



Brazilian Journal of Physics

ISSN: 0103-9733

luizno.bjp@gmail.com

Sociedade Brasileira de Física
Brasil

Salazar Valencia, P. J.; Bolívar Marinez, L. E.; Pérez Merchancano, S. T.
Molecular Modeling of Ammonium, Calcium, Sulfur, and Sodium Lignosulphonates in Acid
and Basic Aqueous Environments
Brazilian Journal of Physics, vol. 45, núm. 6, 2015, pp. 567-574
Sociedade Brasileira de Física
São Paulo, Brasil

Available in: <http://www.redalyc.org/articulo.oa?id=46442560001>

- How to cite
- Complete issue
- More information about this article
- Journal's homepage in redalyc.org

redalyc.org

Scientific Information System

Network of Scientific Journals from Latin America, the Caribbean, Spain and Portugal

Non-profit academic project, developed under the open access initiative

Molecular Modeling of Ammonium, Calcium, Sulfur, and Sodium Lignosulphonates in Acid and Basic Aqueous Environments

P. J. Salazar Valencia¹  · L. E. Bolívar Martinez¹ ·
S. T. Pérez Merchancano¹

Received: 15 June 2015 / Published online: 15 September 2015
© Sociedade Brasileira de Física 2015

Abstract Lignosulphonates (LS), also known as lignin sulfonates or sulfite lignin, are lignins in sulfonated forms, obtained from the “sulfite liquors,” a residue of the wood pulp extraction process. Their main utility lies in its wide range of properties, they can be used as additives, dispersants, binders, fluxing, binder agents, etc. in fields ranging from food to fertilizer manufacture and even as agents in the preparation of ion exchange membranes. Since they can be manufactured relatively easy and quickly, and that its molecular size can be manipulated to obtain fragments of very low molecular weight, they are used as transport agents in the food industry, cosmetics, pharmaceutical and drug development, and as molecular elements for the treatment of health problems. In this paper, we study the electronic structural and optical characteristics of LS incorporating ammonium, sulfur, calcium, and sodium ions in acidic and basic aqueous media in order to gain a better understanding of their behavior and the very interesting properties exhibit. The studies were performed using the molecular modeling program HyperChem 5 using the semiempirical method PM3 of the NDO Family (neglect of differential overlap), to calculate the structural properties. We calculated the electronic and optical properties using the semiempirical method ZINDO / CI.

Keywords Lignosulphonates · Semiempirical methods · Computational chemistry

1 Introduction

The extraction process of lignosulphonates (LS) is known as delignification, and during this process, the electrophilic carbocations produced by breaking the ester bonds react with the bisulfite ions to produce LS, incorporating ions such as calcium, sodium, magnesium, and ammonium. So a detailed theoretical study of the role of these ions into the properties of LS is very interesting; this process can be seen briefly sketched in Fig. 1 [1].

In this process, a new class of polyelectrolyte polymers with a high acidity is obtained by removing the components adhering to the woody tissue; the acidity is due to the presence in their molecular structure groups of highly dissociated sulfonic acid and, unlike lignin in cell walls, are water soluble; this family of molecules are known collectively as lignins [2].

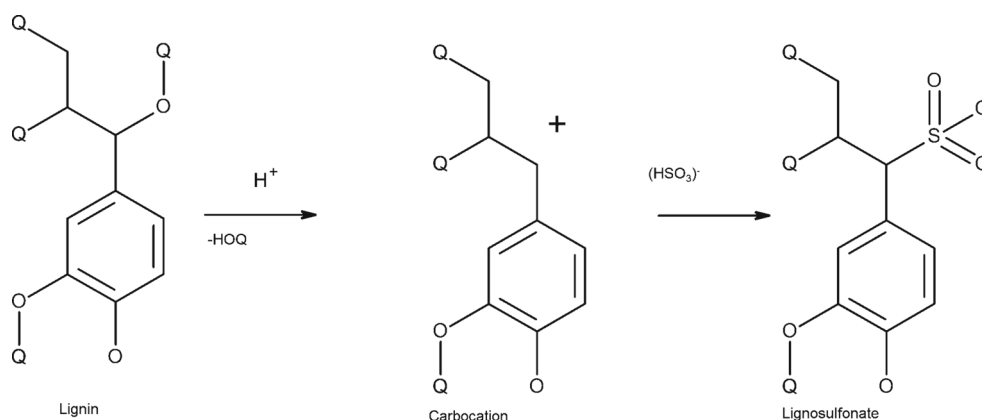
It has also been observed, mostly empirically, that LS have capabilities that make them behave very effectively as free radical scavengers and antioxidants [3]. The importance of studying the interaction between free radicals and LS is based on the role of oxygen-derived free radicals in the origin of many diseases, such as cancer, rheumatoid arthritis, and atherosclerosis, as well as degenerative process associated with aging. Free radicals are generated by metabolic processes from exogenous sources such as foods, medicines, ultraviolet light, ionizing radiation, and environmental pollution [4].

