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The "Xanthene Dye – Surfactant" Interactions: Energy and Structures of Nanoassociates

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Abstract: The study of the "dye – surfactant" interactions is very important in view of its practical application in biochemistry, analytical chemistry and modern pharmaceutical engineering; currently, they are interesting as structural nanosystems. Association between anionic xanthene dyes (Sulfo Rhodamine B, SR, or Ethyl Eosin, EE) and cationic surfactant (cetylpyridinium bromide, CPB) has been studied. In order to optimize the geometry of molecules in this research, the methods of molecular mechanics MM+ and AMBER have been used. Energy (standard enthalpy of formation) and the most probable structure of associates were determined with the help of AM1 and PM3 semiempirical methods. Based on the obtained data, it can be concluded that the formation of associates is energetically determined and for the considered systems, "SR + CPB", "EE + CPB" runs with a large gain in energy. This is especially true for system simulations in the presence of water.

Keywords: Association, Sulfo RhodamineB, Ethyl Eosin, Surfactant, Enthalpy of Formation, Semiempirical Methods

1. Introduction

Scientific interest has recently increased in studying heteroassociation processes between dyes and surfactants. Effective practical applications of these interactions are known in a number of areas. Thus, the known application of "dye–surfactant" systems in biochemistry (modification of DNA structures or determination of components in pharmaceutical preparations), analytical chemistry (quantitative determination of metals, quantitative and qualitative determination of surfactants in aqueous media) and physical chemistry (determination of critical micelle concentration (CMC) of surfactants) [1-4].

The "dye – surfactant" interactions take place even at small concentrations ($5 \cdot 10^{-7}$ M and more) of the colored particles in solutions. Therefore, spectrophotometry, and luminescence analysis are the most suitable instrumental methods for studying the properties of nanoassociates [5].

But recently, computer simulation semiempirical methods have been used also to evaluate the interaction energy, structures and stoichiometry of associates. For example, the thermodynamics of the "bromophenol blue – cetylpyridinium chloride" associates was studied using semiempirical methods [6]. Association constants, parameters ionization of nonyl phenol were determined by AM1 method in various solvents, correlation between the ionization potential of organic solvents and CMC was investigated [7]. The electron density distribution of ionic surfactants was determined using AM1, PM3, MNDO semiempirical methods [8]. Enthalpy of formation of pyrazolinylazo dyes was calculated by PM5 method [9]. Solvatochromy of betaine dyes was studied using the PCM medium model of ZINDO method in various solvents [10].

Earlier it have been investigated the peculiarities of the cation–anion association with the participation of dyes [4, 5, 11]. It was shown that the stability of the ionic nanoassociates formed depends on the magnitude of the charge, the spatial and hydrophobic properties of the ion. This report presents the thermodynamic and structural properties of the nanoassociates between anionic xanthenes Sulfo Rhodamine B or Ethyl Eosin with cationic surfactant cetylpyridinium bromide with the help of AM1 and PM3 methods.

2. Materials and Methods

Ethyl Eosin (EE), C. I. 45386, and Sulfo Rhodamine B (SR), C. I. Acid Red 52, were considered as single-charge anions. Molecular modeling and calculations were carried out with the involvement of the "*HyperChem 8.0*" package for different initial variants of counterions arrangement relative to each other. Geometric optimization of ions was carried out by methods of molecular mechanics MM+ for vacuum and AMBER for water; calculation of *Single-point* (the procedure is the system energy in a fixed state with a certain configuration) was carried out by semiempirical methods AM1 and PM3. The *Periodic Box* function was used to simulate the solvent environment (solvent was water).

The semiempirical AM1 and PM3 methods have been used to estimate the values of ΔH^{o}_{f} for ions and nanoassociates. The parameters of these methods were selected so that they allow us to reproduce the experimental values of ΔH^{o}_{f} of organic substances in the best way. Note that the AM1 and PM3 methods take into account a considerably greater number of parameters than other semiempirical methods (for AM1 the parameters were optimized over 100 molecules, from 7 to 21 parameter per element; for PM3, over 657 molecules, 18 parameters per element) [12]. The values of enthalpies were calculated for the standard conditions. The use of two methods of calculation is associated not so much with the desire to achieve greater reliability in absolute values, but to minimize the systematic error in detecting the course of changes in the enthalpy of formation in the ranks of heteroassociates of different composition. The methods were used to determine the most probable structure of nanoassociates also. Other features of the experiment and principles of implementing simulations of the structures of dyes, nanoassociates, and the interpretation of the obtained results are presented previously [13, 14].

