Dedicated to Prof. Sorin Rosca on the occasion of his 70th birthday

Catanionic Organogelators Derived from D-Sorbitol and Natural Fatty Acids

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*Several catanionic organogelators derived from 1,3 :2,4-bis-O-(p-aminobenzylidene)-D-sorbitol (p-**NH_2-DBS**) and hydroxy derivatives of natural fatty acids were synthesized, characterized and their gelation ability was evaluated. SEM observations of the xerogels formed by association of 1,3 :2,4-bis-O-(p-aminobenzylidene)-D-sorbitol and 12-hydroxystearic acid showed important modifications in the morphology and depend upon the nature of solvent as compared with the xerogels formed by each individual organogelator.*

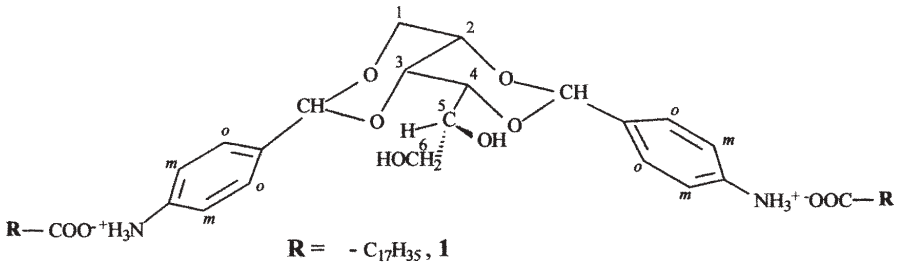
Keywords: catanionic organogelator, 1,3 :2,4-bis-O-benzylidene-D-sorbitol, hydroxy-stearic acids

Low molecular mass organic molecules have attracted in the last fifteen years considerable interest as gelling agent for organic liquids [1,2]. An organogelator is capable of self-organizing into finely dispersed anisotropic aggregates (nanofibers) by noncovalent interactions such as hydrogen bonding, van der Waals, π-stacking, electrostatic and charge-transfer interactions. Noncovalent crosslinks among the nanofibers and/or mechanical entanglements create a three-dimensional network which includes the solvent and so gelation occurs. The network is commonly destroyed by heating but is reformed on cooling thus rendering the system thermoreversible. Organogelators constitute an important class of functional materials with applications in templated material synthesis [2,3], drug delivery systems [4], cosmetics [5], separation technology [6] and biomimetics [7]. 1,3 :2,4-Bis-*O*-benzylidene-D-sorbitol (**DBS**) is known as a versatile gelling agent for a wide range of organic solvents. Recently the gelation ability of **DBS** was extended to more complex systems such as isotactic polypropylene, poly(propyleneglycol), silicone fluids and liquid crystals [8]. We have recently reported the synthesis and characterization of several nitrogen containing derivatives of **DBS (**NO_2, NH_2, NH-C_nH_{2n+1}, n=5, 7, 9) [9]. The attempt to increase the hydrophobicity of the organogelator and consequently to change the aggregation mode by attaching alkyl chains with various lengths to amino group was limited by modest reaction yields. This inconvenient may be surpassed by providing the hydrophobic alkyl chain using the association of 1,3 :2,4-bis-O-(*p*-ammoniumbenzylidene)-D-sorbitol (*p*-**NH_3^+-DBS**) with carboxylate anions of natural fatty acids in 1:2 molar ratio, forming a catanionic organogelator. This technique has been already involved in the synthesis of mixed hydrocarbon/fluorocarbon and other catanionic sugar-derived surfactants [10] or anionic - cationic systems which are homogeneous even at high concentrations (80%) [11]. Catanionic (binary) organogelators composed by cationic gemini surfactants acting as a structure-forming component and tartaric acid acting as a chirality-generating component have been reported by Huc's group [12]. Recently, photo- and thermoresponsive binary organogelators composed of alkylammonium and anthracene-9-carboxylate were reported [13].