LS properties depend, as in any molecular system, on its structure and the characteristics of the individual components, sharing with lignin the basic precursors shape [5] and the linking mechanism [6]. Its molecular structure consists of a series of small aggregates of 2 or 3 precursor units linked through oxygen-carbon bonds in a high proportion of type β -O-4 [7]; other aromatic units are linked to this

✉ P. J. Salazar Valencia
pjsalazar@unicauca.edu.co

¹ Universidad del Cauca, Calle 5 Núm. 4-70, Campus Tulcan, Popayán, Colombia

Fig. 1 Outline of the process of structural formation of a LS



chain as well as a wide variety of substituent groups. In the case of LS, the substituent groups are sulfonates (functional groups containing an SO_3 ion) with other functional groups attached either to the sulfonates, available positions in the carbon chain or simply appear near the structure in a molecular or ionic form. This can be seen in Fig. 2; we have the graphical representation of LS precursor with calcium, which consists of a base unit and Ca atom (which may or may not be ionized) in their vicinity; for other LS, the Ca atom is replaced with other functional groups [8].

The macromolecule then grows in a random fashion, polymerizing into an amorphous, three-dimensional biopolymer that, like lignin, it is difficult to study due to the size and randomness of its structure. Fortunately for us, previous studies have shown that in the case of lignins in general, the properties of the basic units or precursors can easily be extrapolated and used to describe certain characteristics and behavior of the macrostructure [9].

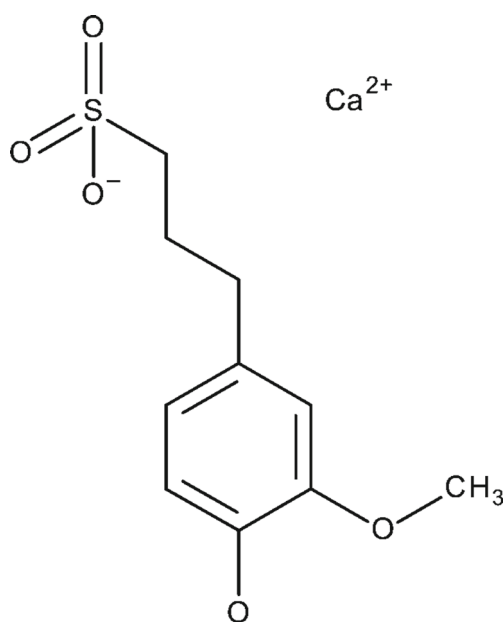


Fig. 2 Graphical representation of an LS precursor

2 Methodology

The molecular geometries and structural and electronic properties of the lignin precursors are known and have been modeled previously. From those studies, we know the most relevant characteristics of the precursor units [10] and polymerization mechanisms. This information will be used to study the growth of LS fragments containing ammonium, sulfur, calcium, and sodium functional groups, up to a size of 3 units connected with the most abundant linking mechanism in lignins, the β -O-4 [11]. The behavior of these fragments in different charged states and in aqueous media both acidic and basic were also studied.

Although, nowadays, the ab initio and density functional methods are widely used with relatively low computational cost and high accuracy, the semiempirical methods have continued to be regarded as a powerful tool. They allow us to study large molecular systems providing high-quality results even when compared with the aforementioned methods; they have also the advantage of working very well with severely limited computational resources. The studies were performed using the semiempirical method PM3 [12] of the NDO (neglect of differential overlap) [13] family. The electronic and optical properties were calculated using the semiempirical method ZINDO/CI [14].

