

Diesters of Pyromellitic Acid – New Amphiphilic Surfactants

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The aim of this work was to synthesize new amphiphilic surfactants – diesters of pyromellitic acid (DEPA). Self-assembled amphiphilic oligomers based on dianhydrides are used as nanoreactors and nanocontainers for many practical applications. Synthesized amphiphilic surfactants contain hydrophilic and lipophilic chains and are soluble in both polar and non-polar solvents, what is achieved through solvation of corresponding fragments. The dependence of surface-active properties, including CMC, maximum adsorption in monolayer and the area in adsorption layer occupied by one molecule at the surface interface solution-air from pH was investigated. The presence of carboxyl groups in the molecule of surfactants leads to a significant dependence from pH and negative ξ -potential of micelles. Micelles of amphiphilic DEPA and their aggregates in aqueous solution can serve as nanocontainers and in organic solvents as nanoreactors.

Keywords: Amphiphilic surfactants, CMC, Micelles, ξ -potential, Solubilization.

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1. STRUCTURE OF NEW AMPHIPHILIC SURFACTANTS – DIESTERS OF PYROMELLITIC ACID

Synthesis of new amphiphilic surfactants is in particular interest due to their ability to form direct and reverse micelles and complexes of micellar structures. Such micellar structures can be used as Nanoreactors or Nanocontainers [1]. Synthesis of new amphiphilic surfactant using interactions between pyromellitic dianhydride (PMDA), polyethylene glycol Monoalkyl Ethers (MPEGM.m.) and aliphatic primary alcohols

(PA): 1-butanol (Byt), 1-octanol (Okt), cetyl alcohol (Cet); amphiphilic diesters of pyromellitic acid (DEPA) were obtained (Fig. 1). By changing molecular weight of PA and MPEG of amphiphilic surfactants the ratio between lengths of lipophilic and hydrophilic fragments was varied and hydrophilic-lipophilic balance (HLB) controlled.

Composition of synthesized DEPA was confirmed by pH-metric titration, IR (Table 1), ^1H NMR spectra and GPS. (Table 2).

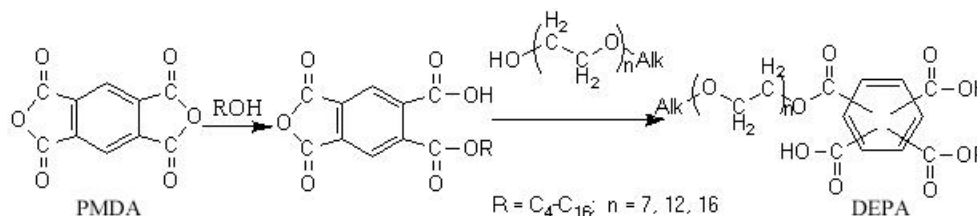


Fig. 1 – Amphiphilic diesters of pyromellitic acid synthesis

Table 1 – Characteristic of IR spectra of DEPC with different lipophilic chain length: butyl (Byt-MPEG550-PMDA), octyl (Oct-MPEG550-PMDA) chetyl (Cet-MPEG550-PMDA)

Wavenumber, cm^{-1}	Group	Wavenumber, cm^{-1}	Group
3426 ÷ 3438	aromatics	1467 ÷ 1456	CH ₂ (alkyl)
2927 ÷ 2921	CH ₃ (alkyl)	1253 ÷ 1249	C-O- (ester)
2854 ÷ 2869	CH ₂ (alkyl)	1106 ÷ 1105	C-O-C (ether)
1729 ÷ 1727	C=O (ester)	760 ÷ 750	CH ₂ (alkyl)
1612 ÷ 1616	aromatics		

Table 2 – Molecular mass of DEPA defined by GPS

Sample DEPA	Mol.mass, g/mol, calculated	Gel permeable chromatography		
		MW	Mn	Polydispersity
Byt-MPEG550-PMDA	842	701	870	1.2
Oct-MPEG550-PMDA	898	928	1015	1.1
Cet-MPEG550-PMDA	1010	1135	1341	1.2

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2. COLLOIDAL PROPERTIES OF DEPA

Obtained amphiphilic surfactants are soluble in both aqueous and organic media. Isotherms of DEPA surface tension show reduce of the surface tension of water to 19-35 mN/m compared to the water with the corresponding pH (Fig. 2).

