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Micellization of polyoxyethylene–polyoxypropylene block copolymers in aqueous polyol solutions

Kazuhiro Kaizu¹, Paschalis Alexandridis^{*}

Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York (SUNY), Buffalo, NY 14260-4200, USA

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ABSTRACT

The micellization of a representative polyoxyethylene–polyoxypropylene–polyoxyethylene (POE–POP–POE) amphiphilic block copolymer (Pluronic P105, EO₃₇PO₅₈EO₃₇) in aqueous solutions of the common excipients glucose, glycerol or ethanol, has been investigated as a function of solute (solvent) concentration, block copolymer concentration, and temperature. The formation of POE–POP–POE micelles is favored in the presence of glucose or glycerol, while ethanol has the opposite effect. ΔH° and ΔS° values derived from analysis of critical micellization concentration (CMC) data are both positive in all mixed aqueous polyol systems. ΔH° and ΔS° decrease slightly with increasing glucose or glycerol content, but increase significantly in the presence of ethanol. A 10- to 100-fold increase of the amphiphilic block copolymer solution viscosity was observed in the presence of glucose or glycerol above a certain temperature. This viscosity increase is indicative of micelle shape changes from spherical to elongated. The CMC and viscosity changes caused by glucose and glycerol are attributed to the enhanced dehydration of the POE block of the polymeric amphiphile. Glucose is more effective than glycerol, apparently due to its higher hydration number.

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1. Introduction

The ability of amphiphiles to self-assemble in aqueous solutions is integral in a variety of products, e.g., pharmaceuticals, skin-care, hair-care, detergents, coatings and inks. Therefore, the elucidation of the self-assembly behavior of amphiphiles under different conditions is of great interest for industrial applications and also for fundamental considerations. Micellar solutions, which are the most common self-assembling systems, have been extensively researched. Several reports have considered solvent effects on micelle formation and structure, the solvent quality being a controlling factor for amphiphile self-assembly [1].

The most commonly examined solvent additives are alcohols and also polyols [1]. Addition of alcohol to aqueous surfactant solutions can result in changes of, e.g., critical micellization concentration (CMC), critical micellization temperature (CMT), micelle molecular weight or association number, micelle radius, micelle shape, and ionization degree or surface density of micelle. These changes are attributed to a decrease of the solution dielectric constant caused by alcohols, and to alcohol penetration in the micelle hydrophobic interior [1–3]. In the case of polyoxyethylene (POE)-containing non-ionic surfactants, the dehydration of POE that is effected by added polyols becomes also important [4–6].

These factors lend complexity to aqueous surfactant systems containing alcohols. For example the effect of ethanol on the CMC of sodium dodecyl sulfate (SDS) or tetradecyltrimethylammonium bromide (TTAB) aqueous solution at 25 °C is non-monotonic: the CMC goes through a minimum at around 4.8 wt.% ethanol and then increases with further increase of the ethanol content [1]. On the other hand, in the case of POE(31)-dodecyl ether, the CMC simply increases with increasing ethanol content at 20 °C [1]. The micelle size decreases and the micelles eventually disappear when sufficient amount of ethanol is added to SDS [1] (around 19 wt.% ethanol) or to cetyltrimethylammonium bromide aqueous solution [7] (around 80 vol.% ethanol). In another example, the addition of glycerol to SDS [8,9] or TTAB [10] aqueous solutions at 25 °C and to POE(8)-dodecyl ether [11] aqueous solution in the temperature range of 25–35 °C leads to an increase in CMC. Moreover, the addition of glycerol to POE(8)-hexadecyl ether results in a shape change of the micelles from spherical to rod-like [4].

We have an on-going interest in our research group on solvent quality effects on the conformation and supramolecular organization of polymeric amphiphiles such as polyoxyethylene–polyoxypropylene–polyoxyethylene (POE–POP–POE) block copolymers (which are commercially available as Pluronics or Poloxamers), poly(dimethylsiloxane)-graft-polyether copolymers, and polysaccharides (e.g., dextran, cellulose ethers). We have shown that the structural polymorphism of polymeric surfactants is richer than that of typical, low molecular weight surfactants [12,13]. Even in dilute solutions, polymeric surfactants have the potential to exhibit complex structures such as flower-like or star-like assemblies [14] due to the conformational

^{*} Corresponding author.

