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3*H*-1,2-Dithiole-3-thione derivatives as novel solvatochromic dyes

Alejandro M. Fracaroli[a], O. Fernando Silva[a], Alejandro M. Granados[a] and Rita H. de Rossi[a]*

The UV–Vis spectrum of 5-(1-butylthio)-3*H*-1,2-dithiole-3-thione (1a) and that of the chromium pentacarbonyl complex of 5-methyl-3*H*-1,2-dithiole-3-thione (3) present significant changes with the solvent polarity. The two absorption bands shown by the compounds in the region above 300 nm were identified by theoretical calculations. For Compound 1a these are n→π^* and π→π^* transitions and for Compound 3 the longest wavelength absorption corresponds to a charge transfer band and shows a remarkably negative solvatochromism. Not only has the wavelength of maximum absorption changed with the solvent but also the ratio of the absorbances at the two wavelengths. The effect of solvents was correlated with solvatochromic parameters such as π^* and α. The spectrum of 5-(1-butylthio)-3*H*-1,2-dithiole-3-one (2) was also measured in different solvents but in this case the changes observed are less significant than for the other two compounds. The spectra of 1a and 3 were also determined in the presence of anionic (SDS), cationic (CTAB), and neutral surfactants (Brig-35) and it is shown that these compounds can be used as probes for the polarity of the binding sites of organized assemblies. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: solvatochromism; thiones; polarity of organized systems

INTRODUCTION

Effects of solvents on reaction rates and equilibria are rationalized in terms of the physicochemical properties of the solvent and its interactions with the species of interest, reactants, activated complexes, and products.[1–5] Information on the effects of medium polarity is obtained most conveniently by studying the spectra (absorption or emission) of certain solvatochromic indicators in solvents and/or in solvent mixtures.

Zwitterionic probes have been employed extensively because of their favorable UV–Vis spectral properties. Examples include 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl) phenolate (Reichardt Betaine, RB), 2,6-dichloro-4-(2,4,6-triphenylpyridinium-1-yl) phenolate (Wolfbeis betaine, WB), 1-methylquinolinium-8-olate (QB), and 4-[2-(1-methylpyridinium-4-yl)ethenyl] phenolate (MePM).[6–14]

The impetus for studying the solvatochromic behavior of these probes is that their ground and excited states differ greatly in polarity, i.e. they serve as models for reactions where there are relatively large differences in polarities between the species of interest, e.g. reactants and activated complexes. Solvatochromic data give information on solvent–probe interactions. For binary solvent mixtures, they shed light on solvent–solvent interactions and on the relationship between the compositions of the probe solvation microsphere and that of the bulk solvent.

Extensive use has been made of an empirical solvent polarity scale, E_T, calculated by Eqn (1):[1]

$$E_T(\text{kcal/mol}) = \frac{28591}{\lambda_{max}}(\text{nm}) \quad (1)$$

This scale converts the electronic transition within the probe into the corresponding intramolecular transition energy in kcal/mol; this allows quantification of the above-mentioned solvent effects.

The use of solvatochromic indicators as models underlines the need for studying probes with widely different structures and hence physicochemical properties. The acid–base character of the indicator is of prime importance, because of solute–solvent hydrogen bonding. Use of a zwitterionic probe like RB whose pKa is relatively high is somewhat limited by the ease of reversible protonation of its phenolate oxygen because the zwitterion is the solvatochromic form. Cases where this problem may arise include the study of relatively acidic solvents,[15] buffer solutions that are employed in the acid region of the pH scale, and solutions of organized assemblies (aqueous micelles, microemulsions, etc.). In the latter case, the charged micelle interface shifts the indicator equilibrium so that the zwitterionic form may be observed only if acid or base is added.[16–19] This procedure (addition of acid or base to the micellar solution) may be problematic because the added electrolyte may change the properties (e.g. the morphology) of the micellar aggregate or lead to the formation of mixed micelles, e.g. alkyltrimethylammonium halide and hydroxide.[19] Use of solvatochromic probes of low pKa is therefore advantageous for the study of both bulk and micellar solutions.

