Chalcogenide Letters Vol. 10, No. 12, December 2013, p.555 - 564

A COMPARISON BETWEEN POLYETHYLENEIMINE AND TRIETHANOLAMINE AS COMPLEXING AGENTS FOR PbS: THEORETICAL PERSPECTIVES

ANED DE LEON*, F. ROCHA-ALONSO, E. F. VELÁZQUEZ,
S. J. CASTILLO[a], A. APOLINAR-IRIBE[a]
Departamento de Ciencias Químico-Biológicas, Universidad de Sonora, Blvd. Luis Encinas y Rosales S/N, Col. Centro, Hermosillo, Sonora, México
[a]Departamento de Investigación en Física, Universidad de Sonora, Blvd. Luis Encinas y Rosales S/N, Col. Centro, Hermosillo, Sonora, México

PbS is a semiconductor with a great variety of applications. Our aim is to propose complexing agents to the chemical bath deposition technique to produce PbS thin films in the future. Thus, we have chosen to study the interaction between PbS and complexing agents. Previously, we have studied triethanolamine as a complexing agent. In this work, we proposed polyethyleneimine as complexing agent and compared the results with those of triethanolamine. The conformational analysis, geometry optimizations and frequencies were calculated at the same level of theory, MP2/LANL2DZ to confirm the isomer stabilities.

(Received May 11, 2013; Accepted December 3, 2013)

Keywords: PbS, Polyethyleneimine, Triethanolamine, Complexingagent

1. Introduction

Semiconductor materials have widespread applications like in the automotive industry, circuit protections, computing, medicine, military and aerospace (1). In particular, we focus on the semiconductor PbS, which can be used as a detection element material. Experimentally, thin films of PbS can be produced through different methods (2) such as metal organic chemical vapor deposition (MOCVD), metal organic vapor phase epitaxy (MOVPE), close spaced sublimation (CSS), molecular beam epitaxy (MBE), screen printing (SP), successive ionic layer adsorption and reaction (SILAR), physical vapor deposition (PVD) and chemical bath deposition (CBD). One of the most common techniques is CBD since it is simple, scalable, the procedure is rather simple and it is not expensive (3).

A main characteristic of the CBD technique is that a solid layer is deposited on substrates immersed in a dilute bath with metal ions. The deposition is thus determined by certain variants. In the past years, the effect of factors such as reagent concentration (4), pH (5), temperature(6) and complexing agents (7-9) on the deposition of semiconductor films has been studied, showing that the structure of the film is influenced by the precipitation of the solid phase. In this particular study we focus on the influence of a complexing agent on PbS. Complexing agents act as a link between the substrate and the solid phase. Some of the most common complexing agents are ammonia. Ethylene-diamine (ED) and ethylene-diamine-tetra-acetic-acid (EDTA) (10).Nevertheless, the use of ammonia has decreased due to its toxicity and volatility. Our group has studied experimentally and theoretically with glycine (7) and acetylacetone (8) as complexing agents for CdS which have shown to yield a good performance. Recently, we have focused on a different chalcogenide, PbS. We started analyzing it by performing quantum mechanical simulations of Pb and PbS with triethanolamine (TEA) as a complexing agent [9]. The results showed stable complexes of Pb(TEA), $Pb(TEA)_2$, PbS(TEA) and $PbS(TEA)_2$ are formed. It did not report complexes with more TEA molecules, since adding more molecules of TEA causes steric hindrance and destabilizes the system. In this work, our aim is to propose a different complexing agent, linear

---

*Corresponding author: d_aned@hotmail.com polyethileneimineand compare the results with those of triethanolamine. In this report we decided to model PEI monomers by adding hydrogen atoms to the tips of the monomers to study the effect of the monomer size and keep the linearity of the molecules (not inducing the formation of rings). Instead of the original formula for PEI, –(C2H5N)–$_n$, we modified it to H[–(C2H5N)–$_n$–]H and refer to it as [PEI]H_2. We look forwardto aid in the experimental setup of the deposition of PbS with [PEI]H_2 and confirm our results with experimental values in the near future.