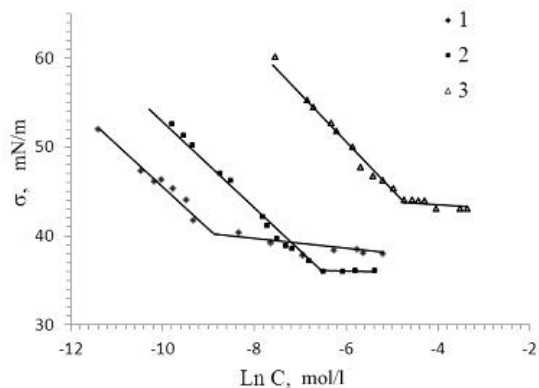


Fig. 2 – Surface tension isotherms of DEPA aqueous solutions: 1. Byt-MPEG550-PMDA (pH 2.2), 2. Oct-MPEG550-PMDA (pH 2.8), 3. Cet-MPEG550-PMDA (pH 3.5)

The presence of two carboxyl groups in the molecule of surfactant leads to a significant dependence of DEPA surface-active properties from pH, including CMC, maximum adsorption in monolayer Γ_{∞} and the area in adsorption layer occupied by one DEPA molecule at the surface interface solution-air A_0 and permit to regulate their by pH of environment.

Increasing of pH is accompanied with growth of CMC and change of Γ_{∞} and A_0 (Table 3), which is associated to increase of DEPA hydrophilicity with increasing of carboxyl groups ionization, their hydration and change of the molecules orientation in the surfactant adsorption layer

Table 3 – Dependence of the colloidal properties of Oct-MPEG550-PMDA from pH of aqueous solutions

№	pH	CMC, mmol/l	$\Gamma_{\infty} \cdot 10^6$, mol/m ²	A_0 , nm ²
1	3,5	1,0	1,55	1,1
2	5,9	5,5	1,35	1,2
3	6,5	10,0	2,20	0,8
4	9,5	11,1	3,26	0,5
5	11,5	16,7	4,68	0,3

ξ -potential of micelles in micellar solutions at pH 6.5, at the concentration lower or close to the CMC (measured on Zetasizer Nano-ZS 90 at 298K) is (-20.8±2,8 mV) for Byt-MPEG550-PMDA, (-29.56±0,97 mV) for Oct-MPEG550-PMDA, (-55.86±2.50 mV) for Cet-MPEG550-PMDA. Due to the presence of carboxyl groups ξ -potential of micelles is negative.

In organic solvents nonpolar DEPA form micelles

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and their aggregates, which solubilize insoluble in these solvents hydrophilic compounds. In particular, benzene solutions of DEPA solubilize insoluble in benzene dye Malachite green (MG). The concentration of solubilized MG increases with increasing of DEPA concentration, at CMC solubilization increases much larger (Fig. 3.a).

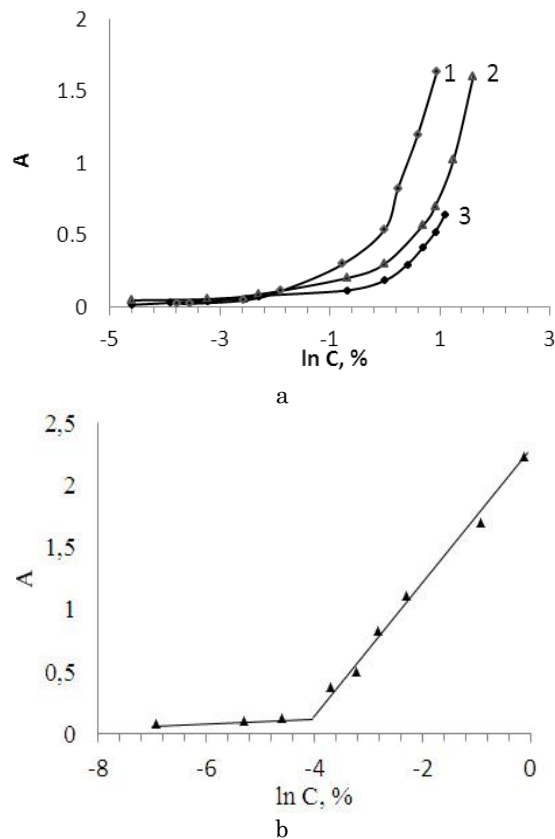


Fig. 3 – Dependence of the intensity of the absorption from concentration of DEPA with solubilized dye: a – MG ($\lambda = 480$ nm) in benzene solution: 1. Byt-MPEG550-PMDA, 2. Oct-MPEG550-PMDA, 3. Cet-MPEG550-PMDA, b – Sudan III ($\lambda = 480$ nm) in aqueous solution-Cet-MPEG550-PMDA

In DEPA aqueous solutions occurring solubilization of soluble in nonpolar solvents and not soluble in water dye Sudan III. At concentrations of Cet-MPEG550-PMDA greater than CMC, solubilization of Sudan III is growing rapidly, as evidenced by the increase of absorption spectra intensity (Fig. 3.b). CMC determined by solubilization of Sudan III in aqueous solutions agreement with the values of CMC obtained by surface tension isotherms.

Thus, micelles of amphiphilic DEPA and their aggregates in aquatic environments can serve as nanocontainers for lipophilic, water insoluble substances, including drugs and biologically active substances, and in organic solvents as nanoreactors for flow reactions of water-soluble reagents, in particular, to obtain nanoparticles of metals and oxides [2].