 1) \cdot [(n^2 - 1)(2n^2 + 1)] \tag{2}$$

It follows from Figs. 1 and 2 that for the studied surfactants there are no linear relationships between I_1/I_3 and $f(D_{exp}, n^2)$ as for a number of conventional organic solvents at 293 K [41] but for Tween 80 the presented relationships can be described by a polynomial function of the second order.

The attention should be also paid to the fact that for Tween 80 and the concentrations higher than CMC and CMC_2, the values of I_1/I_3 decrease with the rising temperature (Fig. 2), similarly to TX114, but this trend is reverse for the concentrations of Tween 80 between CMC_1 and CMC_2. As pointed out by Nakajima [42], this phenomenon can not be explained only by the solvent polarity. According to Ndou et al. this fact is attributed to thermal agitation which reduces short range intermolecular interactions in the solvent [36]. At the intermediate concentration of aqueous solutions of Tween 80, the I_1/I_3 ratio exhibits a remarkably negative slope with T because the instability of pyrene in the micelles by thermal agitation is greater than the effect of solvent polarity. However, when the micelle size reaches a constant value, the temperature dependence of I_1/I_3 ratio shows a positive slope. This can be also connected with the changes of size and/or shape of the Tween 80 micelles as well as disorder of loosely bound water molecules around Tween 80 compared to TX114 [31] and hydration of oxyethylene units in the surfactant molecules. Of the methods presented in the literature to determine hydration numbers, the ultrasonic measurements allow the primary hydration numbers to obtain, n_h, through the expression [43,44]:

$$n_h = \frac{n_W}{n_S} \left(1 - \frac{\kappa_S}{\kappa_{S,0}} \right) \tag{3}$$

where n_W and n_S are the number of moles of water and solute, respectively, and κ_S is the isentropic compressibility which can be determined from the speed of sound (u) and density (ρ) using the Newton-Laplace equation [45]:

$$\kappa_S = \frac{1}{\rho u^2} \tag{4}$$

$\kappa_{S,0}$ is the isentropic compressibility of pure water.

Eq. (3) implicitly assumes that (i) n_h is the number of water molecules in the hydration shell of the solute whose properties are altered with respect to those of the bulk solvent by the presence of the solute, and (ii) these molecules of water are trapped so tightly that they can be considered as incompressible. Taking

Table 2
Values of D_{exp}, φ_K, L_f, Z and [U] for TX114.

T	C [M]	D_{exp}	φ_K 10^{-3} m³/kg	L_f 10^{-10} m	Z 10^6 kg/m²s	[U]
293 K	10^{-4}	70.95	44.56	0.43443	1.48178	12.01
	10^{-3}	34.96	45.58	0.43429	1.48231	1.52
	10^{-2}	34.8	45.61	0.43369	1.48466	0.27
298 K	10^{-4}	69.62	44.08	0.43462	1.49392	8.90
	10^{-3}	31.74	44.8	0.43459	1.49403	0.92
	10^{-2}	31.61	44.87	0.43430	1.49534	0.14
303 K	10^{-4}	66.07	43.58	0.43532	1.50406	7.78
	10^{-3}	30.17	44.20	0.43530	1.50416	0.81
	10^{-2}	30.05	44.26	0.43483	1.50605	0.17
308 K	10^{-4}	65.28	43.12	0.43653	1.51223	7.67
	10^{-3}	27.85	43.72	0.43651	1.51232	0.79
	10^{-2}	26.38	43.78	0.43612	1.51393	0.15
313 K	10^{-4}	64.52	42.73	0.43821	1.51852	8.03
	10^{-3}	26.29	43.36	0.43817	1.51867	0.87
	10^{-2}	25.71	43.42	0.43777	1.52032	0.16
318 K	10^{-4}	63.94	42.48	0.44037	1.52294	8.13
	10^{-3}	25.69	43.11	0.44033	1.52309	0.88
	10^{-2}	23.47	43.17	0.43992	1.52476	0.16

Table 3
Values of D_{exp}, φ_K, L_f, Z and [U] for Tween 80.