2. Results and discussion

Physical properties of the systems analyzed in this study are shown in Tables 1 and 2. Plain numbers indicate systems of Pb/PbS with $[PEI]_nH_2$, whereas numbers followed by * indicate systems of Pb/PbS with TEA. Dissociation energies with zero point and BSSE corrections (ΔE(0K)) are in kcal/mol and HOMO/LUMO gaps (GAP) are in eV. Table 1 displays the properties for the systems of $Pb[PEI]_{n=1-5}H_2$ and $Pb(TEA)_{1,2}$. Table 2 displays the properties for the systems of $PbS[PEI]_{n=1-5}H_2$ and $PbS(TEA)_{1,2}$. The figures display selected geometrical parameters, bond distances are in Angstroms (Å) and angles in degrees (°). Figs. 1 and 2 include the systems for $Pb[PEI]_{n=1-5}H_2$, while$PbS[PEI]_{n=1-5}H_2$ are shown in Fig. 2. The figures for $Pb(TEA)_n$ and $PbS(TEA)_n$ are displayed in ref. (9)

Table 1. Dissociation energies and HOMO/LUMO gaps of the systems of $Pb[PEI]_{n=1-5}H_2$ (configurations 1-17) and $Pb(TEA)_{n=1,2}$ are listed. MP2/LANL2DZ energies with zero-point and BSSE corrections are displayed under ΔE(0K) in kcal/mol and HOMO/LUMO gaps are represented by GAP in eV.

System		ΔE(0K)	GAP	**System**		ΔE(0K)	GAP
Pb[PEI]H_2	1	-14.31	5.31	Pb(TEA)	1*	-15.39	5.62
	2	-13.78	5.26		2*	-15.97	5.44
$Pb[PEI]_2H_2$	3	-14.57	5.36	$Pb(TEA)_2$	3*	-31.34	5.62
	4	-15.06	5.39		4*	-31.07	5.62
	5	-13.99	5.33		5*	-35.57	6.56
	6	-13.98	5.32		6*	-32.17	5.67
$Pb[PEI]_3H_2$	7	-30.13	6.37				
	8	-24.88	6.17				
	9	-25.39	6.15				
	10	-24.73	6.15				
$Pb[PEI]_4H_2$	11	-24.19	6.19				
	12	-24.79	6.17				
	13	-25.21	6.28				
$Pb[PEI]_5H_2$	14	-21.30	5.33				
	15	-22.98	6.16				
	16	-25.08	6.17				
	17	-24.91	6.36				

Table 2. Dissociation energies and HOMO/LUMO gaps of the systems of $PbS[PEI]_{n=1\text{-}5}H_2$ *(configurations 18-32) and* $PbS(TEA)_{n=1,2}$ *are listed. MP2/LANL2DZ energies with zero-point and BSSE corrections are displayed under ΔE(0K) in kcal/mol and HOMO/LUMO gaps are represented by GAP in eV.*

System		ΔE(0K)	GAP	**System**		ΔE(0K)	GAP
$PbS[PEI]H_2$	18	-7.38	8.41	PbS(TEA)	7*	-7.68	8.62
	19	-8.17	8.38		8*	-7.04	8.55
					9*	-9.41	8.65
					10*	-6.92	8.54
$PbS[PEI]_2H_2$	20	-9.08	8.39	$PbS(TEA)_2$	11*	-26.03	10.14
	21	-7.59	8.45		12*	-22.03	9.73
	22	-8.44	8.42		13*	-27.81	10.12
					14*	-31.53	9.74
$PbS[PEI]_3H_2$	23	-10.47	8.43				
	24	-11.30	8.89				
	25	-13.56	8.85				
$PbS[PEI]_4H_2$	26	-22.49	8.86				
	27	-21.75	8.98				
	28	-18.07	8.49				
$PbS[PEI]_5H_2$	29	-12.52	8.86				
	30	-13.39	9.01				
	31	-14.65	9.05				
	32	-11.97	8.89				

Structures 1 and 2 of $Pb[PEI]H_2$ are the most stable systems formed by the interaction with only one monomer of PEI. Both have a contact distance with Pb of 2.53 Å, anyhow, structure 2 has a higher dissociation energy with a value of -13.78 kcal/mol probably due to the fact that the electronic cloud from the nearby hydrogens of CH_2 group repel the metal. Their HOMO/LUMO gaps are alike, due to their resemblance. The energies and HOMO/LUMO gaps are similar to those obtained with Pb(TEA). However, in the case of TEA, Pb interacts with oxygen instead of nitrogen, which yields lower dissociation energies.

Structures 3-6 are formed by $[PEI]_2H_2$ and Pb. They all have a contact distance of 2.54 Å. Their energies are considerably similar to those of the geometries 1 and 2. The configuration 4 is the most stable of the $[PEI]_2H_2$ structures, with a dissociation energy of -15.06 kcal/mol probably due to the fact that it is the only system in which the hydrogens of the amino group interacting with Pb are not facing the metal, reducing repulsion. Systems 3, 4 and 6 all interact with a nitrogen in the end of the chain. Structure 5 interacts with a nitrogen in the middle of the chain with a very similar energy to the other systems. The HOMO-LUMO gaps of the systems as well as the dissociation energies are in the same range as in structures 1 and 2 probably because the interactions involved depend mainly on the interaction with one nitrogen and not with the length of the chain up to this point. In contrast, the dissociation energies of the systems of $Pb(TEA)_2$ are almost doubled compared to Pb(TEA). In these systems Pb interacts with two OH groups (one from each TEA molecule). However, including more TEA molecules causes the system to destabilize due to steric hindrance.

