
AB INITIO STUDY OF MIXED CLUSTERS OF WATER AND N,N'-DIMETHYLETHYLENEUREA

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Intermolecular interactions between a single water and two N,N'-dimethylethyleneurea (DMEU) molecules have been investigated using local and density-fitting approximations of the standard Møller–Plesset perturbation theory (DF-LMP2) with the aug-cc-pVTZ basis set. Six stable configurations have been found. In the first three, the water molecule intercalates between two DMEU molecules. In the next three configurations, the water molecule is attached to a stacked DMEU dimer, and these structures are more stable than the first three. These results support the view that DMEU molecules can form contact pairs in dilute aqueous solutions.

1. Introduction

Weak intermolecular interactions play important roles in a wide range of chemical and biological processes at supramolecular level. These complex systems are generally governed by different types of intermolecular interactions, like hydrogen bonds (H bonds) [1], weak van der Waals forces [2], or charge-transfer complexes [3]. Attractive interactions between aromatic π systems are one of the the most studied non-covalent van der Waals forces responsible for many supramolecular organization and recognition processes. In case of aqueous solutions of non-electrolytes, the strength and the balance of these interactions play role in the mixing behavior of the species, and the often present the self-aggregation of hydrophobic co-solvent molecules.

Aqueous solutions of urea are nearly ideal systems. Other carbamides, containing methyl groups, are more hydrophobic, and their mixing behavior with water is no more ideal. The deviation from ideality correlates with the number of methyl groups and, in general, with the size of the hydrophobic part of a molecule. Aqueous solutions of some of these molecules have been investigated by various physico-chemical methods, revealing a considerable self-association in their dilute solutions

[4–8]. The self-association is the consequence of the hydrophobic interactions that are characteristic of aqueous solutions of all kinds of molecules possessing relatively large hydrophobic moieties.

The character of the self-association of carbamides in these solutions showed certain difference. According to neutron scattering, tetramethylurea (TMU) shows a typical hydrophobic character of self-association, while the self-association of the cyclic molecules of dimethylethyleneurea (DMEU) and dimethylpropyleneurea (DMPU) is not sensitive to temperature [7,8]. Such behavior may indicate that the self-association in these cases is dominated by weak intermolecular forces, which are sufficiently strong to bind these molecules together, so that the role of the hydrophobic effects becomes less important. Recent thermodynamic data on aqueous TMU, DMEU, and DMPU reveal the hydrophobic solvation of all these compounds, which is strongest for TMU and weakens to its cyclic derivatives DMEU and DMPU [9–11].

Quantum chemistry seems to be an appropriate method for getting more insight into the energetics and the structural configurations of the bound complexes. In our previous study [12], we analyzed the configurations of energetically bounded complexes of two types: water and DMEU, and a DMEU dimer. The dimer configurations were found to be relatively strong, suggesting that they may be present in the liquid phase, too.

In the present work, we extended the theoretical modeling to larger complexes consisting of three molecules, aiming to reveal the structural and energetic aspects of these weakly bonded molecular associates.

2. Computational Details

In the past few years, efforts have been made to develop new, efficient approximation techniques in order to re-

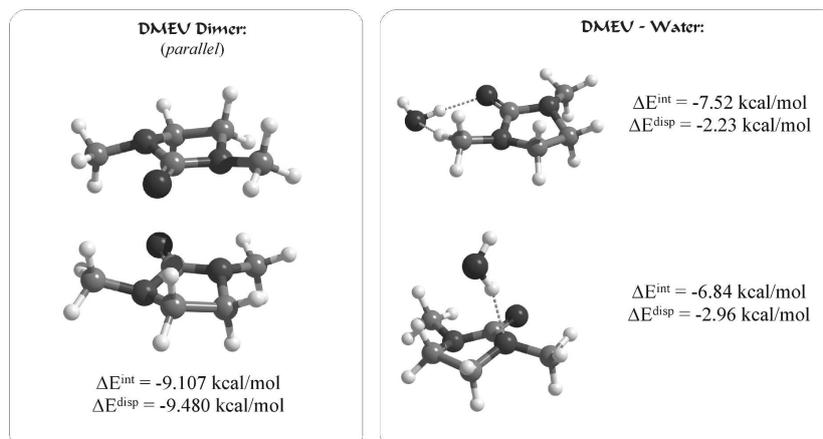


Fig. 1. Optimized geometries of a parallel DMEU dimer and of two DMEU – Water complexes [12]