T	C [M]	D_{exp}	φ_K 10^{-3} m³/kg	L_f 10^{-10} m	Z 10^6 kg/m²s	[U]
293 K	10^{-4}	28.15	44.54	0.43443	1.48180	12.06
	10^{-3}	25.8	45.55	0.43426	1.48252	1.62
	10^{-2}	23.8	45.60	0.43285	1.48855	0.39
298 K	10^{-4}	28.72	44.01	0.43458	1.49405	9.63
	10^{-3}	24.72	44.76	0.43443	1.49470	1.24
	10^{-2}	22.57	44.85	0.43331	1.49975	0.30
303 K	10^{-4}	28.56	43.42	0.43525	1.50432	9.41
	10^{-3}	23.92	44.16	0.43512	1.50489	1.16
	10^{-2}	21.94	44.24	0.43408	1.50964	0.28
308 K	10^{-4}	28.46	43.01	0.43648	1.51241	8.75
	10^{-3}	22.94	43.64	0.43611	1.51381	1.64
	10^{-2}	20.11	43.75	0.43510	1.51843	0.32
313 K	10^{-4}	29.16	42.70	0.43820	1.51857	8.31
	10^{-3}	22.51	43.28	0.43777	1.52015	1.72
	10^{-2}	20.07	43.39	0.43665	1.52516	0.36
318 K	10^{-4}	29.84	42.48	0.44038	1.52293	8.00
	10^{-3}	20.42	43.05	0.44006	1.52414	1.44
	10^{-2}	19.74	43.15	0.43894	1.52908	0.33

into account the measured values of ρ as well as u (Figs. 5 and 6), the values of κ_S and n_h were calculated and are presented in Figs. 7–10. As follows from Figs. 5 and 6 the values of u increase with the increasing temperature and concentration of aqueous solutions of studied surfactants, in contrast to those of κ_S (Figs. 7 and 8). The decrease of κ_S values can result from the combined effects of hydration of surfactant molecules and breaking of three dimensional network of water structure. According to Pasynski [45], with the addition of solute the compressibility of the solvent (water) becomes strongly reduced compared to that of pure bulk water or even becomes zero. The effect of such interactions should always be observed as an initial decrease of compressibility of aqueous solutions with the increasing concentration, both for electrolytic and polar nonelectrolytic solutes. Additionally, it can be found out that for the surfactant concentrations higher than the CMC, as the concentration of the surfactant increases, compressibility of solutions decreases because the decreasing amount of bulk water is offset by increasing the number of micelles in the solution. Therefore the isentropic compressibility of solutions

becomes independent of concentration [46]. From Figs. 7 and 8 it results that at $C = 10^{-3}$ M and T = 293 K κ_S is equal to 4.5432 and 4.5426 for TX114 and Tween 80, respectively and at $C = 10^{-2}$ M: 4.5306 and 4.5132 which confirms that the water around Tween 80 is loosely bound [31]. Also for a given temperature the values of n_h are higher for Tween 80 than for TX114 (Figs. 9 and 10) which means that as amphiphile becomes longer, more conversion to bulk water of the structured water molecules is observed, obtaining lower compressibilities and higher values of n_h.

When the amphiphiles form micelles, the hydrophobic hydration around the alkyl chain disappears and compressibility of the aggregate becomes the dominant factor.

When the aggregate forms, the released water molecules in the vicinity of the hydrophobic part of the molecule become bulk water. The water molecules around the hydrophobic part are highly structured, having a rather low compressibility compared to the bulk water. To obtain more information about the solute-solute and solute-solvent intermolecular interactions in the studied surfactant solutions, the apparent specific adiabatic
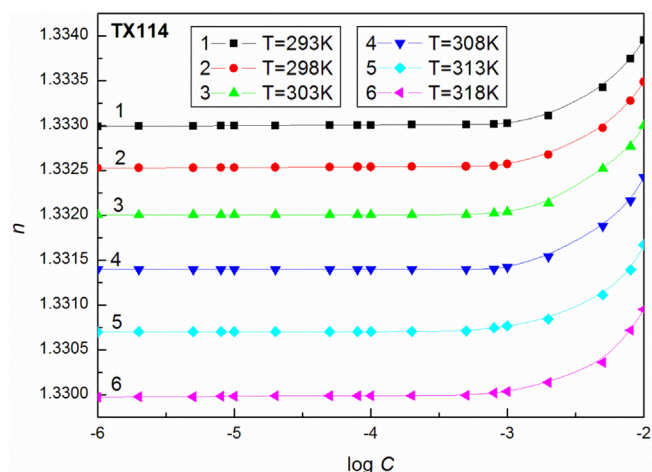
Fig. 3. A plot of the values of n of aqueous solutions of TX114 at T = 293 K (curve 1), 298 K (curve 2), 303 K (curve 3), 308 K (curve 4), 313 K (curve 5) and 318 K (curve 6) vs. log C.
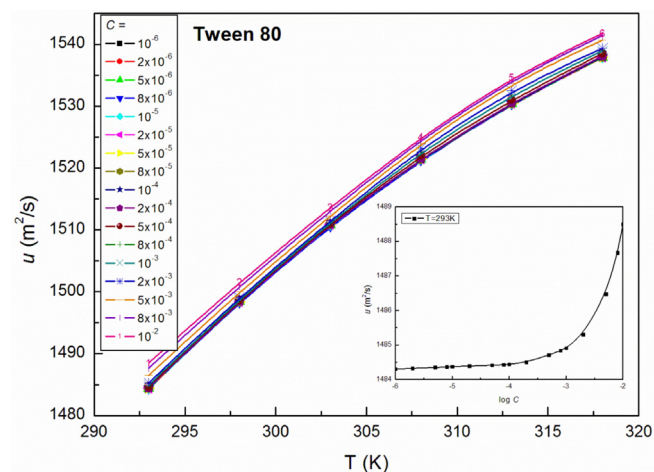

