

Max-Planck-Institut
für Mathematik
in den Naturwissenschaften
Leipzig

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structure of supramolecular nanoaggregates
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by

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Preprint no.: 90

2008



Integral equations study of solvent effects on the structure of supramolecular nanoaggregates formed by cyanine dyes

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We performed a modeling study of the effects of aqueous solvent on the structure of of supramolecular nanoaggregates formed by cyanine dyes. Using a supermolecule approach and the reference interaction site model we calculated optimal structures of hydrated monomer-ion, dimer, and tetramer complexes formed by thea-monomethinecyanine dyes and I^- counter-ions. We calculated the binding and the dimerization energies of the aggregates in vacuum and in water. We found that the most stable structure of all investigated aggregates in vacuum is similar to that of the so-called H-aggregates. However, we observed that the structure of the complexes changes while self-assembling in water. The structure of the most stable dimer in water is found to be also similar to that of the H-aggregates, whereas the tetramer complex shows a structure typical for another structural form of the complexes - J-aggregates. We proposed an explanation of this cross-over transformation. The obtained results correlate well with available experimental data.

I. INTRODUCTION

The aggregation of molecules into well-defined supramolecular assemblies has recently attracted much of attention due to a number of promising nanotechnological applications of these materials. In particular, synthetic cyanine dyes are popular for construction of such self-assembled systems due to a variety of their industrial applications [1]. These dyes can form thread-like supramolecular assemblies in concentrated aqueous solution which can be

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characterized by the appearance of a new distinctive absorption band, which is red-shifted and very narrow with respect to the monomer absorption peak. These assemblies are usually called J-aggregates [1, 2, 24]. In some cases, however, there have been observed cyanine dyes aggregates with the absorption band shifted towards smaller wavelengths (hypsochromic shift) [2]. Such assemblies have been called H-aggregates.

Although the cyanine dyes aggregates have been experimentally studied for more than a half of century and a wealth of experimental data on the behavior of such aggregates has been accumulated up to date, there is a certain lack of information on the supramolecular structure of the aggregates on atomistic level because their noncrystalline nature and large size do not allow one to use the high-resolution X-ray spectroscopy and solution-phase NMR methods of structural investigations.

These days, the modern molecular modeling methods provide an alternative way of studying structural properties of supramolecular aggregates [6–8]. However, the standard methods of direct molecular simulations are hardly applicable to the problem of dyes aggregation in solution because of the large time scales associated with that process (up to several days [3]). The large number of solvent degrees of freedom one has to take into account in the direct simulations makes such calculations practically unfeasible these days. What is why molecular studies of cyanine dyes are mainly limited by dye crystals [4] or cyanine dimers in vacuum [5].

We believe the methods based on the integral equations theory of molecular liquids [9] are more suitable for the computational treatment of self-assembled cyanine aggregates, since computational costs required to treat the solvent effects by this method are less by 2 ÷ 3 orders than it needs in molecular dynamics or Monte-Carlo simulations. Most popular among the integral equation theories is the reference interaction site model (RISM) pioneered by Chandler and Andersen [10] and then extended to the dipolar liquids [11]. The approach is based on calculations of radial distribution functions (RDF) via the site-site Ornstein-Zernike (SSOZ) integral equation.

The goal of this communication is to apply the RISM method to investigate the self-aggregation of cyanine dyes on aqueous solution. We will calculate various thea-monomethinecyanine (TMMC) dye oligomers up to tetramers arising in water under ambient conditions, i.e. normal pressure and temperature equal to 25⁰C. We will consider I^- as a counter-ion to avoid an additional complexity caused by flexibility of structure and peculiar

orientations of molecular contra-ions. Although the hypernetted chain closure (HNC) has been employed in the original RISM procedure [11], the predictions from this method provide only a qualitative picture for hydrated polar solutes. Therefore we will use a modification of the HNC to eliminate this drawback in computations of hydration energies [12–14].