duce the computational cost of the high electron correlation methods. For the computation of intermolecular interactions, local electron correlation methods [13–15] at second-order perturbation theory level have been proved to drastically reduce the computational effort and, at the same time, give values which are very close to the standard Møller–Plesset perturbation theory (MP2) results. By construction, this method is also virtually free of the basis set superposition error (BSSE) [14, 15]. Quasilinear scaling of the computational cost as a function of the system size [16] of the LMP2 method makes it possible to treat larger systems or to use larger basis sets. Using the density fitting (DF) approximation of the electron repulsion integrals [17–19], one can reduce again the computation time by about one order of magnitude, applying it both in the Hartree–Fock (HF) and LMP2 cases (DF-HF and DF-LMP2). In this way, the computational cost is reduced to $\mathcal{O}(N) - \mathcal{O}(N^2)$ without losing much in accuracy compared with the case of the classical second-order Møller–Plesset perturbation theory (MP2), which scales formally with the order of $\mathcal{O}(N^5)$. Furthermore, considering the local character of occupied and virtual orbitals in the local correlation treatment, one can easily obtain also the dispersion part (an intermolecular effect) of the correlation contribution [20].

Using the DF-LMP2 method implemented in the Molpro program package suite [21], we have performed the geometry optimization for different configurations of N,N'-dimethylethyleneurea dimer + water system considering the aug-cc-pVTZ basis set [22, 23]. Taking the program parameters as presented in Ref. [24], we used the following input settings: *i*) we considered the Pipek–Mezey (PM) localization procedure [25]; *ii*) in order to solve the poor orbital localization in the PM

technique when the larger diffuse basis set was used, we eliminated the contribution of the diffuse basis functions to the localization criteria by setting the corresponding rows and columns of the overlap matrix used in the PM localization to zero. Molecular structures were visualized and analyzed using the open source Gabedit molecular graphics program [26].

3. Results and Discussion

3.1. DMEU dimers and DMEU-water complexes

In our previous work [12], we investigated a N,N'-dimethylethyleneurea dimer and N,N'-dimethylethyleneurea-water systems. For the sake of completeness, we repeat briefly the results relevant to the present work. For DMEU dimers, we found three different dimer configurations, which were called *planar*, *parallel*, and *perpendicular* forms. It was established that the parallel and perpendicular configurations of a DMEU dimer are strong enough to support the binding of a further water molecule. The parallel dimer configuration is shown in Fig. 1.

The SAPT method was further applied for the decomposition of the intermolecular interaction energy to physically relevant components. It turned out that dispersion effects were significant for all studied equilibrium configurations, while the contributions of other energy components were smaller. Accordingly, the stability of DMEU dimers is given by the presence of dispersion effects in the molecular interactions.

In case of DMEU-water complexes, two stable configurations called *Structure I* and *Structure II* were found

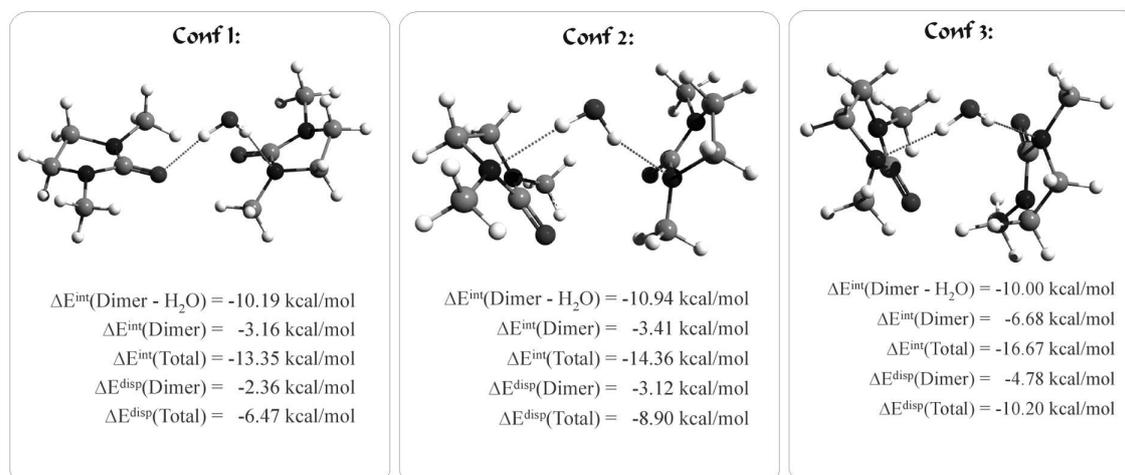


Fig. 2. Geometries of mixed clusters of a water molecule intercalated between two DMEU molecules

(Figure 1). In one case, the water molecule is attached to the C=O group of DMEU, while the O–H...N H-bond is formed in the second case. In both cases, the dispersion-type interaction effects remain important. But, in addition, other contributions like electrostatic or polarization effects became also significant typically for a classical hydrogen bond. Comparing the intermolecular interaction energies for a DMEU parallel dimer and for the DMEU-water systems, one can see that the bonding is stronger in the parallel dimer by about 1.6 – 2.3 kcal/mol. One can expect that, for a larger system, i.e. in the liquid phase, the parallel DMEU configuration can occur with a good chance.

