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The effect of glycols and their ethers on micellar behavior of cetyltrimethylammonium tosylate

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ABSTRACT

The effect of glycols viz., ethylene glycol (EG), diethylene glycol (DEG) propylene glycol (PG), dipropylene glycol (DPG) and their monoalkyl ethers on the morphological features of cetyltrimethylammonium tosylate (CTAT) micelle was examined from viscosity and small angle neutron scattering (SANS) measurements. EG and DEG, and their short chain ethers showed an initial increase in viscosity followed by a decrease while long chain PG, DPG and their ethers showed a monotonous decrease in viscosity. SANS results support the viscosity behavior. These trends are explained on the basis of hydrophobicity of the additives that determines its location in the micelle exerting an effect on micelle morphology. The critical micelle concentrations (CMCs) of CTAT determined tensiometrically for selected systems are also reported. This study helps in fine tuning of rheology of micellar systems in the presence of gycols and their ethers often used with surfactant systems.

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1. Introduction

Worm-like micelles(WLMs) formed by surfactants in aqueous solutions are of great interest due to their rheological and viscoelastic properties. These find applications in drag reduction, enhanced oil recovery, as templates for material synthesis, thickeners for personal and home care products [1–4]. Self-assembly of surfactant molecules in aqueous solution can result WLMs depending on surfactant concentration, solution conditions like pH, temperature and the ionic strength, presence of additives etc. Quaternary ammonium salt based cationic surfactants viz. cetyltrimethylammonium bromide (CTAB) forms WLMs in water much above the critical micelle concentration (CMC) or in the presence of salts such as NaCl, NaBr, $NaNO_3$ and $NaClO_3$ even at concentrations close to CMC [5–7]. Formation of such micelles holds for surfactants having strongly bound organic counterions such as salicylate, tosylate [8,9].

Cetyltrimethylammonium tosylate (CTAT) has p-toluene sulphonate as counterion that being hydrophobic strongly binds to CTAT micelles (CMC ~ 0.26 mM, small surface charge but large Debye screening length) [10,11]. Such characteristic properties of CTAT facilitate the formation of WLMs even at relatively low concentrations (~2 mM) which entangle at ~11 mM exhibiting remarkable viscoelasticity that can be modulated by the presence of additives [12–15]. WLMs of CTAT can be modulated by the presence of various additives such as inorganic salts, polymers, alcohols, etc. [11–13,16–22].

Glycols and their ethers are industrially important additives. Glycols are well known for their use as coolants and antifreezes and find application in pharmaceutical, cosmetics, and food industries [23]. Glycol ethers are useful solvents as cleaners and degreasers for dissolving oil, wax, and resin. Due to their high boiling points, lower evaporation rates, and moderate viscosity, glycol ethers are used as diluents and leveling agents [24].

Previously, we have studied the effect of bile salts, alcohols and block *co*-polymers on worm-like CTAT micelles [12,25]. In continuation to our earlier work, herein we report, how glycols and their ethers affect the size and shape of CTAT micelle. To do this, viscosity and SANS measurement were performed. ^1H NMR was used to examine interaction between CTAT and the additive molecules. Further, as a representative, butyl ethers were examined for their effect on CMC of CTAT by surface tension.

2. Materials and methods

Cetyltrimethylammonium tosylate (Sigma-Aldrich) and glycols/ethers listed in Table 1 were from Fluka/Merck/Sigma and used as received. Deionized water from a Millipore Milli-Q system was used to prepare samples for viscosity and surface tension measurement while D_2O from Sigma was used as solvent for SANS and NMR.

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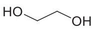
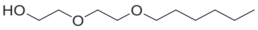
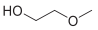
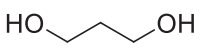
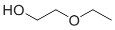
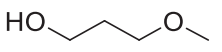
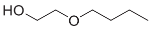
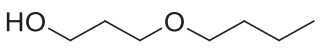
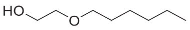
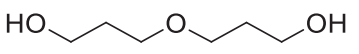
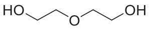
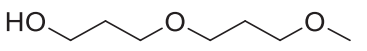
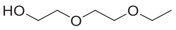
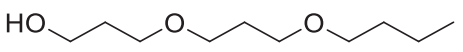
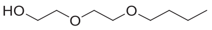
Table. 1
Structures and octanol-water partition coefficient ($\log P_{o/w}$) of glycols and their ethers.

Name	[a]$\log P_{o/w}$	Structure	Name	[a]$\log P_{o/w}$	Structure
EG	−1.36		DEGMHE	+1.70	
EGMME	−0.77		PG	−1.34	
EGMEE	−0.32		PGMME	−0.43	
EGMBE	+0.83		PGMBE	+1.15	
EGMHE	+1.86		DPG	−1.48	
DEG	−1.47		DPGMME	+0.006	
DEGMEE	−0.54		DPGMBE	+1.52	
DEGMBE	+0.56				

EGMME = ethylene glycol monomethyl ether, EGMEE = ethylene glycol monoethyl ether ethylene, EGMBE = ethylene glycol monobutyl ether, EGMHE = ethylene glycol monohexyl ether, EGDME = ethylene glycol dimethyl ether, DEGMME = diethylene glycol monomethyl ether, DEGMEE = diethylene glycol monoethyl ether ethylene, DEGMBE = diethylene glycol monobutyl ether, DEGMHE = diethylene glycol monohexyl ether, EGDME = diethylene glycol dimethyl ether.