3. Results and Discussion

3.1. Features of Applicability of the Methods

Semiempirical methods AM 1 and PM 3 are based on the principles of solving the Schrödinger equation for atoms and molecules with a certain set of approximations and simplifications. For all semiempirical methods, calculations are conducted only for valence electrons, non-optimized basic functions of electronic orbitals and experimentally obtained parameters (parameterization) are used. The AM1 method is an advanced MNDO method, which is widely used to calculate the energy parameters of systems. In this method, the neglect of the differential overlap is used. Changing the part of the theoretical function (first of all, the functions of repulsion of atomic nuclei) and the assignment of new parameters significantly improve the performance of AM1. First of all, it concerns hydrogen bonds and the enthalpy of substance formation (is about 40% better than MNDO), which are fundamentally important parameters in this research. The main disadvantages AM1 relate to the bond "O–O" and "P–O", which are absent in the simulated structures [15-17]. The PM3 method, in turn, was improved AM1. The main difference is that the parameters of PM3 are obtained by comparing much more experimental datum. Therefore, the PM3 method is used for of organic molecules.

In order to optimize the geometry of molecules in this research, the methods of molecular mechanics MM+ and AMBER have been used. In such methods, atoms are considered as Newtonian particles of a certain mass interacting with each other through empirically determined potential fields. The energy of the interaction depends on the interacting atoms, the lengths and angles of the valence bonds and on the non-covalent interactions. The contribution to molecular energy also includes the elasticity of the connection (according to Hooke's law), the bending energy of the valence angles and angular deformation. In such calculations, the forces acting on atoms are represented as functions of the coordinates of the atoms and coefficients of elasticity of the elastic forces that couple the pairs of atoms. Methods of molecular mechanics allow to appreciate the energy of very large systems with minimal time and calculation loss, and the energy of molecules is appreciated taking into account all degrees of freedom. However, they can not be used to simulate systems whose properties are determined by electronic effects or by orbital interactions. MM+ is the suitable method for calculating organic molecules and intermolecular interactions since it has a unique set of parameters for a potential field. But this method can not adequately simulate very polar or charged systems due to the representation of electrostatic interactions as bond dipoles. These parameters are slightly different in the AMBER method, which has been developed for large organic systems such as proteins or nucleic acids. This method was used to model the system with EE. Instead of the dipole bindings, point charges were used, which improves the calculations and reduces the time of optimization of molecules [12, 15, 16].

3.2. Energy and Structure of Nanoassociates

Tables 1 and 2 represent the values obtained in the calculation of the standard enthalpies of the formation of associates with different variants of arrangement of dye molecule and surfactant relative to each other. The tables have the following designations: D is the distance (it is in angstroms) between the oxygen atom of the dye (O) or the nearest atom of the phenyl ring (Ph) and the nitrogen atom in the pyridine of surfactant; dH_{cacl} is the enthalpy of formation of associate; ΔdH is the difference between the total enthalpy of formation of surfactant (dH_{CPB}) and dye (dH_{SR} or dH_{EE}) and the enthalpy of the formation of associate (it is calculated as $\Delta dH = dH_{SR\ (or\ EE)} + dH_{CPB} - dH_{cacl}$).

Table 1. *Energy of «SR + CPB» interaction.*

Version	D, Å	Vacuum				Water (Periodic Box)			
		dH^0_{cacl}		ΔdH^0		dH^0_{cacl}		ΔdH^0	
		AM1	PM3	AM1	PM3	AM1	PM3	AM1	PM3
1	5, 1 (Ph)	-24	-47	80	80	2894	2465	-171	-55
2	5, 2 (Ph)	-32	-54	88	87	–	–	–	–
3	5, 4 (Ph)	23	-5	34	38	3409	2861	344	341
4	4, 4 (Ph)	-12	-42	68	75	2987	2363	-78	-157
5	4, 8 (O)	39	11	17	22	3378	2874	313	354
6	4, 2 (O)	33	7	23	26	2932	2453	-133	-67

Table 2. *Energy of «EE + CPB» interaction.*

Version	D, Å	Vacuum				Water (Periodic Box)			
		dH^0_{cacl}		ΔdH^0		dH^0_{cacl}		ΔdH^0	
		AM1	PM3	AM1	PM3	AM1	PM3	AM1	PM3
1	4, 3 (Ph)	245	205	251	208	2315	1981	-204	-157
2	5, 0 (Ph)	198	167	204	170	–	–	–	–
3	4, 4 (COO^-)	57	47	63	50	1532	1274	-987	-864
4	4, 0 (COO^-)	67	57	73	60	2486	2004	-33	-134
5	5, 6 (O)	53	44	59	47	2496	2003	-23	-135
6	5, 7 (O)	–	50	–	53	2828	2297	309	159

Figures 1 – 4 show the most probable (from the point of view of energy) associate dye – surfactant, for which ΔdH^0 is the largest.