3.2. 2 DMEU – 1 water complexes

Starting from the results obtained for DMEU dimers and DMEU-water systems, we continued our investigation by mixing these two systems. We added a water molecule to the previously obtained parallel DMEU dimer, and a second DMEU molecule to the DMEU-water system. The geometry optimization resulted in six different configurations denoted with *Conf i*, $i = 1 \dots 6$ (Figs. 2 and 3). In each case, the following energy quantities were computed: $\Delta E^{\text{int}}(\text{Dimer}-\text{H}_2\text{O})$ is the intermolecular interaction energy between a water molecule and two DMEU molecules, $\Delta E^{\text{int}}(\text{Dimer})$ is the interaction energy between the DMEU molecules, $\Delta E^{\text{int}}(\text{Total})$ is the total intermolecular interaction energy inside the triplet, $\Delta E^{\text{disp}}(\text{Dimer})$ is the dispersion component of the interaction energy between the DMEU molecules, and $\Delta E^{\text{disp}}(\text{Total})$ is the dispersion component of the total intermolecular interaction energy inside the triplet.

These six configurations are sorted in two groups. In the first group (Fig. 2), the water molecule is trapped between two DMEU molecules, while, in the second case (Fig. 3), the water molecule is H-bonded to one of the molecules of a parallel DMEU dimer. In both graphs, the systems are sorted in descending order according to their total energies.

Group 1. As a starting point, we settled the water molecule between the two DMEU molecules (see *Conf 1* in Fig. 1) in such a way that the water molecule can form two H-bonds similar to what was obtained for the *Structure I* and *Structure II* configurations in [12]. Namely, the water molecule forms O–H...O and O–H...N H-bonds with one of the two DMEU molecules. As can be seen in Fig. 2, the DMEU molecules are quite far from each other. Therefore, the intermolecular energy is mainly given by the sum of contributions of the DMEU-water interactions ($\Delta E^{\text{int}}(\text{Dimer}-\text{H}_2\text{O}) = -10.19 \text{ kcal/mol}$). The direct DMEU–DMEU interaction energy is only -3.16 kcal/mol .

In the next case (*Conf 2* in Fig. 2) instead of a C=O...H–O H-bond, we have an O–H...N H-bond, and the DMEU molecules come a bit closer. The H-bond energy (given by $\Delta E^{\text{int}}(\text{Dimer}-\text{H}_2\text{O})$) is somewhat larger, while the dispersion component of the weak VDW interaction is increased from -6.46 kcal/mol in case of *Conf 1* to -8.90 kcal/mol in the present case. The conformational difference between *Conf 1* and *Conf 2* is -4.74 kcal/mol , mainly due to the stronger dispersion attraction.

The last configuration of the first group is very similar to the previous structure, only the positions of the N...H–O H-bonds are different (see *Conf 3* in Fig. 2). In

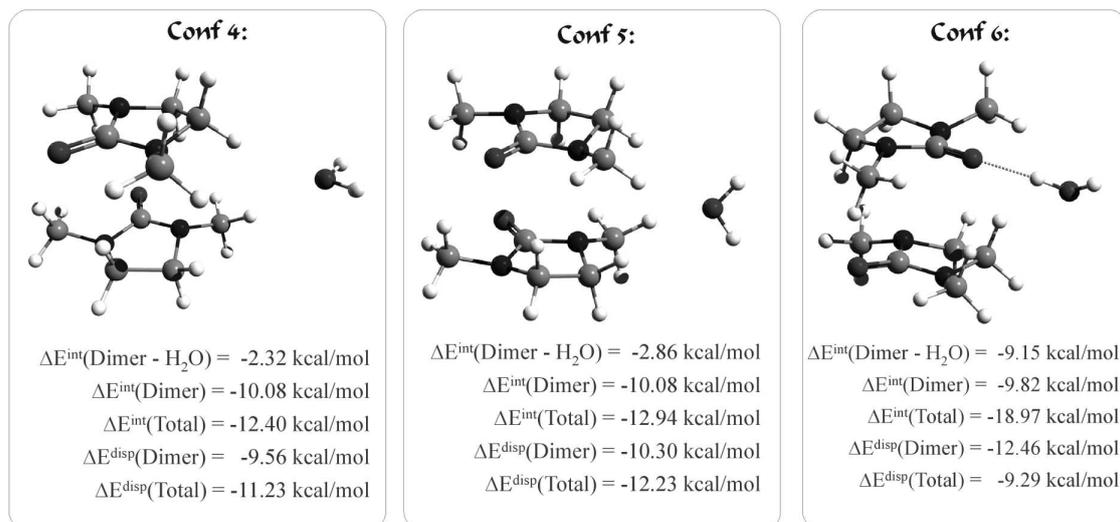


Fig. 3. Geometries of mixed clusters of a parallel DMEU dimer and a water molecule. See the text for the definition of energies