Geometries 7-10 show the interactions between Pb and $[PEI]_3H_2$ through 2 nitrogens. It is interesting to note that in these systems the dissociation energies are highly affected by the interaction between Pb and one more nitrogen, compared to systems 1-6. In the former structures, Pb lies above PEI almost in the center with contact distances of 2.53 Å and 2.55 Å, except for structure 10 with values of 2.55 Å and 2.56 Å. The configuration 7 is the most stable of all of the $Pb[PEI]_nH_2$ systems, with a dissociation energy of -30.13 kcal/mol and a HOMO-LUMO gap of 6.37 eV. This could be due to the fact that the tips of the PEI molecule in structure 7 are arranged in such a way that intramolecular repulsions are minimized. In geometries 8-10, the monomers in the tips are interacting with other monomers in PEI, reducing the stability of the system.

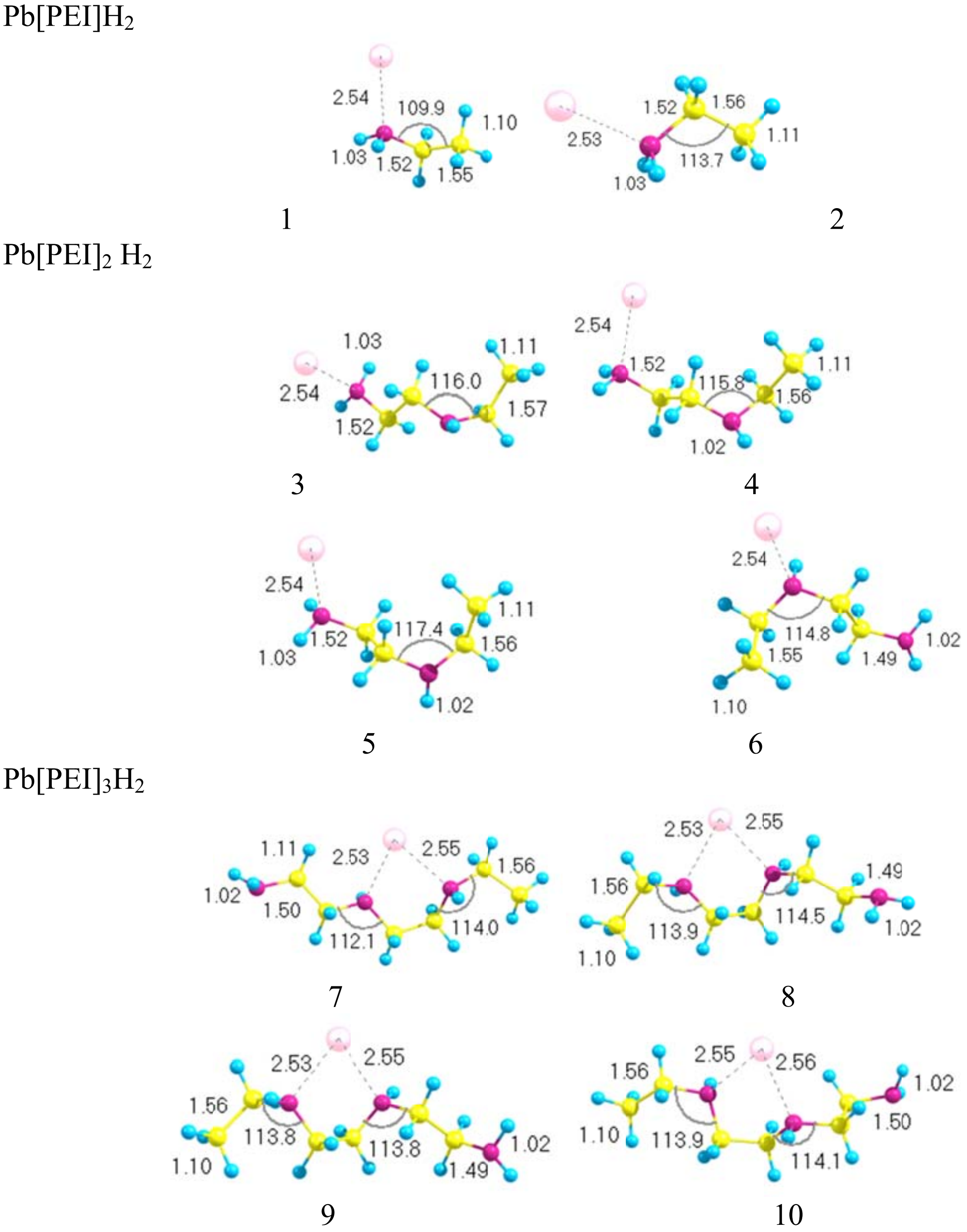
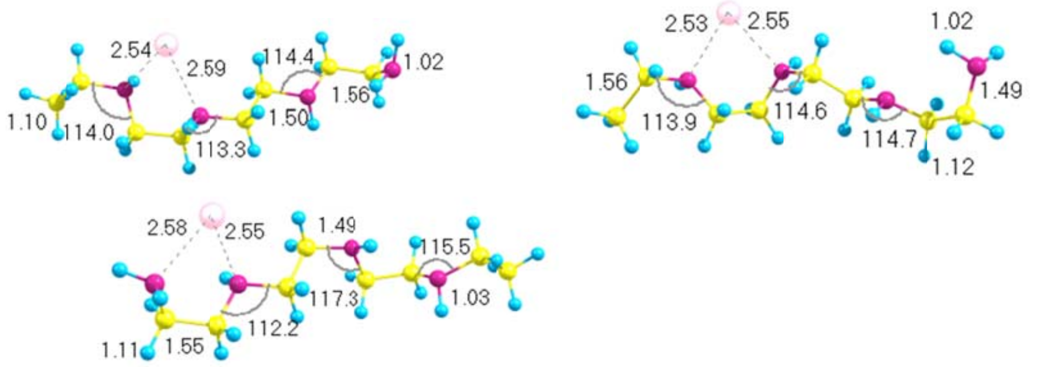