Cationic polymethine dyes, in particular cyanine dyes, are intensively colored and have been frequently used as optical

* *Correspondence to: R. H. de Rossi, Instituto de Investigaciones en Físico Química de Córdoba (INFIQC), Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, X5000HUA Córdoba, Argentina.*
E-mail: ritah@fcq.unc.edu.ar

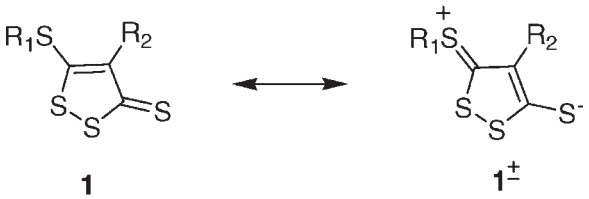
a *A. M. Fracaroli, O. F. Silva, A. M. Granados, R. H. de Rossi*
Instituto de Investigaciones en Físico Química de Córdoba (INFIQC), Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, X5000HUA Córdoba, Argentina

probes in the study of membranes, surfactants, micelles, and dendrimer-based host systems.[20–22]

In solution, the main nonradiative relaxation process for the excited singlet state is the rotation around the conjugated polymethine chain.[23] The quantum yield of fluorescence for this class of dyes increases when the viscosity of the environment increases, because the rotational freedom is restricted.[24]

A large number of fluorescent dyes are used as probes of microenvironments in biological systems or in simpler-organized systems such as micelles and cyclodextrins. Fluorescent electron donor–acceptor molecules display large sensitivity of their emission properties to the polarity of the medium due to the intramolecular charge transfer (ICT) nature of their lowest singlet state; therefore, these compounds are good candidates as fluorescent probes. 4-Amino-phthalimide (AP) shows such an ICT excited state, and stabilization of the ICT state in polar solvents leads to an important Stokes shift of the fluorescence maximum.[25–27] The fluorescence properties of AP are even more sensitive to the hydrogen bonding properties of the solvents.[28] Therefore, the solvatochromism and hydrogen bonding interaction have made AP and its derivatives interesting probes to follow the micellar aggregation process [29,30] and the solvation dynamics in organized systems.[31,32] AP binds to α- and β-cyclodextrins with low association constants (92 and 208 M^{-1}, respectively),[26] and the complex formation leads to a change in the AP fluorescence due to the elimination of water molecules from the surroundings of the probe.[33] The solvation dynamics of dimethylformamide inside the nanocavity have also been studied with AP as a probe.[34] Recently, 3-hydroxyflavone derivatives were proposed to probe hydrophobic sites in microheterogeneous systems.[35]

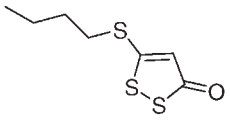
3*H*-1,2-Dithiole-3-thiones are an important class of anticarcinogens that selectively induce the production of phase II enzymes.[36–39] We have developed a method to synthesize a great variety of 3*H*-1,2-dithiole-3-thione (**1**) derivatives substituted at C-5 by arylthio and alkylthio groups and at C-4 by R_2—H, Ph, and OCH_3.[40–42]



1 **1**$^{\pm}$

These compounds have the characteristic of having a donor and acceptor group in the same molecule with an important contribution of structure **1**$^{\pm}$ and as a result they are reactive in front of electrophilic compounds.[43]

Their UV–Vis spectrum shows well-defined absorption at ~320 and ~420 nm. We have shown that upon formation of an inclusion complex of 5-(1-butylthio)-3*H*-1,2-dithiole-3-thione (**1a**) (R_1—Butyl, R_2—H) with β-cyclodextrin the two absorption bands show a bathochromic and hipsochromic shift, respectively.[44] Besides the relative intensity of the bands also changes. These are interesting properties and therefore we explore the behavior of the compound in different solvents with the aim to use it as a polarity probe. We have also prepared 5-(1-butylthio)-3*H*-1,2-dithiole-3-one (**2**)[45] and a pentacarbonyl chromium complex **3**[46] and have studied their spectroscopic behavior in several solvents. It was found that the spectrum of **3** is highly sensitive to the change in solvent.



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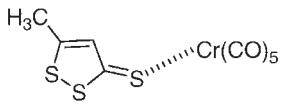

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The results are reported here and it is shown that **1** and **3** can be used as polarity probes and they might be useful for the determination of the polarity of interphases in micelles or other organized systems. Compounds **1** and **3** are small and neutral, therefore they should not perturb the structures of the organized systems.