3 Results

Table 1 shows the values of heat or enthalpy of formation for the sulfonated lignin polymerization, from 1 up to 3 precursor units linked with a β -O-4 type link; functional groups of ammonium, sulfur, calcium, and sodium were added to create other LS. The results show the heat of formation in different charge states. The precursor units have a structure as depicted in Fig. 2 with the aforementioned functional groups replacing the Ca ion.

The results show a progressive decline in the value of the heat of formation, as more units are added to the

Table 1 Heat of formation in kilocalories per mole for the polymerization of the LS studied in different charge states, obtained with PM3 method

LS with	Charge	1 unit	2 units	3 units
Ammonium	+1	−33.16	−200.61	−434.13
	0	−222.79	−418.52	−616.55
	−1	−265.79	−469.76	−674.05
Sulfur	+1	−22.18	−213.49	−398.56
	0	−209.03	−393.95	−580.14
	−1	−257.44	−451.04	−641.17
Calcium	+1	−612.03	−1462.35	−1748.48
	0	−660.41	−1596.68	−1817.11
	−1	−728.58	−1649.98	−1903.79
Sodium	+1	−143.97	−444.94	−658.71
	0	−245.70	−528.33	−816.64
	−1	−303.77	−593.51	−868.73

fragments. The decrease is quite noticeable and covers a range from −200 to −1000 kcal/mol showing a behavior of great structural stability for the fragments. The values of heat of formation obtained for the ionized structures show an improvement for the −1 charge states, confirming the electron acceptor nature of this molecules; however, it is interesting to note that the difference in values between −1 and neutral states is becoming smaller as the fragment

grows, up to the case of the 3 units where the difference is minimal.

In Fig. 3, we have a graphical representation of the molecular structures of the lignosulphonates studied in ideal conditions (vacuum with no electric charge). We see that for the LS with ammonium (a) and sulfur (b), the structure tends to spread along its axis, while for the LS with calcium and sodium, the structure tends to close on itself,

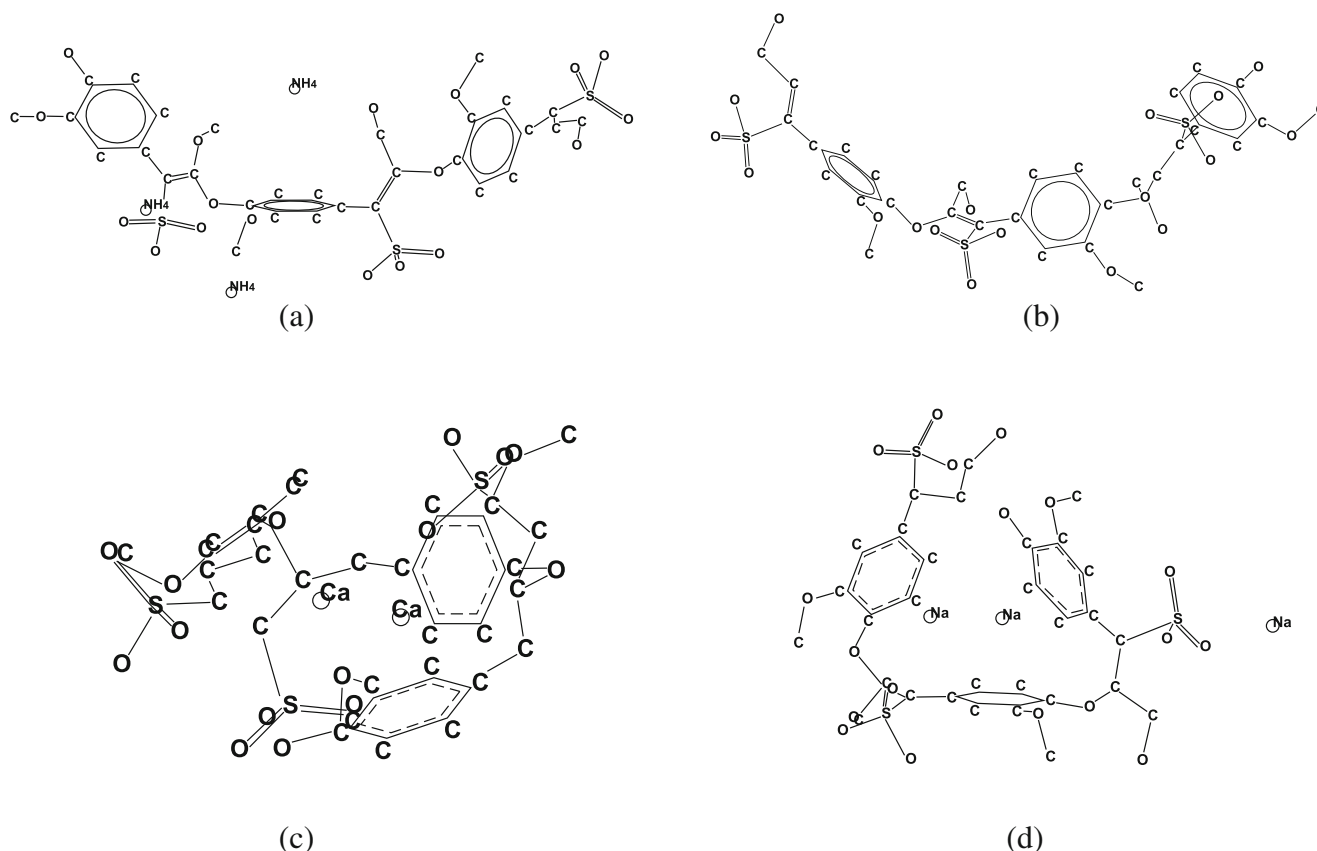
**Fig. 3** Graphical representation of the molecular structure of the LS studied, in vacuum and neutral state of charge. LS with **a** ammonium, **b** sulfur, **c** calcium, and **d** sodium