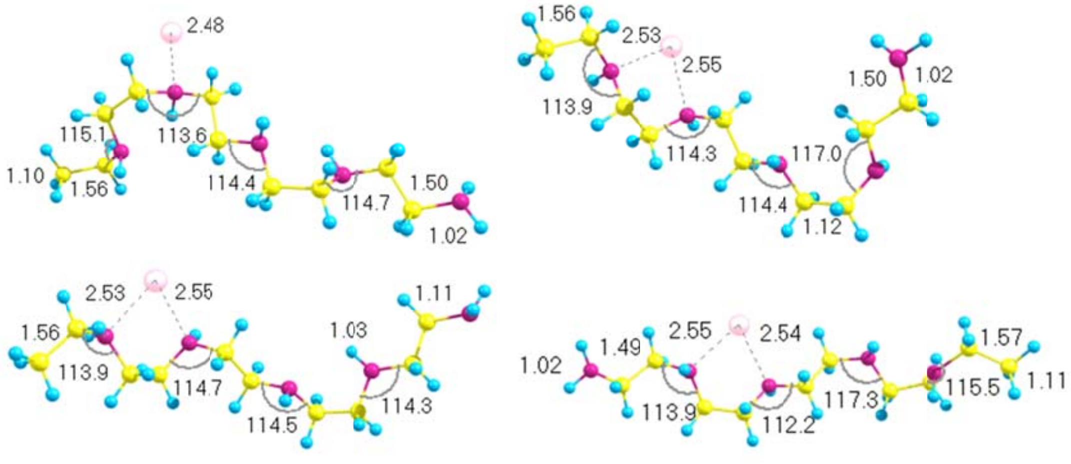
Fig. 1. Selected geometrical parameters of the systems $Pb[PEI]_{n=1\text{-}3}H_2$ (configurations 1-10) whereby bond lengths are in angstroms (Å) and angles in degrees (°).

Pb[PEI]$_4$H$_2$



11 12
13

Pb[PEI]$_5$H$_2$



14 15
16 17

Fig. 2. Selected geometrical parameters of the systems Pb[PEI]$_{n=4,5}$H$_2$ (configurations 11-17) whereby bond lengths are in angstroms (Å) and angles in degrees (°).

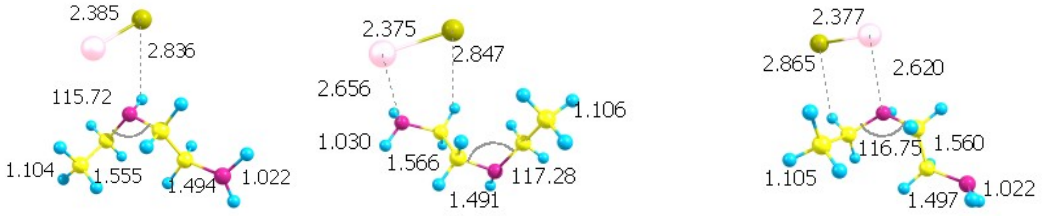
In configurations 11-13 PEI is formed by four monomers. These systems share a similarity with structures 7-10 in that Pb interacts with two nitrogen atoms in PEI. The dissociation energies are similar to the the last group of structures with energies between -24.19 kcal/mol and -25.21 kcal/mol. Since the polymer chain is bigger, the monomers farther apart from the interaction with Pb have higher mobility and thus do not accomplish such a stable configuration as structure 7. Anyway, the dissociation energies are very similar to the ones of systems 8-10 as well as HOMO-LUMO gaps that range from 6.19 eV to 6.28 eV. Of this group structure 13 is the most stable, with a contact distances of 2.58 Å and 2.55 Å, a dissociation energy of -25.21 kcal/mol and a HOMO-LUMO gap of 6.28 eV.