II. METHOD OF COMPUTATION OF SELF-ASSEMBLED AGGREGATES

My main assumption is that arising aggregates can be considered within the framework of a supermolecule approach [15]. Following this method, the aggregate is constructed from molecules of interest and the mean force potential (MFP) between of the associating constituents includes the two contributions:

$$F(\mathbf{R}\Omega) = U(\mathbf{R}\Omega) + \Delta\mu(\mathbf{R}\Omega), \quad (1)$$

where $U(\mathbf{R}\Omega)$ is the direct pair potential between the molecules, which depends on the distance \mathbf{R} and the angular orientation Ω of the molecules, while $\Delta\mu(\mathbf{R}\Omega)$ is the change in the excess free energy due to deposition of the molecules in the solution with a configuration determined by \mathbf{R} and Ω . This excess free energy $\Delta\mu(\mathbf{R}\Omega)$ is written as

$$\Delta\mu(\mathbf{R}\Omega) = \mu(\mathbf{R}\Omega) - \mu(\mathbf{R} = \infty), \quad (2)$$

whereas $\mu(\mathbf{R}\Omega)$ is expressed in terms of RDFs $g_{s\alpha}^{uv}(r) = h_{s\alpha}^{uv}(r) + 1$, which can be calculated within the RISM framework by the solution of the SSOZ equations:

$$h_{s\alpha}^{uv}(r) = \sum_{m,\gamma} \int \int w_{sm}^u(|\mathbf{r} - \mathbf{r}_1|) c_{m\gamma}^{uv}(|\mathbf{r}_1 - \mathbf{r}_2|) \chi_{\gamma\alpha}(r_2) d\mathbf{r}_1 d\mathbf{r}_2, \quad (3)$$

where $\chi_{\gamma\alpha}(r) = w_{\zeta\beta}^v(r) + \rho h_{\zeta\beta}^{vv}(r)$ is the solvent susceptibility, ρ denotes the average solvent density, the superscripts v and u correspond to the solvent and the solute, Latin symbols denote the solute sites and Greek symbols denote the solvent sites. In the above relations, I have introduced an intramolecular correlation function $w_{ij} = \delta_{ij}\delta(r) + (1 - \delta_{ij})\delta(r - L_{ij})/4\pi L_{ij}^2$, where L_{ij} is the distance between the sites i and j of a molecule.

The above equations include also the second unknown variables $c_{m\gamma}^{uv}(r)$ which are the site-site direct correlation functions. A closure relation is required to complete set (3). The simplest closure is given by the HNC approximation:

$$c_{m\gamma}^{uv}(r) = \exp[-\beta U_{m\gamma}^{uv}(r) + \gamma_{m\gamma}^{uv}(r)] - \gamma_{m\gamma}^{uv}(r) - 1, \quad (4)$$

where $U_{m\gamma}^{uv}(r)$ is the intermolecular site-site potential, $\gamma_{m\gamma}^{uv}(r) = h_{m\gamma}^{uv}(r) - c_{m\gamma}^{uv}(r)$ is the indirect correlation function, while $\beta = (k_B T)^{-1}$ where k_B is the Boltzmann constant, and T is the absolute temperature.

The free energy of solvation can be obtained in a closed form within the RISM/HNC theory [10, 11, 16]. However, the RDFs responsible for hydrogen bonding are overestimated by the HNC, whereas the RISM/HNC model is rather poor for thermodynamics of hydrophobic solvation [17]. Much effort has been spent to improve the RISM/HNC approach and develop advanced models capable to provide accurate thermodynamics of hydrated molecules [12, 13]. In our work we are using a so-called Partial Wave expansion [13] which gives one the following expression for the excess chemical potential:

$$\beta\mu_{PW} = \beta\mu_{GF} + 2\pi\rho \sum_{i\alpha} \int_0^\infty \widetilde{h}_{i\alpha}^{uv}(r) h_{i\alpha}^{uv}(r) r^2 dr, \quad (5)$$

where $\widetilde{h}_{i\alpha}^{uv}(r) = \sum_{j\gamma} w_{ij}^{u-1}(r) * h_{j\gamma}^{uv}(r) * w_{\gamma\alpha}^{-1}(r) = \sum_{\gamma\beta} c_{i\gamma}^{uv}(r) * (\delta_{\gamma\alpha} + \rho h_{\gamma\beta}^{vv} * w_{\beta\alpha}^v)^{-1}$.