Table 2 Heat of formation in kilocalories per mole for the polymerization in aqueous environment of the LS studied, in different charge states obtained with the PM3 method

LS with	Charge	1 unit	2 units	3 units
Ammonium	+1	−2156.99	−1888.85	−3722.44
	0	−2321.92	−2107.97	−3938.01
	−1	−2394.50	−2163.43	−4011.67
Sulfur	+1	−2439.65	−2307.57	−3081.13
	0	−2517.81	−1599.16	−3234.59
	−1	−2917.00	−3635.19	−3311.40
Calcium	+1	−2652.95	−3079.56	−2886.98
	0	−2819.23	−4233.09	−8660.77
	−1	−2946.49	−3249.89	−3089.56
Sodium	+1	−2646.73	−2023.53	−2161.18
	0	−1737.70	−3021.14	−7054.17
	−1	−2773.99	−2163.69	−2862.78

surrounding the external elements encapsulating the molecule. The structures are represented not showing the hydrogen atoms for ease of visualization, since otherwise the representation would be crowded and confusing.

Table 2 shows the values of heat of formation for the LS studied, in an aqueous environment and different charge states. The first thing that we notice is the significant reduction in the values for the LS in water and neutral charge state, presenting values greater than −2000 kcal/mol for

most cases; there is also a decrease of the heat of formation values for the charge −1 state, reinforcing the image of electron acceptors that had already been appreciated for the structures in vacuum.

By observing the −1 charge state as the structures grow from 1 to 3 units, we have found that for the LS with ammonium and sulfur, the values of the heat of formation tend to have little variations, indicating that the state of charge does not affect the stability and ion capture

