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Investigations of preferential solvation on some poly(siloxane-azomethine)s containing dihydroxyanthraquinone units

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ABSTRACT

UV/VIS absorption and emission spectra of some polyazomethines containing dihydroxyanthraquinone units and siloxane moieties have been investigated in solvents of different polarities. The Catalan solvent scale was used for describing the solvatochromic shifts of the absorption and emission bands. The influence of the solvent and composition of binary solvent mixtures on the solvation of the absorption and emission maxima have been studied. The following binary solvent mixtures were utilized: methanol-dimethyl sulfoxide (MeOH-DMSO), chloroform-DMSO ($CHCl_3$-DMSO) and chloroform-methanol ($CHCl_3$-MeOH). The preferential solvation parameters local mole fraction (X_2), excess function (δ_{s2}) and preferential solvation constant (K_{PS}) were determined.

1. Introduction

Anthraquinone derivatives are of considerable importance in different fields, like dye industry, synthetic organic chemistry, biology or medicine. These compounds can be utilized in the production of dyes, as catalysts in paper industry to increase pulp production, as corrosion inhibitors or in dyeing of textile materials [1–9]. Anthraquinone-containing compounds are known to play a significant role as anticancer agents [10–12]. They are used as such or incorporated in polymers, either in the main chain, or in side chains, as an electron acceptor moiety due to the strong electron-withdrawing character [8,13,14]. The spectral characteristics of anthraquinone compounds are dependent on the substituent position, the possibility to form hydrogen bonds and the solute–solvent intermolecular interactions.

The study of the physicochemical phenomena in mixed solvent systems and their interpretation in terms of preferential solvation of solutes by one of the component solvents provides valuable information concerning the role of solvent–solvent interactions on the solvation process. By mixing two solvents, solute–solvent and solvent–solvent interactions become more complex and new solvent properties can be obtained, which are not present in single solvents [15,16]. In solvent mixtures, the solute microenvironment may be different in comparison with the bulk solvent composition, due to the difference between the nature and extent of interaction of the solute with component solvents [17]. Mixed binary solvents supply systems in which the polarity can be tuned by mixing solvents having different polarities in various ratios. In this way, it is possible to modify the solvent–solvent interactions in order to understand the role of these interactions in the solvation process and to obtain desired solvent characteristics and improved solubility [18,19].

Two polyazomethines based on 1,4-dihydroxyanthraquinone (quinizarine) and siloxane diamines with different numbers of dimethylsiloxane units (1,3-bis(3-aminopropyl)tetramethyldisiloxane and α,ω-bis(3-aminopropyl)oligodimethylsiloxane having about 12 siloxane units/sequence) were chosen for this study. The alternation of the polar dihydroxyanthraquinoneimine units and highly hydrophobic dimethylsiloxane moieties results in an amphiphilic copolymer, which can behave interestingly in solution. Three solvents were chosen to create a medium with different polarities: DMSO, methanol and chloroform.

Dimethyl sulfoxide (DMSO) is an aprotic polar solvent with high dipole moment and dielectric constant ($\mu = 3.96$ D and $\varepsilon = 47.24$). Methanol is a protic polar solvent having $\mu = 1.70$ D and $\varepsilon = 32.70$. Chloroform is an aprotic nonpolar solvent with a dipole moment of 1.15 and dielectric constant of 4.81. Therefore, a mixture of chloroform and DMSO provides a dielectric constant range from 4.81 to 47.24 in different ratios and the solvent polarity dependent changes may become very interesting.

The influence of solute–solvent and solvent–solvent interactions on the preferential solvation properties of the approached above-mentioned polymers in binary solvent mixtures, for a range of mole fractions, was explored. Also the spectral behavior in single solvents was analyzed. For this purpose, the electronic absorption and fluorescence spectra in different single solvents and binary mixtures were utilized.

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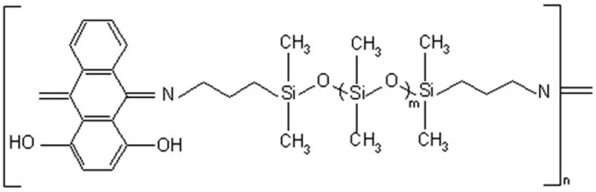

PS1 (m=0); PS2 (m=12).

Fig. 1. Structural formula of poly(siloxane-azomethine)s.

2. Experimental

The polyazomethines, poly{(1,4-dihydroxyanthraquinon)-imine-[1,3-bis(propylene)tetramethyldisiloxane]} – PS1 and poly{[1,4-dihydroxy-anthraquinon)-imine- [α,ω-bis(propylene)oligodimethylsiloxane]} – PS2, have been synthesized based on 1,4-dihydroxyanthraquinone and siloxane diamines differing by the siloxane sequence length (1,3-bis(3-aminopropyl)tetramethyldisiloxane and α,ω-bis(3-aminopropyl) oligodimethylsiloxane having about 12 siloxane units/sequence), and characterized as described elsewhere [20]. Weight molecular masses, as determined by GPC, were 13,300 and 2700 for PS1 and PS2, respectively [20]. All solvents used in the present paper were of spectrophotometric grade. UV/VIS absorption spectra were taken on a Shimadzu 3600 spectrophotometer, using 10 mm quartz cells. Fluorescence emission measurements were performed on a Perkin Elmer LS5 luminescence spectrometer. The excitation wavelength was set at 458 nm for the samples under study. All measurements were made at room temperature. Mixed solvents were prepared by carefully mixing the solvent components by volume at room temperature. Each binary mixture was obtained in volume ratios of 1:5, 2:4, 3:3, 4:2 and 1:5.