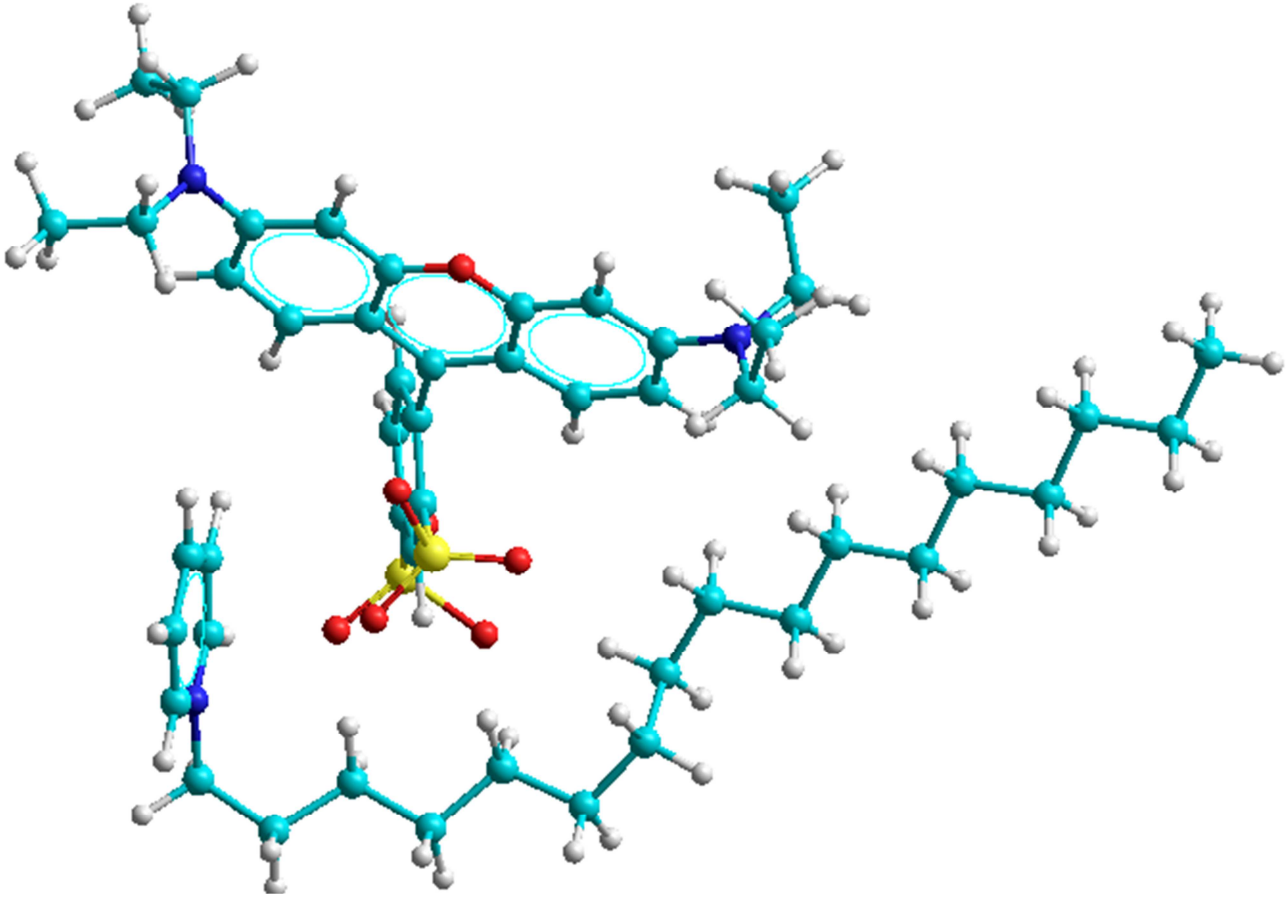

Figure 1. *Associate "SR – CPB" (the structure corresponds to the variant №2 in Table 1; the dye is located at the top).*