E-mail address: palexand@buffalo.edu (P. Alexandridis).

¹ On leave from: Skin Care Labs, Kao Corp., Tokyo 131-8501, Japan.

flexibility conferred by their higher molecular weight and corresponding length.

We have previously reported on the effects of polar organic solvents such as formamide, ethanol, and glycerol on the self-assembly of a POE–POP–POE block copolymer (Pluronic P105, EO₃₇PO₅₈EO₃₇) in aqueous solutions, determined from analysis of small-angle neutron scattering (SANS) measurements [5,15]. We found that the addition of formamide or ethanol led to a decrease in the micelle size and the polymer volume fraction in the micelle corona and core, and an increase in the CMC, while glycerol caused the opposite trend [5,15]. Other groups have reported the effect of 1-butanol on Pluronic F127 (EO₉₉PO₆₅EO₉₉) aqueous solutions [16], and of 1-pentanol on Pluronic P103 (EO₁₇PO₆₀EO₁₇), P105 (EO₃₇PO₅₈EO₃₇), and P108 (EO₁₃₂PO₅₀EO₁₃₂) aqueous solutions [17]. Both 1-butanol and 1-pentanol decrease the CMC and solubilize in the micelle core [17], in agreement with our observations.

We have also reported on the effects of 2-propanol, ethanol, formamide and glycerol on micelles formed by poly(dimethylsiloxane)-graft-polyether copolymers in aqueous solutions. The micelle radii, micelle association numbers, and polymer volume fractions in the micelle corona and core decreased with increasing 2-propanol, ethanol, or formamide content. On the contrary, the addition of glycerol led to an increase of the micelle association number and caused a micelle shape change from sphere to ellipse [6]. Similar shape changes in poly(dimethylsiloxane)-graft-polyether micelles have been reported upon the addition of glucose, 2-butoxyethanol, and polyoxyethylene [18]. It is notable that we found a good correlation between the CMC in the presence of various solvents and the component of the solvent solubility parameter (δ) which accounts for hydrogen bonding [19,20].

Here we focus our attention on polyols such as glucose and glycerol which are widely used as excipients in pharmaceutical, cosmetic, and food formulations [21,22]. We examine the effects of these polyols on the micellization in water of a representative POE–POP–POE block copolymer (Pluronic P105, EO₃₇PO₅₈EO₃₇). In particular, we present information on (i) micelle formation, (ii) thermodynamics of micellization, and (iii) micelle solution properties in aqueous glucose or glycerol solutions, as well as in aqueous mixtures of glucose and ethanol.

2. Materials and methods

2.1. Materials

The Pluronic P105 polyoxyethylene–polyoxypropylene–polyoxyethylene (POE–POP–POE) block copolymer was obtained from BASF Corp. and was used as received. According to the manufacturer it has molecular weight of 6500 and 50 wt.% PEO content and can thus be represented as EO₃₇PO₅₈EO₃₇. Among the various POE–POP–POE block copolymers available commercially, Pluronic P105 is of intermediate hydrophobic/hydrophilic balance and molecular weight. Not coincidentally it exhibits a rich phase behavior in the presence of water and/or non-aqueous polar solvents [23–25]. D(+)-glucose monohydrate (>99.5%) was purchased from Fluka Chemical Corp., Milwaukee, WI. Glycerol anhydrous (>99.5%) was purchased from J. T. Baker, Phillipsburg, NJ. Ethyl alcohol (99.5%) was purchased from Pharmco Products Inc., Brookfield, CT. Millipore-filtered water was used for all samples, which were prepared by weighing appropriate amounts of polymer, solute and water. Appropriate time was allowed for thermodynamic equilibration of the samples. Chemical formulas for the molecules considered here are shown in Fig. 1, and physicochemical parameters are presented in Table 1.

