Computational Studies on Dodecylsulfate-Quaternary Ammonium Herbicides Ion-Associate Formation in Water: A DFT Study

Kassem Kalife Nege[a] (IC), Mateus Ribeiro Lage[a] (PG), Jonas Oliveira Vinhal[b] (PQ), Ricardo Jorgensen Cassella[a] (PQ), José Walkimar de M. Carneiro[a] (PQ)

[a] *IQ, UFF, Campus do Valonguinho, 24020-141, Niterói-RJ, Brasil*
[b] *DQ, UFU - Campus Patos de Minas, 38700-128, Patos de Minas-MG, Brasil*
mrlage@id.uff.br

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INTRODUCTION

Agrochemicals have been becoming important to increase the modern agricultural productivity. However, the use of such compounds is the cause of contamination of aquatic systems, considered as one of the main problems in modern society.[1] Chemicals like paraquat, diquat (DQ) and difenzoquat (DF) are largely employed as herbicides in various types of cultures, but this class of compounds has been proved to be toxic.[1,2,3] In this way, recent works focused in the development of efficient methodologies for the extraction of agrochemicals from water.[3] In the present work we report the study of the ion-associate formation from the interaction of dodecylsulfate (DS) ion with diquat and difenzoquat. Understanding the interaction mechanism between such compounds is important for the development of new extraction methodologies.

METHODS

The association of the well-known DFT functional B3LYP with the 6-31G(d) basis set was employed. CPCM solvation model was employed to simulate the effect of the solvent water. The geometry of each isolated ion and of each ion-associate was obtained in the gas phase and in water. Each successful geometry optimization was followed by calculation of the second order Hessian matrix. The results were analyzed in terms of the computed thermodynamic properties.

RESULTS AND DISCUSSION

The final geometries indicate that the ion associate is mainly stabilized by electrostatic interactions, what was confirmed by analysis of atomic partial charges (Figure 1). The interaction energy (IE) was computed according to the equation: $IE = E_{ION\text{-}ASSOCIATE} - (E_{CATION} + NE_{ANION})$ and are given in kcal/mol in Table 1.

Table 1. IE per number of DS added (N).

N	DQ (g)	DF (g)	DQ (s)	DF (s)
1	-163.63	-87.73	-6.26	-4.72
2	-256.30	-114.85	-8.10	-6.02
3	-288.93	-91.54	-14.71	-5.21
4	-285.58	-56.76	-14.64	-1.11
5	-243.01	-	-11.90	-
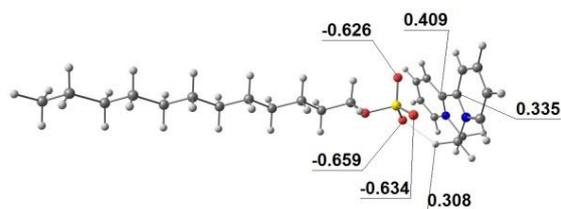
Figure 1. Geometry of DS-DQT ion-associate.

CONCLUSIONS

The results in Table 1 indicate that, for the system containing DQ, increasing the number of DS unities there is an increase in the interaction energy, which is attain the maximum value for 3 or 4 DS unities. For DF the interaction is much weaker and attain the most negative value for two DS unities. This show that for the doubly charged DQ it is needed a higher number of DS unities than for the interaction with DF which has only one positive charge.

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