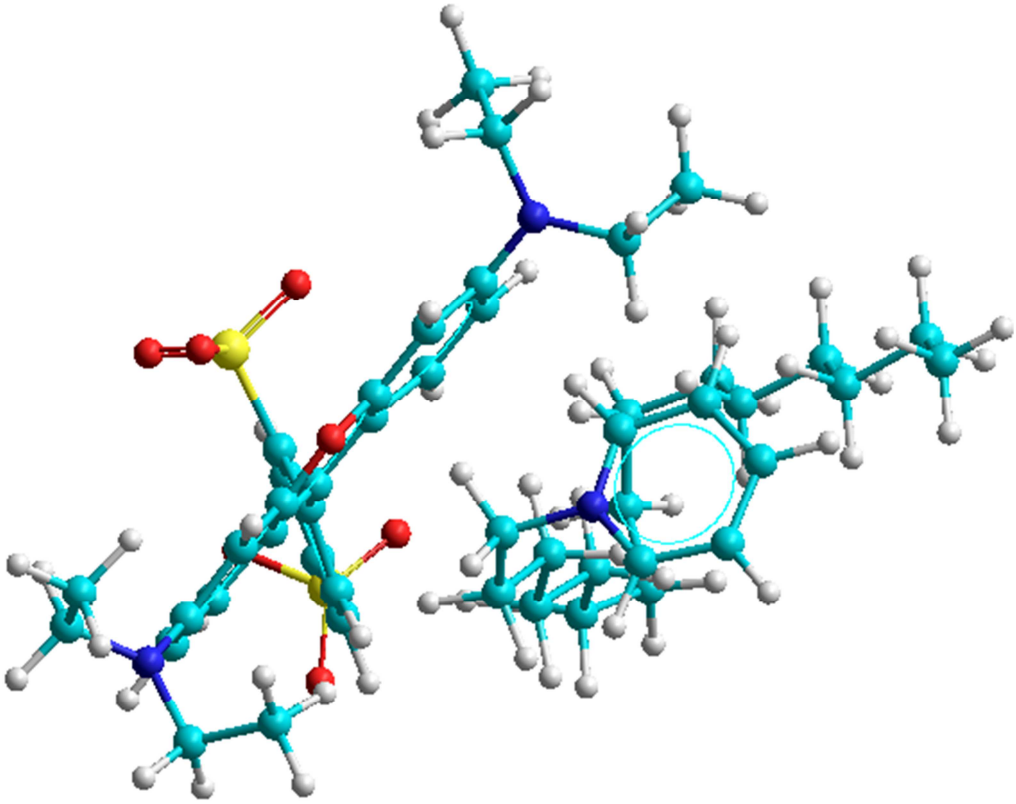

Figure 2. *Associate “SR – CPB” (the structure corresponds to the variant №5 in Table 1; the dye is located on the left).*