2.2. Light scattering

The light scattering intensity of samples was measured with a Brookhaven BI-200SM goniometer (equipped with a Lexel model 95 argon ion laser operating at 514 nm) at 90° detection angle at temperatures varying in the range of 5–45 °C. Previously equilibrated samples

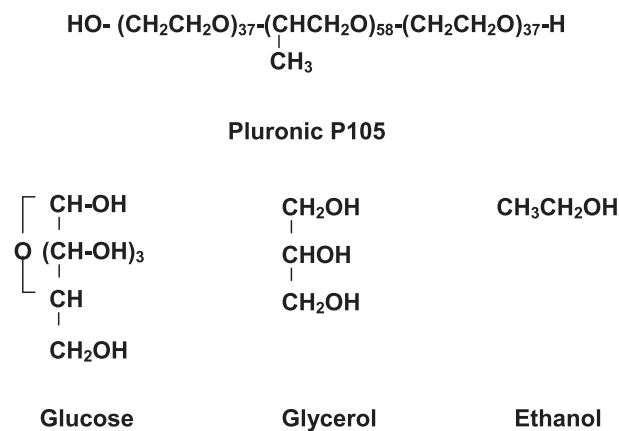


Fig. 1. Chemical structures of the amphiphilic block copolymer and polyols used in this study.

were kept an hour at a specific temperature before measurements. The sample compositions are the following: Pluronic P105 content = 1 or 8 wt.%, solute or solvent (glucose monohydrate, glycerol, or ethanol) content = 0, 20, 30, 40, or 60 wt.%, and the remainder is water.

2.3. Viscosity

Viscosities of aqueous Pluronic P105 solutions were measured with a Cannon–Fenske routine type viscometer at the temperature range of 7–60 °C [20]. The reproducibility of viscosity values was typically $\pm 3\%$. Above certain temperatures the viscosities of these solutions increased dramatically (more than 10-fold), and the measurements in this case were subjected to bigger error. The sample compositions that we considered are: 1 or 8 wt.% Pluronic P105, 0, 20, 30, or 40 wt.% glucose monohydrate or glycerol, or 5, 10 wt.% ethanol, with the remainder being water. The reported relative viscosity denotes the viscosity of the aqueous Pluronic P105 solutions divided by the viscosity of the correspondent solvents (consisting of aqueous solutions of glucose, glycerol, or glucose + ethanol, or plain water).

2.4. Phase behavior

We have already reported ternary isothermal (25 °C) phase diagrams for Pluronic P105–water–glucose, glycerol, or ethanol systems [24]. Normal (“oil”-in-“water”) isotropic micellar solutions as well as micellar cubic, normal hexagonal, normal bicontinuous cubic, and lamellar lyotropic liquid crystalline (LLC) phases have been identified in these phase diagrams. The LLC structures “dissolve” with increasing ethanol content above 25%. It is notable that, with increasing glucose or glycerol content relative to water, the composition range of the normal hexagonal (cylindrical) LLC region expands toward lower block copolymer contents. This signifies a decrease in interfacial curvature (from

Table 1
Physicochemical parameters of the solute and solvents used in this study.

Solvent Solute	m_w^a	Density ^{b,c} (g/cm ³)	Dielectric constant ^{b,c}	Dipole moment ^d	Log P ^e	Solubility parameter ^f (MPa ^{1/2})
Water	18.01	0.9982	78.5	3.11	−1.38	47.8
Glucose	180.16	1.5620		14.1	−3.29	
Glycerol	92.10	1.2567	40.1	2.68	−2.55	36.2
Ethanol	46.07	0.7873	24.3	1.69	−0.32	26.5

^a m_w : molecular weight.

^b Density and dielectric constant values are at 25 °C.

^c Data from Weast [56].

^d Data from McClellan [57].

^e Log P: logarithm of the octanol/water coefficient (data from refs [58,59]).

^f Data from Hansen [60].

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