The configurations of Pb[PEI]$_5$H$_2$ (14-17) also display an interaction between Pb and two nitrogens in PEI, except for structure 14. This could be the reason why it has the highest dissociation energy of this group, with a value of -21.30 kcal/mol and a noticeably different HOMO-LUMO gap of 5.33 eV. The rest of the HOMO-LUMO gaps are between the values of 6.16 eV and 6.36 eV. Systems 16 and 17 are the most stable of this group with dissociation energies of -25.08 kcal/mol and -24.91 kcal/mol. This is probably so because the chains are the most linear and do not lose as much energy in intramolecular repulsions or in the mobility of the monomers farther apart from the nitrogen atoms interacting with Pb.

$PbS[PEI]H_2$

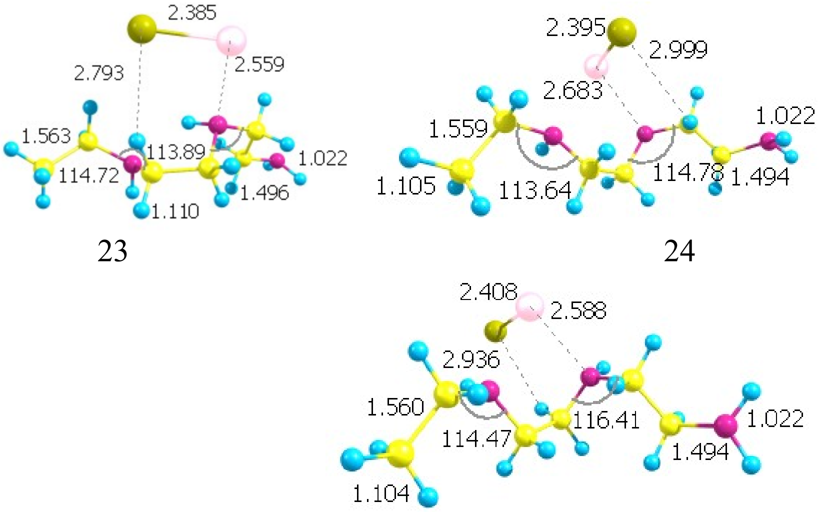
18 19

$PbS[PEI]_2H_2$



20 21 22

$PbS[PEI]_3H_2$

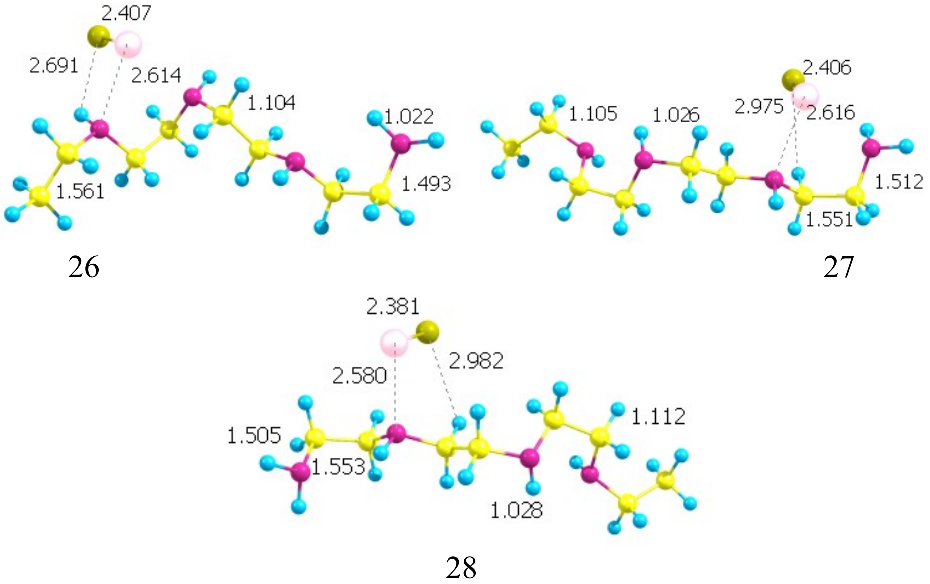


23 24

25

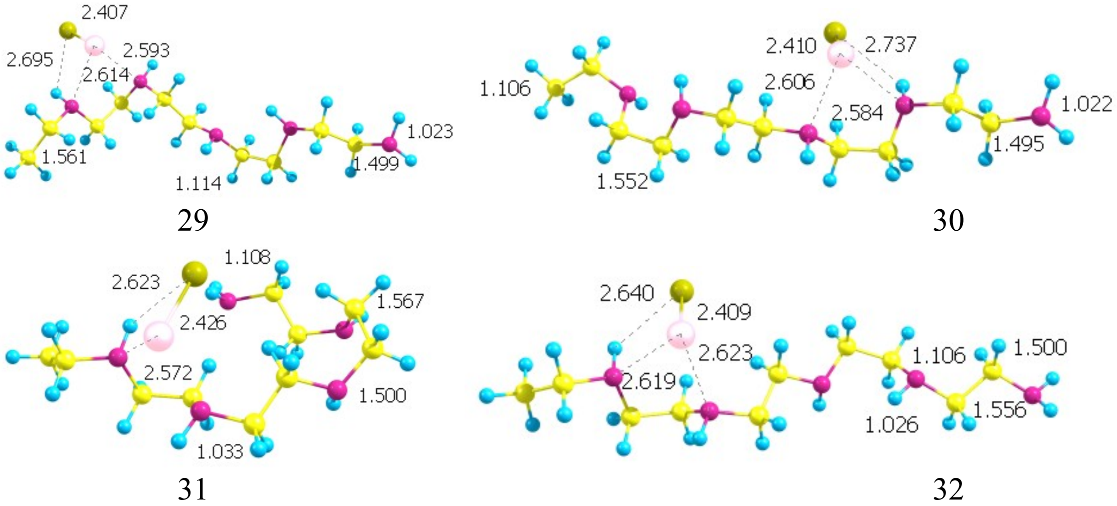
Fig. 3. Selected geometrical parameters of the systems $PbS[PEI]_{n=1-3}H_2$ (configurations 18-25) whereby bond lengths are in angstroms (Å) and angles in degrees (°).

PbS[PEI]$_4$H$_2$



26 27 28

PbS[PEI]$_5$H$_2$



29 30 31 32

Fig. 4. Selected geometrical parameters of the systems PbS[PEI]$_{n=4,5}$H$_2$ (configurations 26-32) whereby bond lengths are in angstroms (Å) and angles in degrees (°).

The rest of the structures (18-32) are formed with PbS. Geometries 18 and 19 of PbS[PEI]H$_2$ form an interaction between the amino group and PbS. Structure 19 has two contact distances with values of 2.901 Å and 2.605 Å which are smaller than those of structure 18. This could be the cause of a lower dissociation energy in configuration 19 of -8.17 kcal/mol compared to that of configuration 18 with a value of -7.38 kcal/mol. Due to their similarity, structures 18 and 19 have comparable HOMO/LUMO gaps with values of 8.41 kcal/mol and 8.38 kcal/mol. In the case of PbS(TEA), structures 7* and 9* are the most stable. In these configurations, the sulfur atom is farther apart from TEA than in 8* and 10*, where the contact distance is of 2.58 Å between sulfur and hydrogen in the OH group in both cases. Anyhow, the HOMO/LUMO gaps remain alike.