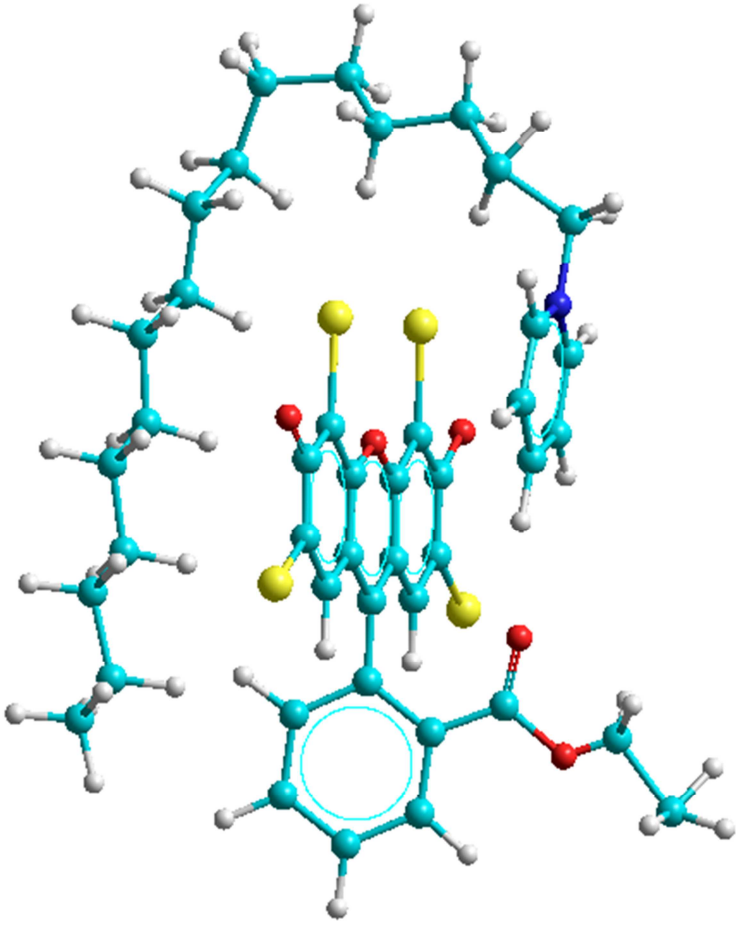

Figure 3. *Associate “EE – CPB” (the structure corresponds to the variant №1 in Table 2; the dye is located at the bottom).*

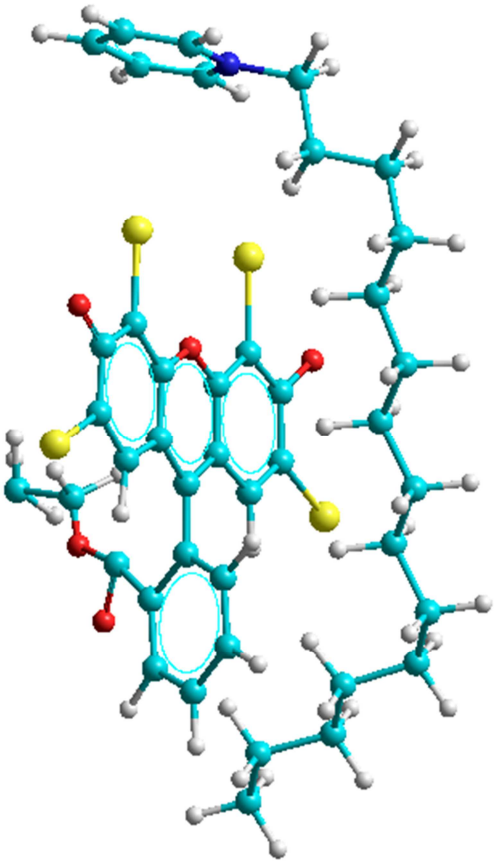

Figure 4. *Associate "EE – CPB" (the structure corresponds to the variant №6 in Table 2; the dye is located on the left).*

Table 3 shows the standard enthalpies of the formation of dye molecules and surfactants, calculated by various methods in vacuum and in water.

Table 3. *Standard enthalpies of the formation.*

A particle	dH^0, kcal/mol, method AM1		dH^0, kcal/mol, method PM3	
	Vacuum	Water	Vacuum	Water
SR	-63	1584	-68	1258
EE	-125	1038	-134	876
CPB	119	1481	131	1262

Tables 4 and 5 show the relative errors of energy calculation for these systems, where $\Delta dH^0 = dH^0_{AM1} - dH^0_{PM3}$.

Table 4. *Relative errors for vacuum.*

A particle	ΔdH^0	$\Delta dH^0 / dH^0_{AM1} \cdot 100\%$	$\Delta dH^0 / dH^0_{PM3} \cdot 100\%$
R200C	5	7,9	7,4
EE	9	6,9	6,7
CPB	12	10	9,2

Table 5. *Relative errors for water.*

A particle	ΔdH^0	$\Delta dH^0 / dH^0_{AM1} \cdot 100\%$	$\Delta dH^0 / dH^0_{PM3} \cdot 100\%$
P200C	326	20,6	25,9
EE	162	15,6	18,5
CPB	219	14,8	17,4

For modeling in a vacuum, the error does not exceed 10%, and 25% in water (Tables 4, 5). These values do not exceed the calculated errors of the calculation methods used. Note that the analysis of spectral changes [5, 11, 13, 14] that accompany cation-anion interactions also indicates the formation of SR or EE associates in aqueous solution. Thus, the obtained calculated data are consistent with the previously spectrophotometrically established facts [18] of the formation of associates between SR or EE and cationic surfactant.

4. Conclusion

Based on the obtained data, it can be concluded that the formation of associates is energetically determined and for the considered systems, "SR + CPB", "EE + CPB" runs with a large gain in energy. This is especially true for system simulations in the presence of water. The latter emphasizes the important role that water molecules play in the process of associative formation. Thus, the calculated data on the manifestation of cation-anion interactions are consistent with

the experimental data, which have been obtained on the basis of measuring the absorption spectra of "an ion dye – an ion surfactant" systems.

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