In this paper we present the synthesis and characterization of four new catanionic organogelators composed of 1,3 :2,4-bis-O-(p-ammoniumbenzylidene)-D-sorbitol, (p-**NH_3^+-DBS**) and carboxylate anions of stearic acid (**SA**), 12-hydroxystearic acid (**HSA**), erytro-9,10-dihydroxistearic acid (**DHSA**) and erytro,eryth- 9,10:12,13-tetrahydroxystearic acid (**THSA**) in a 1:2 molar ratio (fig. 1).

Experimental part

^{1}H-NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer. Approximately 0.2M (for ^{1}H-NMR spectra) solution in DMSO-d_6, TMS as internal standard was



R = - $C_{17}H_{35}$, **1**
- $(CH_2)_{10}CH(OH)-(CH_2)_6-CH_3$, **2**
- $(CH_2)_7CH(OH)-CH(OH)-(CH_2)_7-CH_3$, **3**
- $(CH_2)_7CH(OH)-CH(OH)-CH_2-CH(OH)-CH(OH)-(CH_2)_4-CH_3$, **4**

Fig. 1- General structure of catanionic organogelators derived from D-sorbitol and natural fatty acids

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Table 1
GELATION TESTS FOR **1-4** IN ORGANIC LIQUIDS (3.0% (WT/VOL)) AT 25°C

Ent.	Organic solvent	*p*-NH_3^+-DBS/HA 1	*p*-NH_3^+-DBS/HSA 2	*p*-NH_3^+-DBS/DHSA, 3	*p*-NH_3^+-DBS/THSA, 4
1.	Hexane	I	I	I	I
2.	Cyclohexane	I	I	I	I
3.	Benzene	I	I	I	I
4.	Toluene	I	I	I	I
5.	Chloroform	G	G	G	I
6.	Methylene chloride	P	P	P	I
7.	Tetrahydrofurane	S	S	S	S
8.	Methanol	P	P	P	P
9.	Ethanol	P	G	P	P
10.	*n*- Butanol	P	P	P	P
11.	Ethyl acetate	P	G	P	S
12.	Acetonitrile	P	G	P	P
13.	Dimethylsulfoxide	S	S	S	S

G = gel; I = insoluble; P = precipitation; S = solution

used. Reported date refer to chemical shifts (ppm, TMS), multiplicity, intensity of the signal and attribution. IR spectra were recorded on FTIR Bruker Equinox 55 equipment in KBr. GC-MS analyses were performed using a Varian 3400 gas-chromatograph coupled with Saturn II mass spectrometer provided with ion trap. SEM pictures of the xerogels were obtained using a Hitachi S-900S scanning electron microscope.

Melting points were determined using a Boetius type microscope with electric plate and are uncorrected. Solvents were purified according to procedures described in literature and kept on 4Å molecular sieves.

Commercially available stearic acid (**SA**) and 12-hydroxystearic acid (**HSA**) were used after purification by recrystallization from ethanol. The structure was confirmed by ^{1}H-NMR and IR spectra.

1,3 :2,4-bis-O-(p-aminobenzylidene)-D-sorbitol, (*p*-**NH_2-DBS**, **5**), was synthesized according to the method described previously [9] and identified by ^{1}H-NMR and IR spectra.

^{1}H-NMR (δ, ppm, DMSO-d_6): 3.47 - 3.62 (m, 2H ,CH_2 - sugar, H^6); 3.79 (m, 1H ,CH - sugar, H^5); 4.02 (s, 1H, CH – sugar, H^4); 4.07 (s, 1H, CH – sugar, H^2); 5.11 (m, 3H, CH_2 - sugar, H^1 and CH – sugar, H^3); 5.45 (s, 2H, Ph-CH); 6.53 (d, J=8Hz, 4H, *p*-NH_2Ph - H^m); 7.09 (d, J=8Hz, 2H, *p*-NH_2Ph - H^o) and 7.11 (d, J=8Hz, 2H, *p*-NH_2Ph - H^o).