EXPERIMENTAL

The solvents were purified by the recommended procedures.[47] Their purity was established from the agreement between their experimental $E_T(30)$[48] and published data.[49]

Compounds **1–3** were available in the laboratory from previous work and their purity was checked by thin layer chromatography and NMR.

For the preparation of the solutions, 100 μl of the probe dissolved in hexane or methanol was pipetted into 10 ml volumetric flask followed by solvent evaporation first with N_2 and then under reduced pressure.

The solvent was added and the probe was dissolved, at a final concentration of 1–3 $\times 10^{-5}$ M.

A Shimdzu 2101 PC spectrophotometer was used and the spectrum was run twice at 0.1 nm intervals and constant temperature (25.0 ± 0.1) °C maintained with an external circulating bath.

RESULTS AND DISCUSSION

5-(1-Butylthio)-3*H*-1,2-dithiole-3-thione (1a)

The UV–Vis spectrum of this compound is shown in Fig. 1. It is seen that **1a** has two absorption bands: one at around 320 nm (λ_1) and the other at 420 nm (λ_2).

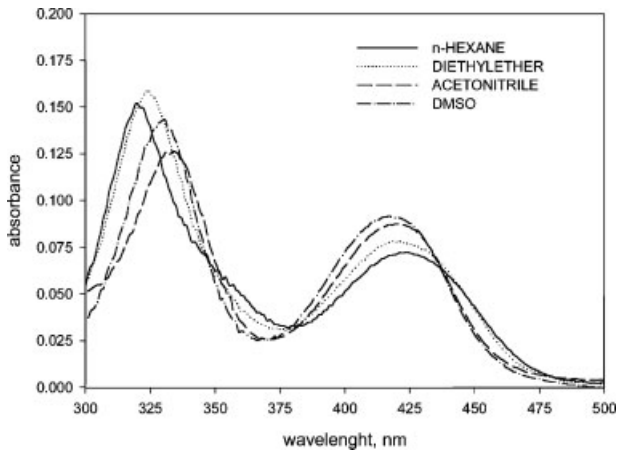

Figure 1. Spectrum of thione (**1a**) (1,2 $\times 10^{-5}$ M) in solvents of different polarities

It is known that thiocarbonylic groups, in molecules such as thioadamantanol or thiocamphor, the lowest energy absorption bands are of type n→π^* and $\pi\rightarrow\pi^*$.[50] We have assigned bands 1 and 2 to $\pi\rightarrow\pi^*$ and n→π^* transitions, respectively based on theoretical calculations using the time-dependent density functional theory (TD-DFT)[51] and natural bond order (NBO)[52–55] methods with hybrid functional B3LYP[56–58] and the 6-31+G* bases set[59] included into the Gaussian 03 package. Band λ_1 shifts from 318 nm in hexane to 333 nm in DMSO while λ_2 moves from 423 to 418 nm (Table 1) in the same solvents. This absorption band is wider than the other; therefore the precision in the determination of its maximum is lower (Table 1).

It is also noteworthy that the relative intensity of the two bands changes considerably with the change in solvent so, A_1/A_2[60] is 2.28 in hexane and 1.44 in DMSO. The change in ratio is because band 2 increases as the polarity increases and at the same time band 1 shows the opposite behavior (Table 1).

The change in λ_2 to shorter wavelengths from hexane to DMSO may be explained by a higher stabilization of the ground state compared with the excited state due to the lower dipolar moment of the latter state. On the other hand, since λ_1 corresponds to a $\pi\rightarrow\pi^*$ transition, it is reasonable to have a batochromic shift from hexane to DMSO due to higher stabilization of the excited state as the solvent polarity increases.[61]

Using Eqn (1) we have calculated the energy for the transition for bands 1 and 2 ($E_T(1)_1$ and $E_T(1)_2$, respectively), and we correlated those values with solvatochromic parameters such as $E_T(30)$.

$E_T(1)_2$ gives a very good correlation with $E_T(30)$ (Fig. 2) while the correlation is poor for $E_T(1)_1$.