[a] Data taken from [26,27].

2.1. Viscosity

Viscosity of solutions was measured using suspended level capillary viscometer. The clean, dry viscometer was vertically suspended in a thermostat at 30 °C. Flow time of solutions was measured with respect to pure water by means of a calibrated stop watch to determine relative viscosity (η_{rel}). The CTAT concentration (15 mM) was such that solutions showed Newtonian flow.

2.2. Small angle neutron scattering (SANS)

SANS measurements on 15 mM CTAT solutions in D_2O at 30 °C were carried at Dhruva reactor, BARC, Mumbai, India. The solutions were kept in sample holders (5 mm path length) and sample to detector distance was 1.8 m. The range of wave vector transfer Q is 0.017 to 0.35 $Å^{-1}$, where $Q = 4\pi \sin(\theta/2)/\lambda$, here θ is the scattering angle and λ is the incident neutron wavelength. The experimental data were corrected for background, empty-cell contribution sample transmission and normalized to absolute cross-section units. The differential scattering cross section, $d\Sigma/d\Omega$ per unit volume of solution for micelles is given by

$$\left(\frac{d\Sigma}{d\Omega}\right)(Q) = nV^2\left(\rho_p - \rho_s\right)^2 P(Q)S(Q) + B \qquad (1)$$

where, n indicates the number density of the micelles having volume V, ρ_p and ρ_s indicate scattering length densities of the micelle and solvent, respectively. $P(Q)$ is single-particle (intraparticle) structure factor and $S(Q)$ is the interparticle structure factor. B is a constant that signifies the incoherent scattering background, which is due to hydrogen in the sample.

2.3. ^{1}H NMR

^{1}H NMR experiments on sample solutions in D_2O were carried out on a Bruker, Avance II spectrometer (500 MHz).

2.4. Surface tension

The surface tension measurements of CTAT solutions for a wide concentration range in the presence of glycol ethers were carried on Kruss Model K9 Tensiometer, Germany. All the measurements were performed at constant temperature (30 °C within ±0.1 °C). To maintain equilibrium the solutions were kept for at least 15 min before each measurement.

3. Results and discussion

It is well documented that CTAT in water forms rod-like micelles at about 1.9 mM [3,28]. With further increase in concentration, these micelles transform into flexible worm-like morphology forming highly viscous or viscoelastic solutions [25,29]. Keeping this in mind and in order to monitor the effect of glycols and their ethers on WLMs, we determined relative viscosity of 15 mM CTAT solution in the presence of glycol additives. Figs. 1(a, b) and 2(a, b) represent relative viscosity in

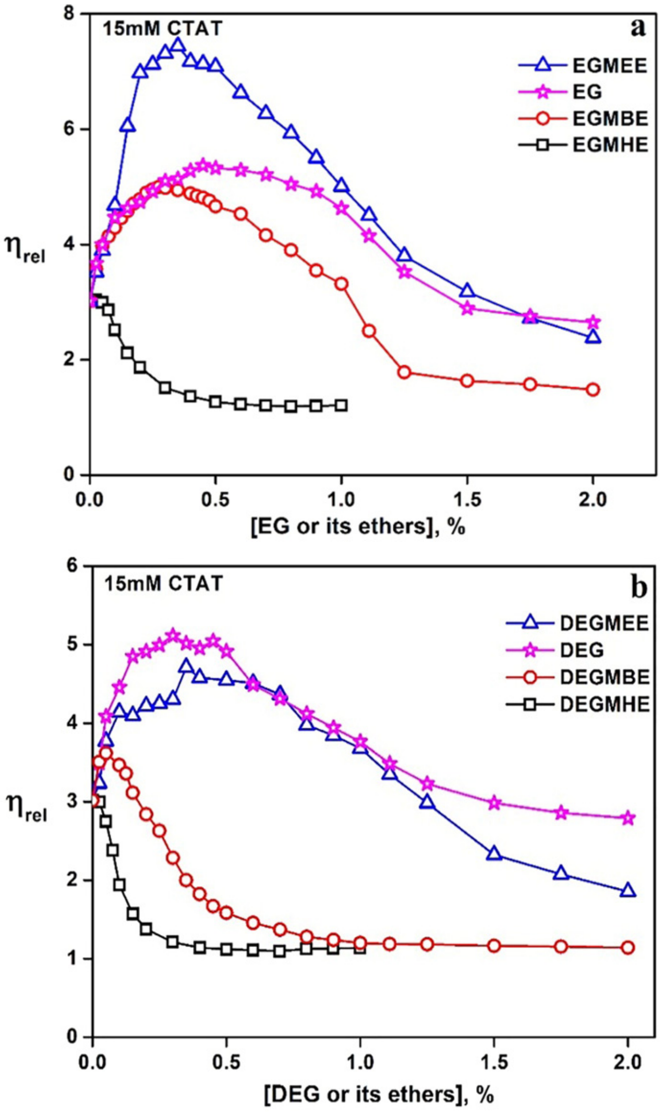


Fig. 1. Relative viscosity (η_{rel}) of 15 mM CTAT in the presence of (a) EG its ethers, (b) DEG and its ethers.

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