this way, the trimolecular complex becomes more compact, and the DMEU molecules get even closer than in the previous case. Accordingly, the weak VDW attraction increases: from -8.90 kcal/mol (*Conf 2*) to -10.20 kcal/mol , and the H-bond contribution just slightly decreases. We consider *Conf 3* to be the most stable structure amongst those where a water molecule intercalates between DMEU molecules.

Group 2. In the first configuration of the second group, the water molecule leaves the internal space between the two DMEU monomers (see *Conf 4* in Fig. 3). The DMEU monomers join together into a parallel configuration, and the water molecule binds to the hydrophobic part of one of the DMEU monomers by a weak VDW interaction. The nature of this interaction is characterized by the comparison of $\Delta E^{\text{int}}(\text{Dimer} - \text{H}_2\text{O})$, on the one hand, and the difference between $\Delta E^{\text{disp}}(\text{Total})$ and $\Delta E^{\text{disp}}(\text{Dimer})$, on the other hand. One can see that this difference between the total dispersion and dimer contributions accounts for more than 70% of the DMEU dimer–water interaction energy. The total energy of this configuration is only a little less than that of the previous one, the difference is only -1.75 kcal/mol . Namely, this is the energy which derives from the geometry reorganization when the H-bond bridge built by the water molecule is destroyed and is replaced with a stacking interaction of the DMEU monomers.

The next configuration presents a high similarity with the previous one and differs only in the different position of the water molecule (see *Conf 5* in Fig. 3). The water

molecule is placed now at the hydrophobic side of the DMEU dimer, between the two DMEU molecular planes. In this way, both weak VDW effects, coming from the monomers, will give contributions to the DMEU dimer–water interaction. The conformational energy difference shows that, in this case, not only the dispersion effect as the main part of the weak VDW binding is significant, but other contributions like the electrostatic and dipole-dipole interactions are important, as well.

The most strongly bound trimolecular system is obtained for *Conf 6*. Here, in addition to the strongly bound parallel DMEU dimer, a $\text{C}=\text{O} \cdots \text{H}-\text{O}$ H-bond is also present. In this way, the VDW contribution remains important and is completed by the strong H-bond interaction: $\Delta E^{\text{int}}(\text{Dimer} - \text{H}_2\text{O}) = -9.15 \text{ kcal/mol}$. Interestingly, this is only slightly below the energy given by two H-bonds found in cases of *Conf 1–Conf 3*. We think that this is due to the three-body effect of the electron correlation, though the further detailed investigations are needed to elucidate its origin.

4. Conclusions

Considering together the six geometries of DMEU dimer and water complexes, one can conclude that a water molecule can intercalate between two DMEU monomers only with a small probability, while the parallel DMEU dimer with a water molecule bounded to one of them is more preferred. The dispersion effects of the van der Waals interaction play an important role in the formation of different small clusters, both in cases of DMEU–

DMEU and DMEU–water interaction. These findings are interesting from the point of view of the clustering of DMEU molecules in their dilute aqueous solutions. The *ab initio* results show that contact DMEU dimers are relatively strong, and it can be assumed that such clusters are present also in aqueous solutions. This is contrasting to the case of aqueous TMU, in which water-separated TMU pairs have been suggested with regard for neutron scattering data [4].

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ДОСЛІДЖЕННЯ ІЗ ПЕРШИХ
ПРИНЦИПІВ ЗМІШАНИХ КЛАСТЕРІВ
ВОДИ І N,N'-ДИМЕТИЛЕТИЛЕН СЕЧОВИНИ

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Резюме

У межах стандартної теорії збурення Меллера–Плессета у локальному і з підгонкою щільності наближеннях досліджено взаємодію молекули води з молекулами N,N'-диметилетилена сечовини (ДМЕМ) в aug-cc-pVTZ базисі. Знайдено шість стабільних конфігурацій. У трьох із них молекула води внесена між двома ДМЕМ молекулами. В інших, більш стабільних трьох конфігураціях, молекула води зв'язана з ДМЕМ димером у формі стопки. Ці результати засвідчують, що ДМЕМ молекули можуть утворювати контактні пари у розбавлених водних розчинах.