Since Compound **1a** is very insoluble in water the value of E_T could not be determined directly in this solvent. Therefore, we prepare solutions of the compound in mixtures of MeOH/water and acetonitrile/water with the concentration of the organic cosolvent less than 20% and the values of λ_1 and λ_2 in the different solvents were plotted against the percentage of the organic solvent. The line obtained was extrapolated to pure water. The values obtained are very similar in the two solvents so for acetonitrile/water the extrapolated values are 71.16 and 85.07

Table 1. Maximum wavelength (λ_1 and λ_2), and absorbance (A_1 and A_2) for Compound **1a**

Solvent	λ_1 (nm)	A_1	λ_2 (nm)	A_2
n-Hexane	318	0.166	423	0.073
Diethyl ether	324	0.159	421	0.078
2-Propanol	326	0.220	417	0.138
Ethyl acetate	326	0.230	420	0.123
THF	328	0.217	419	0.116
Benzene	328	0.247	418	0.138
MeOH	329	0.201	417	0.129
Acetone	329	0.221	419	0.129
Acetonitrile	330	0.137	415	0.085
DMF	331	0.120	420	0.075
DMSO	333	0.131	418	0.091
Water	336[a]	0.304[a]	402[a]	0.313[a]

[a] Value extrapolated from MeOH/water mixtures.

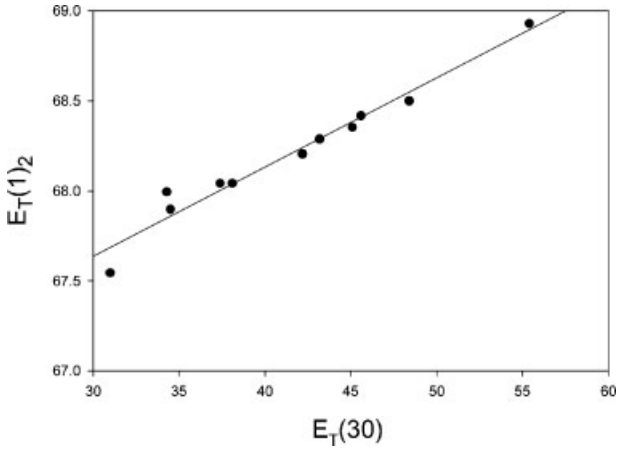

Figure 2. Relationship between E_T for λ_2 of Compound **1a** and $E_T(30)$

for $E_T(1)_2$ and $E_T(1)_1$, respectively. The corresponding values extrapolated from MeOH/water solutions are 70.5 and 85.17.

The value of $E_T(1)_2$ correlates well with the solvatochromic parameters π^* and α (Eqn (2)). The dependence of $E_T(1)_2$ on the α parameter indicates that the *n* electrons of the sulfur of the thiocarbonyl group are involved in the electronic transition and they are partially hydrogen bonded to the proton donor solvents

$$E_T(1)_2 = 0.73\,\pi^* + 0.82\,\alpha + 67.62 \quad (2)$$
$$r = 0.989,\ n = 11$$

On the other hand, $E_T(1)_1$ correlates well with the parameter π^*, Eqn (3), Fig. 3.

$$E_T(1)_1 = -3.7\,\pi^* + 89.5 \quad (3)$$
$$r = 0.988,\ n = 11$$

The ratio of the intensity of absorbance at λ_1 and λ_2, A_1/A_2 correlates very well with parameters π^* and α according to Eqn (4)

$$A_1/A_2 = -0.75\,\pi^* - 0.31\,\alpha + 2.25 \quad (4)$$
$$r = 0.989,\ n = 11$$

It should be noted that the coefficients for π^* and α are negative in Eqn (4) indicating that the increase in polarity/

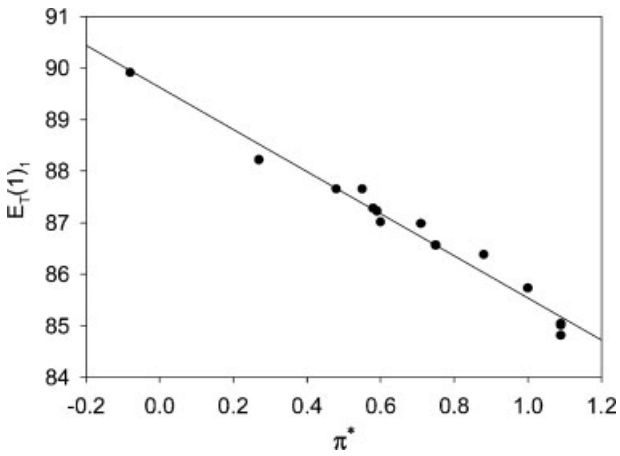

Figure 3. Linear correlation between E_T for λ_1 of Compound **1a** and the π^* parameter

polarizability (π^*) or hydrogen bond donor ability (α) of the solvent produces a decrease in the ratio of absorbances.