Fig. 6. A plot of the values of u of the aqueous solutions of Tween 80 in the concentration range from 10^{-6} to 10^{-2} M vs. T as well as the values of u for the aqueous solutions of Tween 80 at T = 293 K vs. log C.
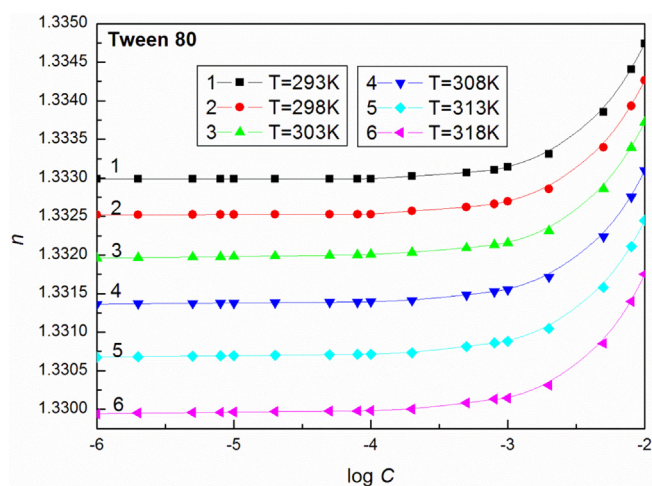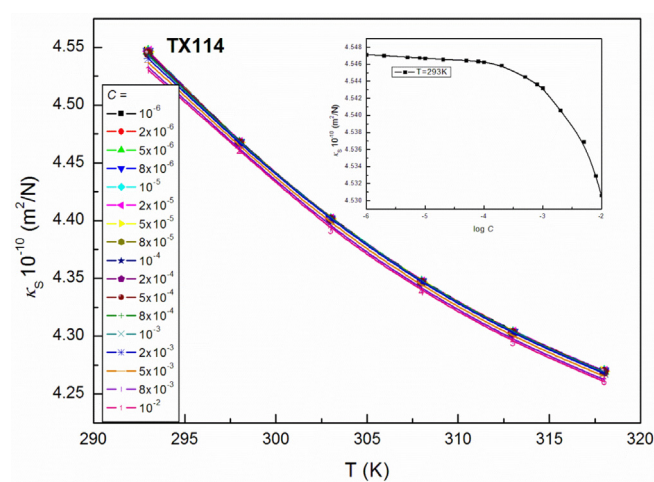

Fig. 4. A plot of the values of n of aqueous solutions of Tween 80 at T = 293 K (curve 1), 298 K (curve 2), 303 K (curve 3), 308 K (curve 4), 313 K (curve 5) and 318 K (curve 6) vs. log C.

Fig. 7. A plot of the values of κ_S of the aqueous solutions of TX114 in the concentration range from 10^{-6} to 10^{-2} M vs. T as well as the values of κ_S for the aqueous solutions of TX114 at T = 293 K vs. log C.
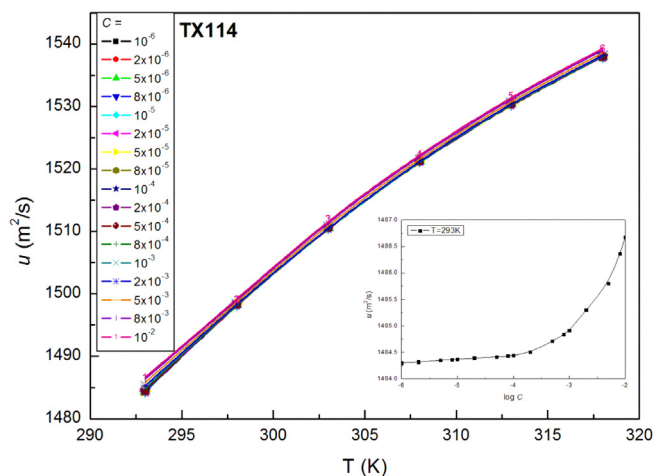