IR (cm^{-1}, KBr): 3200-3600 (ν_{O-H} and ν_{N-H}); 3104 (ν_{Car-H}); 2922 and 2876 (ν_{Csat-H}); 1618 (δ_{N-H}); 1342 (ν_{Car-N}); 1293 (ν_{Car-N}, primmary amine); 1092 (ν_{C-O}).

erytro-9,10-Dihydroxistearic acid (**DHSA**, **6**), was prepared with 65% yield by $KMnO_4$ /NaOH oxidation in aqueous solution [14] of technical grade oleic acid (80% oleic acid, as determined by NMR [15]). The crude **DHSA** was purified by refluxing several times with benzene, filtration and recrystallization from ethanol as white solid, m.p. =126°C.

^{1}H-NMR: 0.87(t, 3H,CH_3); 1.25 (m, 20H, CH_2 psn.4-7 and 12-17); 1.49 (m, 6H, CH_2 psn.3, 8 and 11); 2.28 (t, 3H, CH_2 psn.2); 3.20 (t, 2H, CH-OH); 4.20 (s, broad, 2H, OH); 11.9 (s, broad, 1H, COOH).

IR: 3200-3400 cm^{-1}, broad, $\nu_{O-Hasoc}$; 2938 cm^{-1}, $\nu_{CH3\,as}$; 2917 cm^{-1} $\nu_{CH2\,as}$; 2849 cm^{-1} $\nu_{CH2\,sim}$; 2500-2700 cm^{-1}, broad, $\nu_{O-Hasoc\ fromCOOH}$; 1700 cm^{-1}, $\nu_{C=O}$; 1467 cm^{-1}, δ_{CH2} ; 1073 cm^{-1}, ν_{C-O}.

Erytro,erytro-9,10:12,13-tetrahydroxistearic acid (**THSA**, **7**) was prepared with 30% yield by $KMnO_4$ /NaOH oxidation in aqueous solution [14] of commercial sunflower oil. The initial composition of the starting material was determined by GC-MS analysis of the mixture of methyl esters resulted on transesterification in basic medium [16]: 58,5% linoleic acid, 29,9% oleic acid and 11.6% palmitic acid. The same result was obtained by multiple integrations of the signals in the ^{1}H-NMR spectrum of the sunflower oil [15]. The raw **THSA** was purified by recrystallization from ethyl acetate and resulted as a white solid, m.p. 176°C.

^{1}H-NMR: 0.78 (t, 3H, CH_3); 1.25 (m, 20H, CH_2 psn.4-7 and 15-17); 1.44-147 (m, 8H, CH_2 psn.3, 8, 11 and 14); 2.48 (t, 3H, CH_2 psn.2); 3.21 (t, 4H, CH-OH); 4.20 (s, broad, 4H, OH); 11.9 (s, broad, 1H, COOH).

IR: 3200-3400 cm^{-1}, broad, $\nu_{O-Hasoc}$; 2917 cm^{-1} $\nu_{CH2\,as}$; 2849 cm^{-1} $\nu_{CH2\,sim}$; 2500-2700 cm^{-1}, broad, $\nu_{O-Hasoc\ fromCOOH}$; 1701 cm^{-1}, $\nu_{C=O}$; 1467 cm^{-1}, δ_{CH2} ; 1046 cm^{-1}, ν_{C-O}.

General procedure for the preparation of catanionic organogelators, 1-4: a mixture of **p-NH_2-DBS** and natural fatty acid derivative (**SA, HSA, DHSA, THSA**) in 1:2 molar ratio was dissolved in boiling THF and refluxed for 2 h. The resulted solution was concentrated under reduced pressure and the residue was washed several times with chloroform. Catanionic organogelators **1-4** were obtained in quantitatively yields as light-yellow solids.