5-(1-Butylthio)-3*H*-1,2-dithiole-3-one (2)

The change of a thione group for a carbonyl group produces a significant change in the spectrum (compare Figs 1 and 4). This compound has a maximum absorption at around 280 nm and a shoulder at 310 nm. According to the theoretical calculations, λ_1 (280 nm) corresponds to a $\pi \rightarrow \pi^*$ transition while λ_2 (310 nm) corresponds to an $n \rightarrow \pi^*$ transition. In order to have a better measure of the maximum absorption, the absorption band was deconvoluted into two Gaussians and the change in the maximum of each one and also the change in the absorption ratio of the two bands was determined in different solvents (Table 2). There is no significant change in λ_2 with solvent and $E_T(2)_1$ correlates well with α and π^*, Eqn (5), but the coefficient for π^* is about three times that of α indicating that the polarity/polarizability is the more important factor in determining the change in spectrum in agreement with the $\pi \rightarrow \pi^*$ nature of the transition.

$$E_T(2)_1 = -2.5\,\pi^* - 0.8\,\alpha + 10.2 \quad (5)$$
$$r = 0.977,\ n = 9$$

The absorbance ratio of the two bands correlates with parameters α and π^*, Eqn (6), similar to the behavior of Compound **1**

$$A_1/A_2 = -0.56\,\pi^* - 0.38\,\alpha + 1.52 \quad (6)$$
$$r = 0.977,\ n = 9$$

Analysis of the specific solvent effect based on solvent acidity parameter "α" indicated that the position of the bands, particularly their intensity ratio are strongly sensitive to hydrogen bonding. Increase in the solvent polarity and the formation of hydrogen bonds produce spectral changes in the opposite direction: the shift of the band to a shorter wavelength and the increase in the absorption intensity ratio. This property can be applied to detect the penetration of polar and protic solvents such as water into microscopic particles and nanocomposites.

Pentacarbonyl chromium complex 3

This compound also shows two absorption bands in the visible region: one at ~350 nm (λ_1) and other at ~500 nm (λ_2) (Fig. 5).

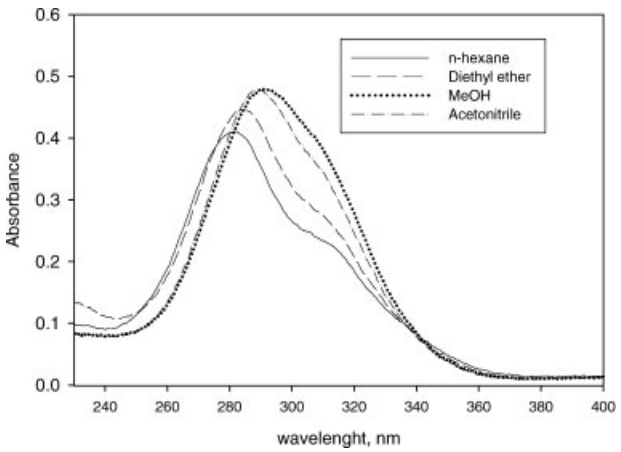

Figure 4. Spectrum of Compound **2** in different solvents

Table 2. Maximum wavelength (λ_1 and λ_2) and absorbance (A_1 and A_2) for Compound **2**

Solvent	λ_1 (nm)	A_1	λ_2 (nm)	A_2
Diethyl ether	281	0.360	308	0.261
Acetonitrile	284	0.341	308	0.313
MeOH	285	0.304	308	0.355
2-Propanol	285	0.316	308	0.338
Ethyl acetate	282	0.362	308	0.277
n-Hexane	279	0.348	307	0.228
DMF	286	0.330	309	0.330
THF	283	0.260	308	0.213
DMSO	287	0.570	309	0.630

The longest wavelength changes very much with the solvent and it is visible to naked eye (Fig. 6). The wavelength of maximum absorption of both bands shifts to shorter wavelengths when the polarity of the solvent changes from hexane to DMSO (Table 3). The wavelength change towards blue of approximately 70 nm for λ_2 can be explained considering that the absorption band corresponds to a charge transfer band which is known to show important negative solvatochromism.[62,63]

We have determined that the changes in the absorption are not due to ligand exchange because when a solution of the complex in hexane or methanol is evaporated and then redissolved in a different solvent, the spectrum obtained is the same as that obtained directly from the dissolution of the solid compound.