Fig. 5. A plot of the values of u of the aqueous solutions of TX114 in the concentration range from 10^{-6} to 10^{-2} M vs. T as well as the values of u for the aqueous solutions of TX114 at T = 293 K vs. log C.
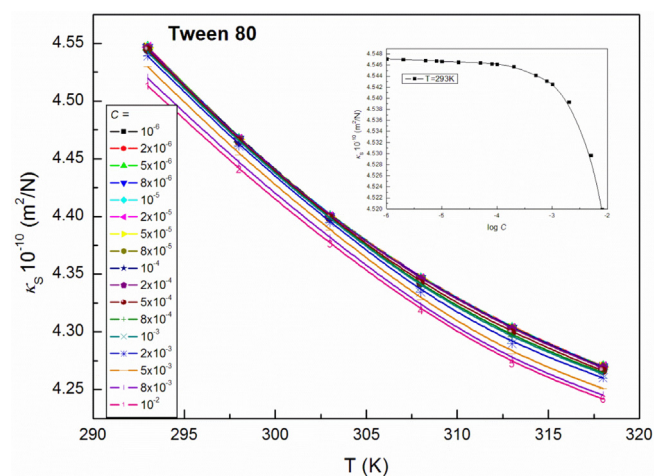

Fig. 8. A plot of the values of κ_S of the aqueous solutions of Tween 80 in the concentration range from 10^{-6} to 10^{-2} M vs. T as well as the values of κ_S for the aqueous solutions of Tween 80 at T = 293 K vs. log C.
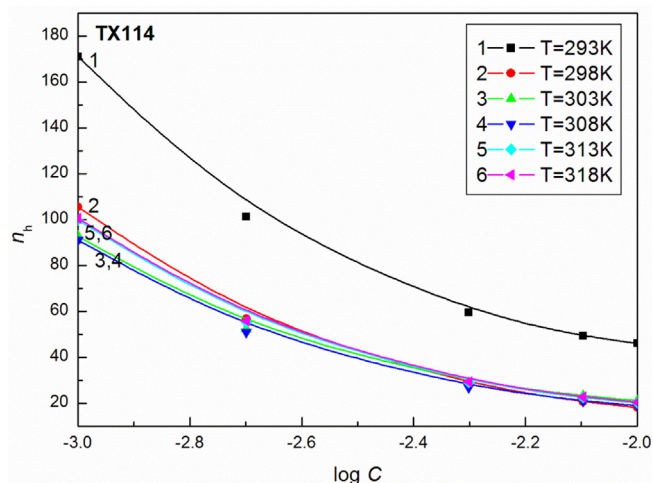
Fig. 9. A plot of the values of n_h of the aqueous solutions of TX114 in the concentration range from 10^{-3} to 10^{-2} M at T = 293 K (curve 1), 298 K (curve 2), 303 K (curve 3), 308 K (curve 4), 313 K (curve 5) and 318 K (curve 6) vs. log C.

Fig. 10. A plot of the values of n_h of the aqueous solutions of Tween 80 in the concentration range from 10^{-3} to 10^{-2} M at T = 293 K (curve 1), 298 K (curve 2), 303 K (curve 3), 308 K (curve 4), 313 K (curve 5) and 318 K (curve 6) vs. log C.
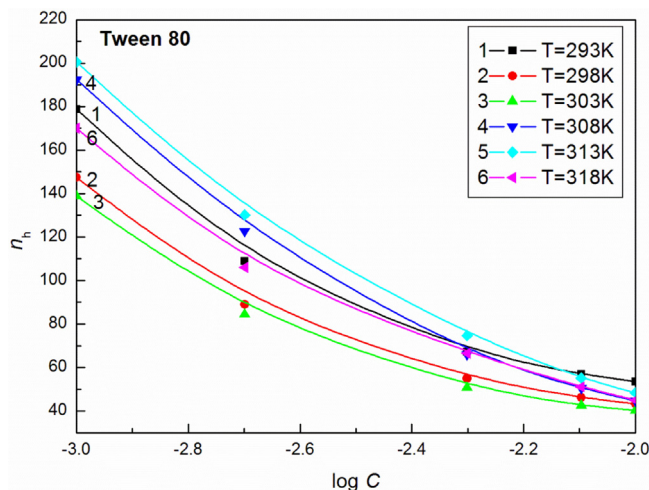
compressibility of a solute, φ_K, was calculated from the expression [47]:

$$\varphi_K = \kappa_{S,A}\varphi_V \tag{5}$$

where φ_V is the apparent specific volume which can be calculated from the expression:

$$\varphi_V = \frac{1}{\rho_0} - \frac{\rho - \rho_0}{\rho_0 C} \tag{6}$$

and $\kappa_{S,A}$ is the adiabatic compressibility of a solute which is equal to

$$\kappa_{S,A} = \frac{\kappa_S - \kappa_{S,0}(1 - C\varphi_V)}{C\varphi_V} \tag{7}$$

As results from Tables 2 and 3 the φ_K values for TX114 and Tween 80 are positive at all temperatures, for a given concentration of surfactants they decrease with the increasing temperature, but at a given T they increase with the increasing surfactant concentration. Also those values are very close for the two surfactants.

To provide more detailed explanation about intermolecular interactions of solution components, the intermolecular free length L_f was calculated from the expression [48]:

$$L_f = K\sqrt{\kappa_s} \tag{8}$$

where $K = [(93.875 + 0.375)T \cdot 10^{-8}]$. L_f is the distance between the surfaces of two molecules. When the isentropic compressibility, κ_S, decreases, free length also decreases and vice versa [49]. For the studied solutions of surfactants the L_f values show a regular decrease with the increasing concentration of a given surfactant (Tables 2 and 3), but as T increases, the values of L_f increase. This indicates that the structural readjustment in the studied solutions proceeds towards the less compressible phase or closer packing of the molecules. It should be also remembered that the expansion of liquids results in loosening of the molecular packing and increase in the intermolecular spacing. Due to this, each sample becomes more and more compressible with the rise in T [50]. Compressibility in each sample depends on two factors namely, effect of T on compressibility of hydrocarbon tail part of the surfactants and the interaction among the head groups of the neighbouring molecules, as the head of each molecule is polar in nature [51]. As T increases, the cohesive force between the neighbouring molecules in a liquid decreases making molecular bond relatively weaker. This is the reason for the increase in L_f with T in all samples according to the Eyring and Kincoid model [52]. In fact for a given concentration and temperature, the values of L_f for TX114 are higher than for Tween 80. It is quite contrary in the case of acoustic impedance values (Z) calculated from the expression [48]:

$$Z = u \cdot \rho \tag{9}$$

Z is the ratio of the effective sound pressure at a point to the effective particle velocity at that point or the impedance offered to the sound wave by the solution components. In other words, the acoustic impedance targets on the molecular packing of the system in terms of different types of interactions. For the studied systems the pattern of Z at all concentrations is similar to density and speed of sound which increases with the increase in the concentration of a given surfactant (Tables 2 and 3). These values increase also with T and are higher for Tween 80 than for TX114 at a given concentration and temperature. The increase of Z values with the surfactant concentration can be attributed to the effective solute-solvent interactions [53]. On the other hand, the values of molar sound number [U] (Tables 2 and 3) calculated from the expression:

$$[U] = (u - u_0)/(u_0 \cdot C) \tag{10}$$

are also higher for Tween 80 than for TX114. It should be noticed that for both TX114 and Tween 80 at a given temperature the values of [U] at $C = 10^{-4}$ M are much greater than those at higher surfactant concentration. However, with the rise in temperature, the values of [U] decrease and next increase depending on the surfactant type or its concentration indicating the role of the intermolecular hydrophobic interactions among surfactant molecules.

4. Conclusions

In the paper some physicochemical properties of aqueous solutions of the nonionic surfactants, Triton X-114 (TX114) and Tween 80, are singled out, discussed, and compared on the basis of density, speed of sound and refractive index measurements as well as the emission spectra of pyrene. From the presented data and calculations, it is evident that the combined effect of hydration of surfactant molecules and breaking of three-dimensional network of water structure influence on the values of CMC of studied surfactants. As amphiphile becomes longer, that is for Tween 80, more conversion to bulk water of the structured water molecules is

observed, obtaining lower compressibilities and higher values of hydration number.

Acknowledgments

References

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