Gelation test. A sample of gelator (15 mg) was mixed with the dried organic solvent (0.5 mL) in capped test tube, sonicated and heated on an oil bath until a solution was obtained. The solution was cooled at room temperature for 1h and the tube was inverted. Gelation was considered successful if no sample flow occurred.

SEM measurements. A Hitachi S-900S scanning electron microscope was used for taking the SEM pictures. The gel (3%wt/vol) was prepared in a sample tube and frozen in liquid nitrogen. The frozen specimen was evaporated by a vacuum pump for 3-5 h. The dried sample thus obtained was shielded by gold. The accelerating voltage of SEM was 5kV and the emission current was 10μA.

Results and discussion

Catanionic compounds **1-4** were prepared in quantitatively yield in THF from **p-NH_2-DBS** and stearic acid (**HA**) or its hydroxy-derivatives (**HSA, DHSA** and **THSA**, respectively) in 1:2 molar ratio. The formation of the association was proved by ^{1}H-NMR spectra as follows: transformation of the amino groups (from the para position in **p-NH_2-DBS**) into ammonium determined an important deshielding of the aromatic protons (from 6.53 ppm at 7.55 ppm for H^m and 7.11 ppm to 7.68 ppm for H^o, respectively). Dissociation of the carboxylic acids into the carboxylate anionic group determined shielding of the signal for the protons of the methylene group in alpha position: from 2.33

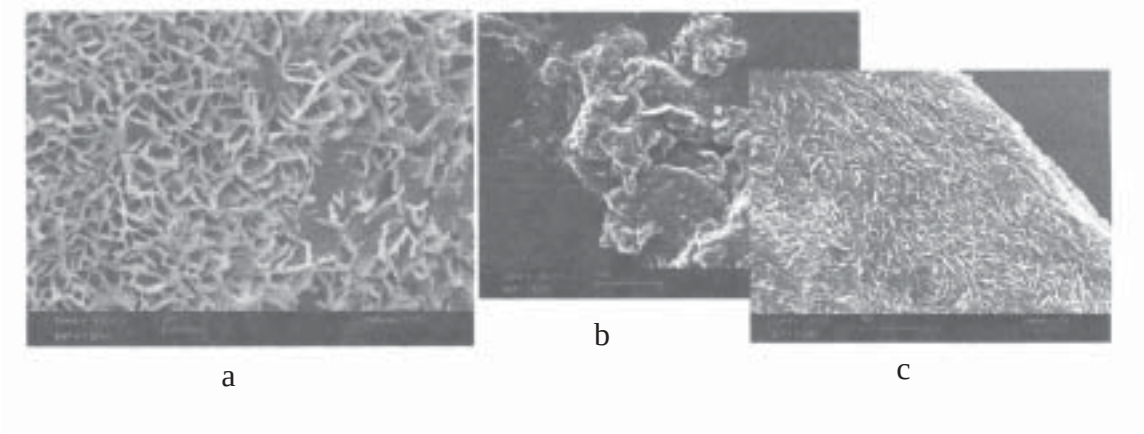

Fig. 2. SEM picture of a dried gel in ethyl acetate of: (a) p-**NH_3^+-DBS/HSA**; (b) **p-NH_2-DBS** and (c) **HSA**