The dissociation energies of the configurations 20 and 22 of PbS[PEI]$_2$H$_2$ are lower than those of PbS[PEI]H$_2$, with values of -9.08 kcal/mol and 8.44 kcal/mol, respectively. These configurations show an interaction with the nitrogen that connects the monomers of polyethileneimine. On the other hand, when PbS interacts with two molecules of TEA, the dissociation energy changes dramatically. This trend could also be observed for Pb. Their dissociation energies range from -22.03 kcal/mol to -31.53 kcal/mol. Structure 14* is the most stable structure since its dissociation energy is the lowest. This can be explained by the fact that PbS is sandwiched between two TEA molecules, maximizing interactions between the TEA molecules and with PbS. However, this behavior cannot be observed in the case of$[PEI]_2H_2$since the monomers are attached covalently to each other and in the case of TEA, they interact though van der Waals forces.

The energy minima structures of $PbS[PEI]_3H_2$ show an interaction between PbS and a nitrogen in the center of the molecule. In structure 23, Pb has a contact distance of 2.559 Å with nitrogen, while sulfur has a contact distance of a distant hydrogen, causing it to have a dissociation energy of -10.47 kcal/mol and a HOMO/LUMO gap of 8.43 eV. In structure 24, PbS lies parallel to the C-N bond with which it interacts, yielding a dissociation energy of -11.30 kcal/mol and a HOMO/LUMO gap of 8.89 eV. The difference in dissociation energy between this configuration and structure 23 can be acquainted to the fact that in structure 23 the atoms PbSinteracts with are far apart, causing $[PEI]_3H_2$ to reorganize, consuming energy in the process. The most stable structure of the $[PEI]_3H_2$systems is 25, with a dissociation energy of -13.56 kcal/mol and a HOMO/LUMO gap of 8.85 eV. In this geometry, PbS also interacts with a nitrogen and hydrogen nearby with a Pb-N contact distance of 2.588 Å which is shorter than in structure 24.