Recently, we have improved the free energy expression by semiempirical corrections accounting properly for excluded volume and the hydrogen bonding effects [14]. The expression for the excess free energy reads in this case:

$$\mu_{PWC} = \mu_{PW} + a\beta^{-1}\rho V_u + b\delta_{iOH}. \quad (6)$$

In this equation, a and b are fitting coefficients, and $V_u = \rho^{-1} + h^{vv}(k=0) - h^{uv}(k=0)$ is the partial molar volume, where $h^{vv}(k=0)$ and $h^{uv}(k=0)$ are the Fourier transforms of the relevant total correlations functions at $k=0$. The last term is a correction due to the presence of the hydroxyl oxygen, while δ_{iOH} means the function equals unity in the case of hydroxyl oxygen, and zero in other cases. This term suppresses the effect of the overestimated hydrogen bonding.

To calculate the optimal configuration of the supermolecule, we need to evaluate $F(\mathbf{R}\Omega)$ at various \mathbf{R} and Ω and then to find the global minimum of the MFP. An initial guess is required for \mathbf{R} and Ω . As it will be shown, the configurations corresponding to the local minima of $U(\mathbf{R}\Omega)$ in vacuum can be used for this purpose, since electrostatic interactions between the cations and contra-ions are the driving force of the aggregation. Furthermore, the hydration of the complexes do not result in a new minimum, but lead to small changes in stable and metastable configurations. These changes determine the polarization energy E_p , i.e. variations of the intramolecular energy of the supermolecule due to displacement of

its constituents. Thus, the final relation for the MFP is rewritten as:

$$F(\mathbf{R}\Omega) = U(\mathbf{R}_{vac}\Omega_{vac}) + \Delta\mu(\mathbf{R}_{vac}\Omega_{vac}) + E_p(\Delta\mathbf{R}\Delta\Omega). \quad (7)$$

At the same time, the computational procedure for revealing the structure of the arising aggregates is summarized as follows: (i) *calculate minima $U(\mathbf{R}\Omega)$ in vacuum for the chosen supermolecule by conventional molecular mechanics*, (ii) *calculate $\Delta\mu(\mathbf{R}_{vac}\Omega_{vac})$ by (3) in water with configuration $\mathbf{R}_{vac}\Omega_{vac}$ corresponding to a local minimum of U in vacuum*, (iii) *find changes in the MFP and evaluate E_p caused by the solvent effect*.

We use the OPLS-UA force field [18] for interaction potentials, they are listed in the support information. The partial charges have been calculated with the use of Gaussian quantum chemistry package. The solute-solvent intermolecular potentials are represented by the Lennard-Jones (LJ) and the Coulomb terms, with the LJ parameters σ_{uj} and ε_{uj} are determined according to the combining rules: $\sigma_{uj} = (\sigma_u + \sigma_j)/2$ and $\varepsilon_{uj} = \sqrt{\varepsilon_u\varepsilon_j}$. I employ the RISM to calculate the water susceptibility and apply the modified SPC/E model of water [17]. These calculations reproduce the main experimental characteristics of bulk water, namely, its dielectric permittivity, positions and amplitudes of RDF responsible for hydrogen bonds, etc [19]. The solute-solvent and solvent-solvent functions have been calculated by the wavelet algorithm [20], which proposes the expansion of site-site correlation functions into the wavelet series and further calculations of the approximating coefficients (see, [20, 21]). As the molecular conformation of the TMMC dye is very stiff we will use a rigid model of this molecule in our calculations.