Both absorption bands correlate with the π^* parameter according to Eqns (7) and (8) but they do not correlate satisfactorily with $E_T(30)$ as expected since $E_T(30)$ depends on α parameter.

$$E_T(3)_1 = 2.8\,\pi^* + 81.4 \quad (7)$$
$$r = 0.938,\ n = 10$$

$$E_T(3)_2 = 7.1\,\pi^* + 55.5 \quad (8)$$
$$r = 0.977,\ n = 10$$

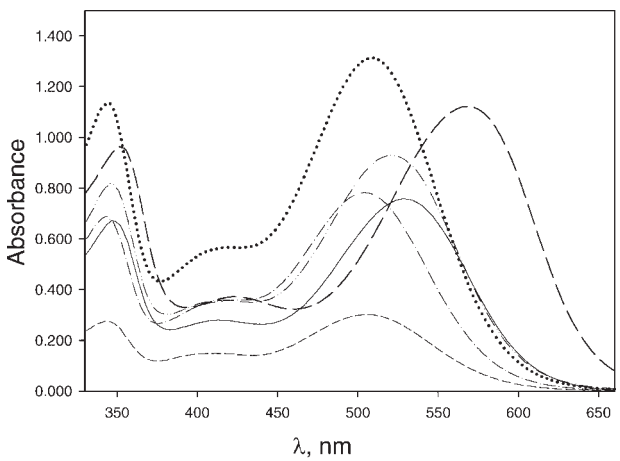

Figure 5. Spectrum of the chromium complex **3** in different solvents. Diethyl ether –; acetonitrile – – –; methanol . . . . .; 2-propanole -..-..-..; acetone -.-.-; *n*-hexane — — —

Journal of Physical Organic Chemistry

Figure 6. Picture of solutions of the chromium complex **3** in different solvents ordered from left to right according to their increasing π^* values: hexane, ether, 2-propanol, ethyl acetate, THF, methanol, acetone, ACN, DMF, DMSO

This result is in agreement with our previous results[46] which indicate that the chromium is bonded to the lone pair of electrons in the thione group; therefore, the nonbonding electron pair of sulfur in the thiocarbonyl group is not available to interact with hydrogen donor solvents.

Studies in micelles

Micelles formed by surfactant molecules are self-assembled structures that are characterized by a strong gradient of polarity from polar interface exposed to aqueous solvent to hydrophobic core formed by hydrocarbon chains. In addition to many industrial applications, such as micellar catalysis and biocatalysis, micelles serve as simple models of biomembranes and test systems for probe development for biomembrane research. Probes that incorporate into the hydrophobic core of micelles and biomembranes and report in a two-band wavelength-ratiometric manner on polarity and hydration at their binding sites are in high demand. For this reason we undertook a series of experiments on the incorporation of synthesized dyes into micelles formed by a cationic (CTAB), an anionic (SDS), and a neutral surfactant (Brig 35) (Fig. 7).

Table 3. Maximum wavelength (λ_1 and λ_2) and absorbance (A_1 and A_2) for Compound **3**

Solvent	λ_1 (nm)	A_1	λ_2 (nm)	A_2
n-Hexane	352.1	0.9630	567.3	1.1220
Diethyl ether	346.8	0.6730	529.3	0.7580
2-Propanol	345.6	0.8190	520.5	0.9300
Ethyl acetate	347.1	0.2960	514.9	0.3230
THF	346.6	1.0830	513.9	1.2290
MeOH	344.1	1.1380	508.9	1.3130
Acetone	342.9	0.6890	503.8	0.7830
Acetonitrile	342.4	0.2770	505.3	0.3020
DMF	341.5	0.3240	495.7	0.3530
DMSO	338.2	0.2660	492.1	0.1790
Water[a]	341.7	N.D.[b]	503.2	N.D.[b]

[a] Value extrapolated from acetonitrile/water solutions.
[b] Value not determined.