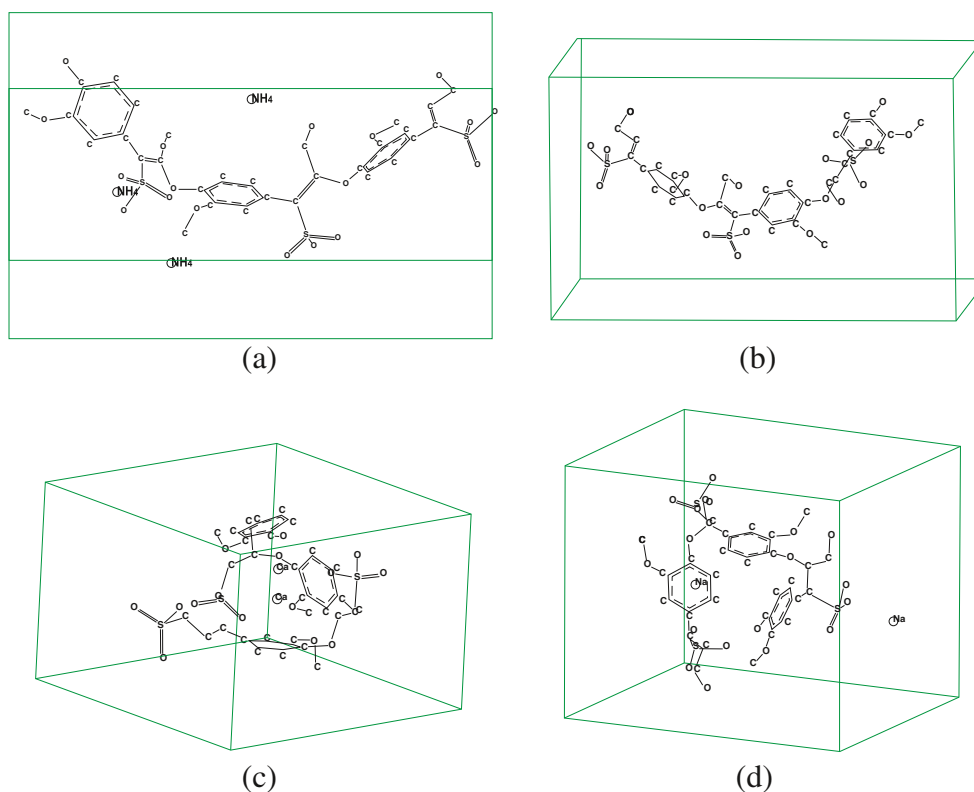


Fig. 4 Graphical representation of the molecular structure of the LS studied in aqueous environments and neutral state of charge; water molecules are not shown to aid visualization of the structures. LS with **a** ammonium, **b** sulfur, **c** calcium, and **d** sodium

Table 3 Heat of formation in kilocalories per mole for the LS studied in a number of basic and acid aqueous media

Environment	LS with			
	Ammonium	Sulfur	Calcium	Sodium
Vacuum	−616.55	−580.14	−1817.11	−816.64
H ₂ O	−3938.01	−3234.59	−8660.77	−7054.17
H ₂ O+H ₂ SO ₄	−3177.18	−3475.96	−7186.21	−2868.06
H ₂ O+HCl	−2795.04	−2931.83	−6851.75	−4560.08
H ₂ O+HNO ₃	−3059.42	−2729.72	−6409.62	−3309.98
H ₂ O+NaOH	−3426.71	−4400.44	Fail	−4917.86
H ₂ O+NHO ₄	−3158.39	−2684.38	−5728.40	−3450.25

Neutral charge state, values obtained by the semiempirical method PM3

properties of the LS. On the other hand, we have the LS with calcium and sodium with a great variation for the +1 and −1 state; also, it is interesting to see for this two LS; the neutral state has a lower heat of formation compared with +1 and −1.

For the LS with calcium and sodium, this behavior indicates that the presence of aqueous medium favors the formation of the molecular structures and presents them as very good candidates to be used as a means of targeting other molecular species. Overall, the results obtained indicate that the LS ionized on aqueous environments are good ion scavengers, capturing both electrons and protons. Graphical representations of the LS in an aqueous medium can be seen in the Fig. 4.

In Table 3, we have the heat of formation values for LS in acid and basic aqueous media; for the neutral charge state, the structures consist of three units linked by β-O-4 mechanism. The new environments that were chosen for these

simulations incorporate some of the most common acidic and basic solvents used in any chemistry lab; also, they can be found in a wide spread of commercial products. We choose these solvents in order to gain a better understanding of the behavior that could be found if this observation was to be undertaken in a real lab, and to gain insight in the LS potential to be used as molecular scavengers in fields such as the treatment of residual or contaminated waters. The simulations were built upon a modification of those that incorporated water molecules, replacing some of them with the basis and acids molecules chosen for the study.