III. RESULTS AND DISCUSSION

Initially, we calculate the hydration of a TMMC monomer and contra-ion (Table 1). The RDFs obtained for TMMC are typical for organic solutes. Comparing the calculated hydration energies with the experimental data [22], we conclude that relations (??) and (6) yield the values close to the experimental one in the case of I^- . There are no available experimental data on TMMC, but the double hydration energy of 3-methylindole [23] can be used as a reasonable estimate. The comparison of the calculated results with this value indicates that the PWC approximation leads to reliable estimates for TMMC.

Next, we have estimated a monomer-ion formation. There are five minima of U for this

complex	U	$\Delta\mu$				E_p				F			
		HNC	GF	PWC	PW	HNC	GF	PWC	PW	HNC	GF	PWC	PW
I^-		-62.9	-69.0	-63.0	-59.6								
TMMC ⁺		70.9	-19.9	-27.0	-1.7								
proto-H	-62.9	64.3	57.4	53.5	52.9	-0.2	-0.6	-0.4	0.0	1.2	-6.1	-9.8	-10.0
proto-J	-48.0	47.4	44.1	39.0	40.0	-0.4	-0.8	-0.5	-0.2	-1.0	-4.7	-9.5	-8.2
DH	-158.1	142.1	118.1	130.3	108.0	-9.8	-7.5	-3.6	-2.3	-25.8	-47.5	-31.4	-52.4
DJ	-142.7	156.5	108.9	125.6	99.9	-5.5	-7.0	-4.4	-2.7	8.3	-40.8	-21.5	-45.5
TH	-340.0	245.3	202.4	262.4	188.3	-0.9	-2.2	-0.7	-0.7	-95.6	-139.8	-78.3	-152.4
TJ	-303.7	222.8	160.4	224.4	149.3	-0.1	0.7	-0.8	1.0	-81.0	-142.6	-80.1	-153.4

Таблица I: The mean-force potential (F) and its contributions for various hydrated aggregates of TMMC dyes, calculated by the RISM with the use of several modifications of the HNC expression for the excess free energy.

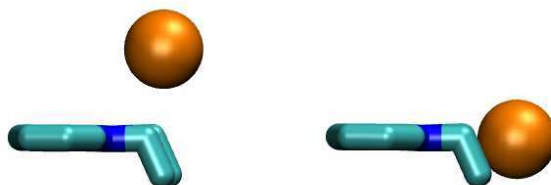


Рис. 1: Optimal structures of the hydrated proto-H (left) and proto-J (right) monomer-ion complexes. The heavy atoms are only indicated, carbons by cyan, nitrogen by blue, and sulfur by yellow colors. The contra-ion is depicted by orange color.

complex in vacuum, three of them lie in the main plane of the monomer, whereas other two minima have off-plane configurations. The global minimum corresponding to the most stable complex arises when the contra-ion is located at distance 3.5 Å above the main molecular TMMC plane and between the nitrogen atoms in the off-plane configuration (Fig. 1b) The conformation with the asymmetrical on-plane location of the contra-ion is the least stable

(Fig. 1a). The difference between these minima is about 15 kcal/mol in vacuum but decreases down to $1 \div 2$ kcal/mol in water (Table 1). I refer these configurations as proto-H and proto-J complexes, since they seem to be prototypes of such aggregates. The number of minima for monomer-ion complexes does not change after dissolution of the complexes, although the contra-ion shifts slightly with respect to the monomer and the polarization energy is small, i.e. $|E_p| \ll |U|$. The HNC expression does not yield correct values for the MFP, while the results obtained by the GF, the PW, and the PWC models are more or less comparable.