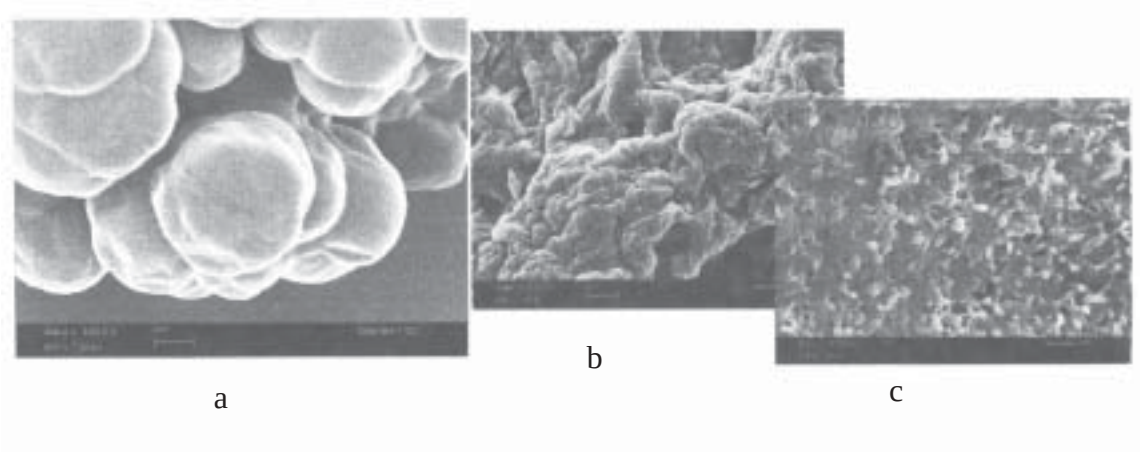

Fig.3. SEM picture of a dried gel in ethanol of: (a) p-**NH_3^+-DBS/HSA**; (b) **p-NH_2-DBS** and (c) **HSA**

ppm for **HA** and **HSA**, 2.37ppm for **DHSA** and 2.48 ppm for **THSA** to 2.17 ppm for all the compounds **1-4**. Dissociation of the carboxylic acid group was also proved by the apparition of a strong $\nu_{C=O}$ band at 1596 cm^{-1}.

The gelation tests for the synthesized compounds **1-4** were carried out for 13 typical organic solvents according to a method previously described [17] and the results are presented in table 1.

The results presented in table 1 show that association of **p-NH_2-DBS** with fatty acids and their hydroxy-derivatives to form catanionic (binary) gelators do not improve the gelation ability of the resulted compounds. As it was shown previously [9], the mechanism of gelation for **DBS** and its derivatives is based mainly on the overlapping of the benzene rings. Introduction of additional positive charges due to the formation of ammonium moiety in the association with fatty acids leads to a disruption of the overlapping of benzylidene groups. Additional van der Waals forces and hydrogen bonding brought by the hydroxyl-derivatives of fatty acids do not compensate this effect and consequently do not improve the gelation ability of the synthesized compounds. An exception is represented by compound **2** (*p*-**NH_3^+-DBS/HSA**) which formed gels in chloroform, ethanol, ethyl acetate and acetonitrile, probably because 12-hydroxystearic acid (**HSA**) a natural compound, constituent of castor oil, has well-known gelation abilities of its own.

Visual insights into the aggregation mode in the gel phase of the compound **2** (*p*-**NH_3^+-DBS/HSA**) were obtained by examining dry samples (xerogels) using SEM (Scanning Electron Microscopy). The morphology of xerogels obtained from compound **2** differs with the nature of the solvent: an alveolar structure with 0.5-1mm unit for the xerogel formed in ethyl acetate (fig. 2a) and a dramatic globular structure with diameters around 4-6 μm for the gel obtained in ethanol (fig. 3a).For comparison pictures of xerogels formed separately by p-**NH_2-DBS** and **HSA** in ethyl acetate (fig. 2b,c) and ethanol (fig. 3b,c) are presented.

Conclusion

We present four new catanionic (binary) organogelators derived from 1,3 :2,4-bis-O-(*p*-aminobenzylidene)-D-sorbitol, (*p*-**NH_2-DBS**) and natural stearic acid and its hydroxy-derivatives. The formation of the association between ammonium positive ion and carboxylate anions of derivatives of stearic acid was demonstated from NMR and FT-IR spectra. The gelation ability was investigated for some typical organic solvents. Transformation of the amino into ammonium group determines a disruption of the overlapping of benzylidene groups and affects the gelation ability. Xerogels obtained from *p*-**NH_3^+-DBS/HSA** in ethyl acetate and ethanol present interesting modification of the morphology as compared with the starting organogelators.

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