Overall, the results show a consistent improvement of the heat of formation regardless of the environment and the solvent; for three out of four LS considered, the best solvent is water, excluding only the LS with sulfur. These results allow us to conclude that in any aqueous media, the lignosulphonates can perform very interesting functions,

Table 4 Energy GAP in electronvolts for the LS studied in vacuum and various charge states, obtained with the method ZINDOS CI configuration

LS with	Charge	1 unit	2 units	3 units
Ammonium	+1	5.54	6.11	5.01
	0	8.36	8.03	7.95
	−1	3.40	1.15	1.46
Sulfur	+1	5.80	5.34	5.80
	0	8.25	7.87	8.09
	−1	2.91	1.19	1.30
Calcium	+1	2.24	2.58	2.69
	0	7.68	7.20	7.46
	−1	2.38	2.25	2.15
Sodium	+1	4.66	2.77	5.23
	0	12.42	6.24	7.00
	−1	2.66	0.95	1.82

Table 5 Gap energy in electronvolts for the LS studied in aqueous media and various states of charge, obtained by the CI method ZINDOS configuration

LS with	Charge	1 unit	2 units	3 units
Ammonium	+1	5.57	5.95	6.15
	0	8.41	8.22	7.86
	−1	2.91	1.05	1.33
Sulfur	+1	5.53	5.78	5.84
	0	8.14	7.60	7.77
	−1	2.98	1.28	1.29
Calcium	+1	3.36	2.78	2.93
	0	7.87	7.54	7.58
	−1	2.39	2.48	2.26
Sodium	+1	3.02	2.46	5.16
	0	6.85	6.24	7.75
	−1	3.76	2.17	2.63

Table 6 GAP energy values in eV for the LS studied in acidic and basic environment, values obtained with the ZINDOS method in CI configuration

Environment	LS with			
	Ammonium	Sulfur	Calcium	Sodium
Vacuum	7.95	8.09	7.46	7.00
H ₂ O	7.86	7.77	7.58	7.75
H ₂ O+H ₂ SO ₄	7.96	8.08	7.75	6.19
H ₂ O+HCl	7.77	7.83	6.34	6.53
H ₂ O+HNO ₃	6.35	6.34	7.38	6.93
H ₂ O+NaOH	6.86	6.52	FAIL	6.38
H ₂ O+NHO ₄	7.94	7.88	6.76	6.40

especially LS like the ones with calcium and sodium that tend to embrace the molecules in their vicinity. This behavior explains the stabilization properties that make some LS widely used in the industry as flocculants and stabilizers; also, this allows us to theorize that this LS can perform other functions such as capturing of molecular contaminants. According to these results, this behavior can be enhanced by using substances that incorporate such acids and bases.

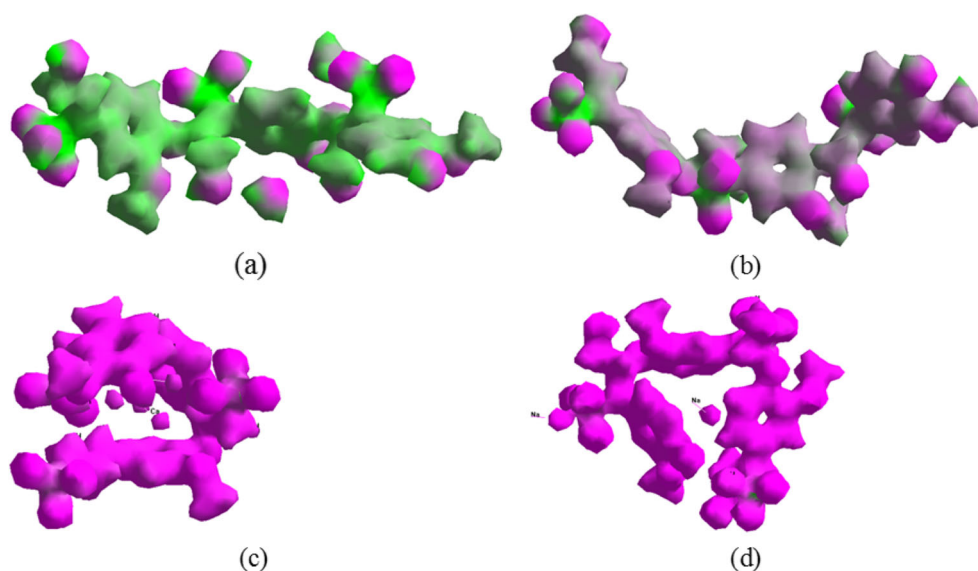
The GAP energy values in electron volts (eV) for LS with a size range from 1 to 3 units are presented in Table 4 in vacuum and several charge conditions. The energy GAP is understood as the difference between the auto energy values corresponding to highest occupied orbital (HOMO) and lowest unoccupied orbital (LUMO). This value gives us a very good idea of how the electrical conduction in a molecular structure behaves and can classify them according to their value in conductors, semiconductors, and insulators. The values obtained show that for the neutral charge state,