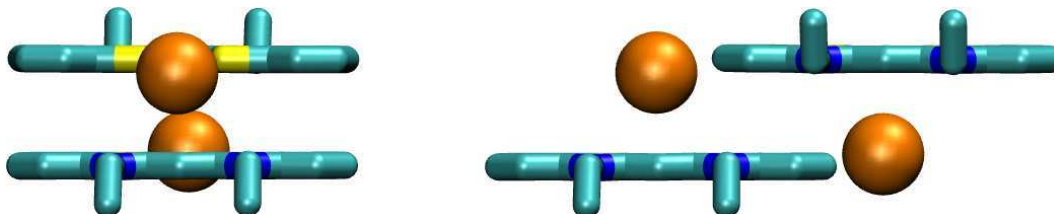


Рис. 2: Optimal structures of the hydrated H- (left) and J- (right) dimers. The notions are the same as in Fig. 1.

At the next stage we treated the dimer formation. The calculated contributions to the MFP are listed in Table 1 for dimers obtained from proto-H and proto-J complexes. The magnitude of the contributions is the same as for monomer-ion complexes, however the polarization energy is larger and about of 4-7 kcal/mol. As it is seen from Table 1, my estimates yield that the dimerization energy of H-dimers is about of -12 kcal/mol (PWC), whereas the dimerization energy is less by 7-10 kcal/mol than that of J-dimers. These estimates are in agreement with experimental data $F_{DH} - 2F_H = -13$ kcal/mol, and $F_{DH} - F_{DJ} = -9.5$ kcal/mol obtained for indocyanine [24] and correlate well with the experimental dimerization enthalpy for a wide class of cyanine dyes [25]. The calculated structures of H- and J-dimers are depicted in Fig. 2. The plane-to-plane distance in the dimers is approximately 3.9 Å, while slipping angle is about of 26° for J-dimers, that correlates also with the value of 22° obtained by minimizing of the Madelung energy of crystal dyes [26]. I note also that J-dimers has nonzero dipolar momentum in contrast to H-dimers. It is due to that contra-ions bind to monomers from the side of ethanol groups. Apart from the considered complexes, there is a large number of various dimers different by orientations of the monomer planes and side groups, the MFP of the complexes is higher than that of H-dimers by 6-12 kcal/mol.

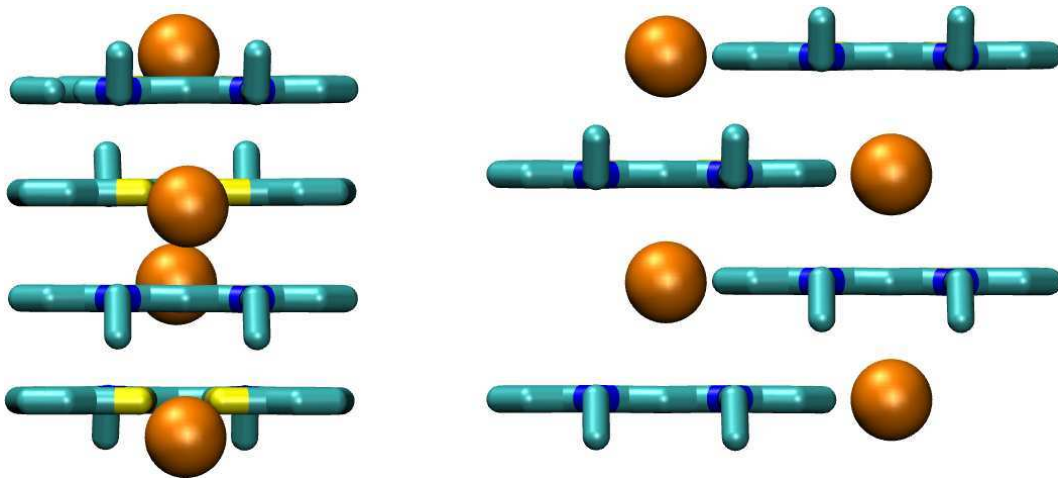


Рис. 3: Optimal structures of the hydrated H- (left) and J- (right) tetramers. The notions are the same as in Fig. 1.