3. Results and discussion

3.1. Spectral behavior in single solvents

It is known that due to the extremely low polarity, polysiloxanes are incompatible with almost any organic system [21]. As a result, most of the copolymers consisting in dimethylsiloxane and organic sequences are amphiphilic, being able to self-assemble in a selective solvent. Isolated copolymer molecules can form monomolecular copolymer micelles, where the block with the least affinity for the solvent forms a compact coil protected from contact with the solvent by a corona constituted by the block with the most affinity for the solvent [22]. A very large number of copolymer molecules can also self-assemble in micelles or higher aggregates depending on the nature of the blocks and solution concentration. The changes in properties that occur as micelle form are marked by sharp transitions in many physical characteristics, such as surface tension, viscosity, conductivity, turbidity, nuclear magnetic resonance or fluorescence spectra of the solution [23]. Photophysical processes may exhibit special characteristics at the interfaces. The micelles produce nonpolar–polar interfaces where absorption and emission properties of the dye, for example, become enhanced or quenched [24]. Various techniques to reveal these changes have been reported, and thoroughly reviewed in literature [25].

Table 1
UV/VIS absorption and emission spectral data of siloxane-azomethine derivatives in various solvents.

No.	Solvent	PS1		PS2	
		$\tilde{\nu}_{abs}$ (cm^{-1})	$\tilde{\nu}_{em}$ (cm^{-1})	$\tilde{\nu}_{abs}$ (cm^{-1})	$\tilde{\nu}_{em}$ (cm^{-1})
1.	Toluene	19011; 17921	18302; 17120	20492	18073sh; 17295
2.	Chloroform	19048; 17921	18512; 17259	20576	18646; 18639; 17535
3.	Tetrahydrofuran (THF)	19011; 17921	18536;17203	20661	18587; 18574; 17419
4.	Dichloromethane	18939; 17889	18755; 17247	20747	18709; 18702; 17708
5.	Methanol	18975; 17953	18716; 17141	20790	18692; 18688; 17602
6.	Acetonitrile	19121; 18018	18653;17126	20833	18650; 18639; 17615
7.	DMF	18868; 17857	18495; 17203sh	20661	18471; 18467; 17516sh
8.	DMSO	18727; 17762	18376; 17056sh	20661	18328; 18315; 17238sh

In this paper, we have chosen to study by spectral methods the influence of solute–solvent and solvent–solvent interactions on the preferential solvation properties of the segmented polyazomethines containing dihydroxyanthraquinone units and dimethylsiloxane moieties with different lengths and the structure as presented in Fig. 1. In these polymers, flexible, nonpolar siloxane-aliphatic moieties alternate with rigid, polar dihydroxyanthraquinone units within the backbone and are linked by polar azomethine groups. Our hypothesis is that a tendency to associate in a selective solvent could manifest for this compound, even though it is not a block copolymer and our previous studies on similar structures have demonstrated this [26,27].

The UV/VIS absorption and fluorescence spectroscopy techniques are used in this paper to investigate the behavior of the poly(siloxane-azomethine)s in solvents of different polarities, which are sensitive to the solvent–polymer interactions, and the self-assembling phenomenon occurring in solution [22,28].

Poly(siloxane-azomethine) PS1 shows a broad absorption band in the visible region 400–700 nm with three characteristic vibrational

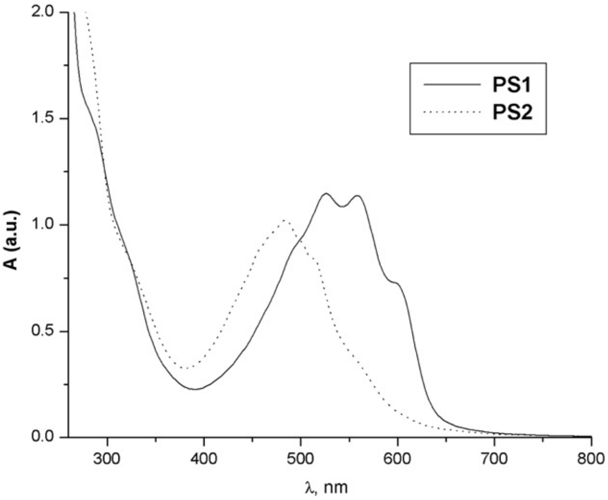

Fig. 2. Electronic absorption spectra of siloxane-azomethine derivatives in THF.

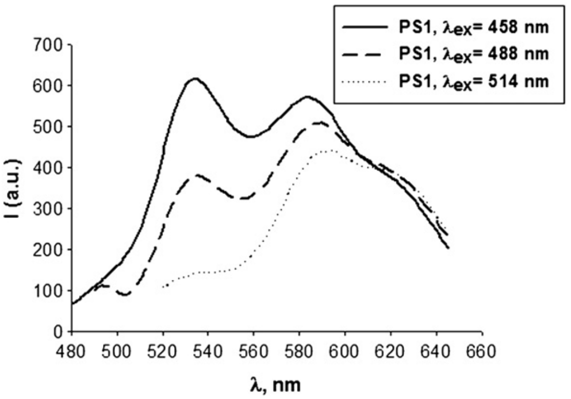

Fig. 3. Fluorescence spectra of PS1 in methanol at different excitation wavelengths.