The group of structures of $PbS[PEI]_4H_2$ yieldsthe most stable systems. Overall, structure 26 is the most stable system of the $PbS[PEI]_nH_2$ structures. PbS interacts with polyethyleneimine with contact distances of 2.691 Å and 2.614 Å. In this structure, PbS interacts with the atoms in a N-H bond. This allows the chain to adopt a stable configuration. Anyhow, in configurations 27 and 28, the contact points between PbS and the chain are not with a N-H bond, but with a nitrogen and a hydrogen that are not bonded to each other. This constrains the chain to a configuration that is not as stable as structure 26. Nevertheless, structures 27 and 28 are still among the most stable systems, with dissociation energies of -21.75 kcal/mol and -18.07 kcal/mol and HOMO/LUMO gaps of 8.98 eV and 8.49 eV, respectively.

The dissociation energy in structures of $PbS[PEI]_5H_2$ rises notably probably due to the rearrangement the chain suffers when PbS interacts with atoms that are not near each other. It is interesting to note that for $Pb[PEI]_nH_2$, when Pb interacts with two nitrogens the dissociation energy decreases, yet for $PbS[PEI]_nH_2$, this is not so because sulfur repels the nitrogen atoms and forces the polyethylene chain to modify its configuration. In cases 29, 30 and 31, PbS interacts with two separate nitrogens, causing the polyethylene chain to bend and thus lose energy. These geometries had dissociation energies of -12.52 kcal/mol, -13.39 kcal/mol and -11.97 kcal/mol and HOMO/LUMO gaps of 8.86 eV, 9.01 eV, 8.89 eV. The most stable structure of this group was structure 31, with a dissociation energy of -14.65 kcal/mol and 9.05 eV. Its lower dissociation energy can be explained by the fact that it only interacts with one nitrogen in the chain. However, its lower stability than the geometries of $PbS[PEI]_4H_2$ is most likely owed to the semicircular configuration of the polyethylene chain.

3. Conclusions

In this paper, we performed quantum mechanical calculations at the MP2 level for the systems of $Pb[PEI]_{n=1\text{-}5}H_2$, $PbS[PEI]_{n=1\text{-}5}H_2$, and compared them to the results of our previous study (9) of $Pb(TEA)_{n=1,2}$ and $PbS(TEA)_{n=1,2}$. In the case of polyethylene, we observed that the dissociation energies decrease from n=1-3 and then slowly increase. As it is seen the interaction between Pb and two nitrogens starts when n=3, which stabilizes the systems. Structure 7 is the most stable of the $Pb[PEI]_nH_2$ systems. In this case, the chain is spatially set in such a way that steric hindrance is minimum, yielding a dissociation energy of -30.13 kcal/mol. In the case of $PbS(TEA)_1$, the dissociation energies are similar to those of $Pb[PEI]H_2$, but for $PbS(TEA)_2$, the dissociation energies decreased radically and where very different than those of $Pb[PEI]_2H_2$. The energies for $Pb[PEI]H_2$ and Pb(TEA) are comparable because in both cases Pb interacts with only one atom (nitrogen in the case of $[PEI]H_2$ and oxygen for the case of TEA). However, for $Pb[PEI]_2H_2$Pb only interacts with one nitrogen atom, while Pb in $Pb(TEA)_2$ forms two interactions with the TEA molecules and the TEA molecules form hydrogen bonds that stabilize the complexes. Its most stable structure has a dissociation energy of -35.57 kcal/mol.

The systems of $PbS[PEI]_nH_2$ were less stable than those of Pb. This was expected since it also happened with the $PbS(TEA)_n$ systems due to the repulsion exerted by sulfur. For the case of $PbS[PEI]_nH_2$ the dissociation energies decrease from n=1-4 and then start to decrease. This can be attributed to the interaction between PbS and atoms that are near each other. This allows PbS to interact only at one site of the chain, allowing the rest of the polyethylene chain to assume a stable configuration. Similarly to the structures obtained with Pb, $PbS(TEA)_2$ yielded the most stable systems. Its most stable structure was 14*, with a dissociation energy of -31.53 kcal/mol, while for $PbS[PEI]_nH_2$its most stable system was geometry 26, with a dissociation energy of -22.49 kcal/mol.