At the last stage, we calculated tetramers formed from the H- and the J-dimers (TH and TJ in Table 1, respectively). The most accurate estimates have been obtained with the use of the GF and the PWC approximations as in the case of dimers. Following my calculations the J-tetramers have the lowest MFP in water, though H-tetramers are more stable in vacuum and have the lowest interaction energy U . The difference between H- and J-tetramers is about $1 \div 3$ kcal/mol, whereas the binding energy of J-dimers is about of -37 kcal/mol. The last value exceeds sufficiently the experimental estimates $E_{ag} = E[(N + 1) * DJ] - E[N * DJ] = -12$ kcal/mol [9]. However, the experimental data are obtained for binding to large J-aggregate but not for a tetramer, and hence my estimate of E_{ag} is only the low bound of this energy, since the binding energy is to decrease as the size of J-aggregate rises. Figure 3 shows the optimal structure of the hydrated J- and H-tetramers. The later have a staircase structure, while the J-tetramers are arranged in a brickwork structure. The structural parameters of tetramers (slipping angle and plane-to-plane distance) are similar to that of the dimers.

We have calculated the oligomers including about 200 atoms, however the method can be extended to the oligomers consisting from dozens and even hundreds of monomers without a sufficient increase of computational costs. We notice, that we treat the monomer as a rigid molecule. But the developed approach can be extended to the case of flexible CH-groups. The flexibility of the groups (especially connected rings of the monomer) can change the flat structure of the monomer and result in tubular forms. To account the flexibility, we need to

add the terms responsible for intramolecular interactions to potential W and then optimize the structure of the oligomers with the use of the developed method. An alternative way may be the energy representation formalism accounting flexibility of solutes [27].

According to our evaluations, we propose the following scenario of the aggregation of TMMC dyes. It seems to be a two-level process. First, a formation of dimers is required. It is controlled by a hydrophobic-hydrophilic balance [25], which is a competition of various factors including nonlinear and nonlocal electrostatic effects [28]. The second step is the J-aggregation. Although H-aggregates having the optimal charge distribution are most stable in vacuum, there is a large number of other metastable oligomers with a higher binding energy. The J-aggregates belong to this class of aggregates, since the charge distribution in these aggregates is not optimal (their dipole momentum is not zero). Although the hydrated H-dimers are more stable than the hydrated J-dimers due to this profit, the J-aggregation may dominate for complexes including more than 2 dimers, since the hydration energy is quadratically proportional to the dipole momentum of the oligomers. Therefore, this step as well as the critical number of dimers required for the J-aggregation is controlled by peculiarities of molecular structure of cyanine dyes, whereas specific types of J-aggregation (tubular, brickwork, etc) depend on the presence of charged side groups and flexibility of molecular structure. The detailed study of these effects will be provided elsewhere.

IV. CONCLUDING REMARKS

Using the integral equations theory of molecular liquids and the supramolecular approach, we have investigated important steps in the process of self-aggregation of cyanine dyes in water, namely, formation of monomer-ion complex, dimers, and tetramers. We have found the energetically favorable structures of the complexes in vacuum and then calculated the optimal structure of the complexes in water by minimization of the MFP. Thus, we have evaluated not only the optimal structure of the complexes, but also a large number of various metastable conformations of the aggregates. The calculated values for the binding and the dimerization energies correlate well with the experimental data, and explain why the H-band corresponding to the stable H-dimers is observed in extremely diluted solutions, while the J-band is revealed only in concentrated solutions. Our estimates are in agreement with the results obtained by the Monte-Carlo simulations [29] and with the experimental data on the

dimerization energies [24].

Acknowledgments

We are thankful to M. V. Basilevsky for fruitful discussions of the work. We acknowledge E. Nikitina for providing us data on partial charges of TMMC.

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