the compounds behave as insulators, with values that tend to stabilize between 7 and 8 eV. For the charge states +1 and −1, the GAP energy is lower, reaching 1.3 eV for the −1 state of charge for the LS with sulfur and 1.46 eV for the LS with ammonia. This shows that the LS behave not only as electron acceptors but they are also very good candidates to perform as organic semiconductors when they are doped with sulfur and ammonia.

In the case of LS in an aqueous medium with different electric charge conditions, the optical gap in electronvolt obtained (Table 5) confirm what was observed in the previous case, showing that these materials behave as charge acceptors independently of the environment into which they are.

As we have seen above, the environment influences the behavior of the molecular structures; in Table 6, we have the values of the GAP energy electronvolt for the LS studied in the acidic and basic environments we have considered in this work. The values obtained show a uniform behavior with all structures appearing as insulators with GAP values ranging between 6 and 8 eV. Other charge states could not be evaluated due to the limitations of the computational system used to perform the simulations; nevertheless, the behavior observed for the precursor units has a very good chance to be found in bigger polymers due to the similitude between the properties of lignosulphonates and the properties of the lignin precursor units.

Something important to consider are the difficulties encountered in this work when studying the LS with calcium and the environments incorporating sodium hydroxide. When studying the LS with calcium in vacuum, the PM3 method performs adequately but once these molecules are placed in the environment containing water and sodium

Fig. 5 Graphical representation of the electrostatic potential of the LS studied in vacuum and neutral charge state. LS with **a** ammonium, **b** sulfur, **c** calcium, and **d** sodium. The degree of electronegativity is represented by color, from less (green) to most (purple)

hydroxide molecules, the simulations fail to find a stable geometry, probably due to the lack of molecular settings suitable for this combination of elements.

Graphical representations of the electrostatic potential, also known as potential energy maps, illustrate molecular charge distributions in two or three dimensions, allowing us to visualize how these are distributed and how regions of electrically charged molecules behave and interact with each other.

These representations are used to illustrate other characteristics such as polarity, electronegativity, or qualities of the bonds, using the charge distribution that is innately linked to these characteristics, and since there is no exact equation that predicts these properties for complex molecules, such representations are the best way to analyze the characteristics mentioned above. In organic chemistry, these representations are quite useful because there are no equations describing the complexities of the interaction between molecules with sufficient quality, providing a tool to identify the sites either nucleophilic reagents (proton affinity) or electrophilic (electron affinity) and how they change as the molecules interact. The importance of these reactive sites becomes more obvious to note that it is in these places where the functional groups are bonded or lost by the molecules.

Graphical representations of the electrostatic potential obtained from the molecular geometries of the LS studied are shown in Fig. 5; these representations show the regions of the molecular system that are most repulsive or attractive, i.e., sites where a greater likelihood for different molecular systems to interact and form some kind of link or bond. For the LS studied in this work, we have found that the most reactive structures correspond to the LS with calcium and sodium and the less reactive structures are the LS with ammonia and sulfur. This behavior for the LS with calcium and sodium is consistent with what is known about these two LS, as they are widely used as desiccants and coagulants agents; this advantage can be related to the high reactivity they exhibit.

4 Conclusions

Studying the molecular structure of the lignosulphonates considered in this work, we have found that the LS become more structurally stable, from the energy point of view as they grow, just like lignin, presenting a significant and steady decline in the heat of formation value for both vacuum and various acidic and basic aqueous environments. By ionizing the structures, we have found that in the vacuum, there is no significant change of the heat of formation, while when placed in an aqueous environment, those LS incorporating calcium and sodium show significant improvement in values for the state of charge of -1 , which

shows the LS affinity with the free radical mechanism, a characteristic that shows its possibilities as a molecular scavenger.