4. Computational Methods

Gaussian 09 software (11) was employed to perform the quantum chemical ab-initio computations. The results were obtained with the second order perturbation MøllerPlesset MP2 (12) method with the LANL2DZ (13) basis set. In order to assure precision, we employed global orbital cutoffs and fine convergence criteria. In addition, we selected minimum energy configurations by examining the Hessian matrix. The selected minimum energy species had only positive vibrational frequencies. This confirms the structures are not transition states, as it happens when a system has at least one negative vibrational frequency. In addition, Basis set superposition error (BSSE) calculations and zero-point energies were employed to correct the energies.

Dissociation energies (ΔE) are obtained from:

$$\Delta E = E_{Pb/PbS[PEI]_nH_2} - E_{[PEI]_nH_2} - E_{Pb/PbS},$$

Where $Pb/PbS[PEI]_nH_2$ refers to the system formed by Pb or PbS (Pb/PbS) and $[PEI]_nH_2$ where n indicates the number of monomers. In this study we report the interaction between Pb/PbS with PEI with n=1-5.

Acknowledgements

CONACyT and ACARUS of the University of Sonora are thanked for their support.

References

[1] B.Yacobi, Semiconductor Materials, An Introduction to Basic Principles, Springer US: 2003, ISBN: 978-0-306-47361-6 (Print) 978-0-306-47942-7.

[2] H. Zhang, X. Ma, D. Yang, Mater.Lett.,**58**, 5-9.2004

[3] G.Hodes, Chemical Solution Deposition of Semiconductor Films; Marcel Dekker Inc.: New York, Basel, 2003.

[4] C.Guillén, M.A.Martínez, Herrero, J. Thin Solid Films, **35**, 37(1998)

[5] J.Barman, J.P.Borah, K.C. Sarma, Chalc. Lett.,**5**, 265(2008)

[6] S.J. Castillo, M.Sotelo-Lerma, I.A. Neyra, R.Ramírez-Bon, Espinoza, F.J. Mater. Sci. Forum, **287**, 343**(**1998).

[7] A.de Leon, M.C.Acosta-Enríquez, S.J. Castillo, D.Berman-Mendoza, A.F. Jalbout, J. Mol. Struct. THEOCHEM, **951**, 34-36**(**2010).

[8] A.de Leon, M.C.Acosta-Enríquez, A.F.Jalbout, A.Apolinar-Iribe, S.J. Castillo, J. Molec. Struct. THEOCHEM, **957**, 90 (2010)

[9] A.de Leon, M.C. Acosta-Enríquez, S.J.Castillo, A.Apolinar-Iribe, J. SulfurChem., **33**, 391**(**2012).

[10]S.Soundeswaran, O. Senthil Kumar, R.F. Dhanasekaran, Mater. Lett.,**58**, 2381(2004).

[11] M.J. Frisch, G.W. Trucks, H.B.Schlegel, G.E.Scuseria, M.A.Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B.Mennucci, G.A.Petersson, H.Nakatsuji, M.Caricato, X. Li, H.P.Hratchian, A.F.; Izmaylov, J.; Bloino, G.; Zheng, J.L.Sonnenberg, M.; Hada, M.; Ehara, K.; Toyota, R.; Fukuda, J.; Hasegawa, M.; Ishida, T.; Nakajima, Y.; Honda, O.; Kitao, H.; Nakai, T.; Vreven, J.A.; Montgomery, Jr., J.E.; Peralta, F.; Ogliaro, M.; Bearpark, J.J.; Heyd,E.; Brothers, K.N.; Kudin, V.N.; Staroverov, T.; Keith, R.; Kobayashi, J.; Normand, K.; Raghavachari, A.; Rendell,J.C.; Burant, S.S.; Iyengar, J.; Tomasi, M.; Cossi, N.; Rega, J.M.; Millam, M.; Klene, J.E.; Knox, J.B.; Cross, V.; Bakken, C.; Adamo, J; Jaramillo, R; Gomperts, R.E.; Stratmann, O; Yazyev, A.J.; Austin, R.; Cammi, C.; PomelliJ.W.;,Ochterski, R.L.; Martin, K.; Morokuma, V.G.; Zakrzewski, G.A.; Voth, P; SalvadorJ.J.;, Dannenberg, S.; Dapprich, A.D.; Daniels, O.; Farkas, J.B.; Foresman, J.V.; Ortiz, J.; Cioslowski, D.J.; Fox, Gaussian 09; Gaussian, Inc.:Wallingford, CT, 2010.

[12] Head-Gordon, M.; Pople, J.A.; Frisch, M.J. Chem. Phys. Lett., **153**, 503**(**1988)

[13] T.H., Dunning, Jr.; P.J. Hay, In Modern Theoretical Chemistry; Schaefer III, H.F., Ed.; Vol. 3; Plenum Press: New York, 1976; pp. 1-28.