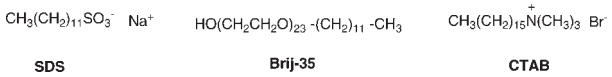

Figure 7. Surfactants used in this study

In the case of the chromium complex **3** it is noteworthy that the intensity of the band with maximum around 400 nm is much stronger than that at 500 nm and this occurs with all types of detergents (Fig. 8 is representative). On the other hand there is no significant change in the maximum absorption. The absorbance ratio decreases as the concentration of the detergent increases. This new band corresponds to the maximum absorption of the thione ligand and it might be that at the interface, some part of the complex decomposes by ligand exchange with the water. According to the values of absorbance in detergent solutions (Table 4) we conclude that the polarity of the binding sites of the micelles is: CTAB > Brig-35 > SDS, which probably indicates that the complex penetrates more deeply in the anionic micelle of SDS. According to the literature[64] the polarity sensed by the Reinchart dye is: SDS > CTAB > Brig 35. The different behavior is reasonable considering that the latter dye is a zwitterion and is likely to interact with the polar headgroup of SDS and CTAB.

Compound **1a** which is also very hydrophobic and so water insoluble dissolves in the presence of detergents. In this case the polarity sensed by the probe (Table 4) is: CTAB ≅ SDS > Brig 35 which is reasonable considering that the dipolar moment of **1a** is relatively high and so it might interact favorably with the polar headgroup of the detergents.

In conclusion we found that Compounds **1a** and **3** are convenient probes to determine the polarity of the binding sites

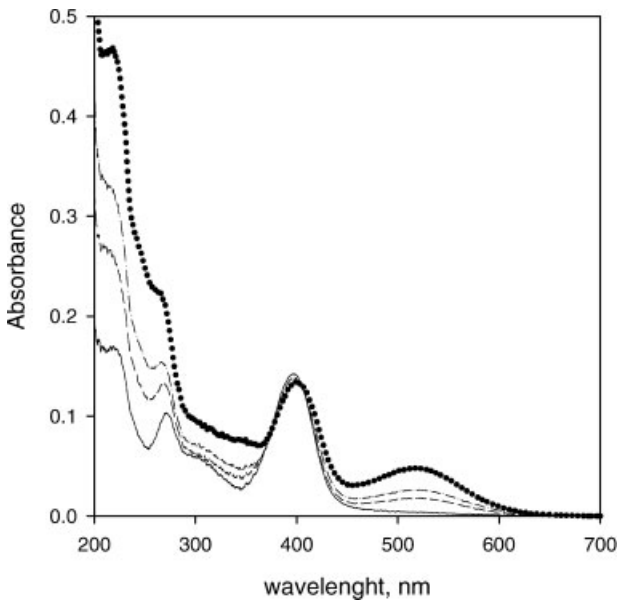

Figure 8. Spectrum of Compound **3** in solutions of different SDS concentrations: 1 mM –, 10 mM ––; 20 mM -.-.-.; 40 mM . . ....

Table 4. Effect of surfactants on the absorption spectrum of Compounds **1a** and **3**

Surfactant	Concentration (mM)	λ_1 (nm)	λ_2 (nm)	A_1/A_2
	Compound **3**			
SDS (cmc = 8 mM)	1		503[a]	
	10		517.6	
	20		518.6	
	40		518.7	
CTAB (cmc = 19 mM)	0.5			
	30		508.3	
	50		506.4	
	100		507.3	
Brij 35 (cmc = 0.1 mM)	0.5			
	1		511.5	
	10		509.8	
	Compound **1a**			
SDS (cmc = 8 mM)	1	334.5	402.3	1.05
	10	332.8	410.3	1.257
	20	332.5	412.4	1.289
	40	332.4	412.5	1.300
CTAB (cmc = 19 mM)	0.5	334.9	398.6	
	30	331.9	414.0	1.368
	50	332.7	414.2	1.364
	100	330.3	414.5	1.415
Brij 35 (cmc = 0.1 mM)	0.5	334.9	339.7	
	1	328.9	412.0	1.37
	10	328.4	419.1	1.554
	20	328.5	419.5	1.555

[a]The compound is completely insoluble under these conditions; this value was extrapolated from data in MeOH/water mixtures.

of organized systems and they have the advantage that are neutral compounds which will not change the charge distribution at the interphases.

Acknowledgements

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