The graphical representations of the molecular structures obtained for LS studied in vacuum and in acidic and basic aqueous media shows that in general, the LS with ammonia and sulfur tend to stretch, forming long chains, in contrast to the behavior observed for LS calcium and sodium whose molecular structures tend to close on themselves surrounding molecules or ions present in their environment. This allows us to conclude and confirm [15] that the LS with calcium and sodium show the best molecular capture capabilities. Graphical representations of the electrostatic potential show that the higher reactivity LS are those incorporating calcium and sodium, disregarding the environment and solvent used with nearly all parts of the molecular structure showing a high electronegativity. This shows that the molecular structures of the LS considered in this work have enormous potential to be subject to electrophilic attack, and in addition, the results obtained for electronic GAP in aqueous environment show a significant decrease of this value for the charge state -1 or, in the presence of an electron, confirmed the excellent reactivity of the treated media LS.

Also, it was found that the LS with calcium and sodium share a behavior as they tend to surround the molecules found in the environment, and the resulting molecular systems presented not only excellent results in terms of heat of formation but also attracted all the molecules in their environment. When studied in acidic and basic aqueous environments, it was found that a more acidic media promotes the molecular capture by the LS, particularly those incorporating sulfuric acid and hydrochloric acid, which are present in a wide range of products.

Acknowledgments The authors wishes to thank the Vicerrectoria de Investigaciones of the Univesity of Cauca for the support in the development of this work under the research project ID4064.

References

1. E. Sjöström, *Wood chemistry: fundamentals and applications* (Gulf Professional Publishing, 1993). Chapter 11
2. G. Brunow, Methods to reveal the structure of lignin, in *Lignin, humic substances and coal*, ed. by M. Hofrichter, A. Steinbüchel, Vol. 1 (Wiley-VHC, Weinheim, 2001), pp. 89–116
3. G. Richardson, Y. Sun, M. Langton, A.-M. Hermansson, Effects of Ca- and Na-lignosulphonate on starch gelatinization and network formation. *Carbohydr. Polym.* **57**, 369–377 (2004)
4. J. Ralph, G. Brunow, W. Boerjan, *Lignins* (eLS. John Wiley & Sons Ltd, Chichester, 2007). doi:[10.1002/9780470015902.a0020104](https://doi.org/10.1002/9780470015902.a0020104)
5. P.J. Salazar-Valencia, S.T. Pérez-Merchancano, L.E. Bolívar-Marinéz, Optical properties in biopolymers: lignin fragments. *Braz. J. Phys.* **36**(3B) (2006)

6. A. Steinbüchel, M. Hofrichter, Biopolymers, vol. 1. Lignin, humic substances and coal (Wiley – Vch, 2001)
7. J. Paul Simon, K.-E.L. Eriksson, The significance of intramolecular hydrogen bonding in the β -O-4 linkage of lignin. *J. Mol. Struct.* **384**, 1–7 (1996)
8. K.V. Sarkanen, C.H. Ludwig, *Lignins, occurrence, formation, structure and reactions* (Wiley-Interscience, New York, 1971)
9. G. Milczareka, T. Rebisa, J. Fabianskab, One-step synthesis of lignosulphonate-stabilized silver nanoparticles. *Colloids Surf. B Biointerfaces* **105**, 335–341 (2013)
10. R. Vanholme, K. Morreel, J. Ralph, W. Boerjan, Lignin engineering. *Curr. Opin. Plant Biol.* **11**, 278–285 (2008)
11. C.J. Houtman, What factors control dimerization of coniferyl alcohol. *Holzforschung* **53**(6) (1999)
12. J.J.P. Stewart, Optimization of parameters for semiempirical methods I. Method. *J. Comb. Chem.* **10**, 209 (1989)
13. HyperChem(TM) Professional 5, Hypercube, Inc., 1115 NW 4th Street, Gainesville, Florida 32601, USA
14. W.M. Fabian, AM1 Calculations of rotation around essential single bonds and prefer conformations in conjugated molecules. *J. Comb. Chem.* **9**, 369 (1988)
15. P. Miretzky, A. Fernandez Cirelli, Cr(VI) and Cr(III) removal from aqueous solution by raw and modified lignocellulosic materials: a review. *J. Hazard. Mater.* **180**, 1–19 (2010)