

Global Reactivity Descriptors, Optimized Parameters and Hydration Free Energy of Sodium and Potassium Salt of Amino Acids

^{*1}Mahendra Bapurao Dhande, ²G Krishna Chaitanya, ³Dipak Tukaram Tayade ,
³Sugan Z. Jadhao

^{*1}Department of Chemistry, HPT Arts and RYK Science College, Nashik-422005, India

²School of Chemical Sciences, SRTM University, Nanded-431 606,

³Department of Chemistry, Institute of Science, Nagpur, 440012, India

Corresponding Author: Mahendra Bapurao Dhande

Abstract

In the present study, using Gaussian 09 software, Global Reactivity Descriptors and optimized parameters like hydration free energies, total dipole moment, HOMO/LUMO band gap energy, C=O vibration of COOH group, bond lengths and bond angles were calculated sodium L-alaninate, sodium L-valinate, potassium L-alaninate, and potassium L-valinate. Study shows that the energy bandgap for potassium salts is less than that of corresponding sodium salts. From result it could be stated that the change of alkali metal (Na / K) in amino acid salts are changing the physical structural and vibrational characteristics of amino acid salts. This study is helpful for their applications in various fields.

Keywords: Amino acid salt; CO₂; Hydration free energies; total dipole moment;

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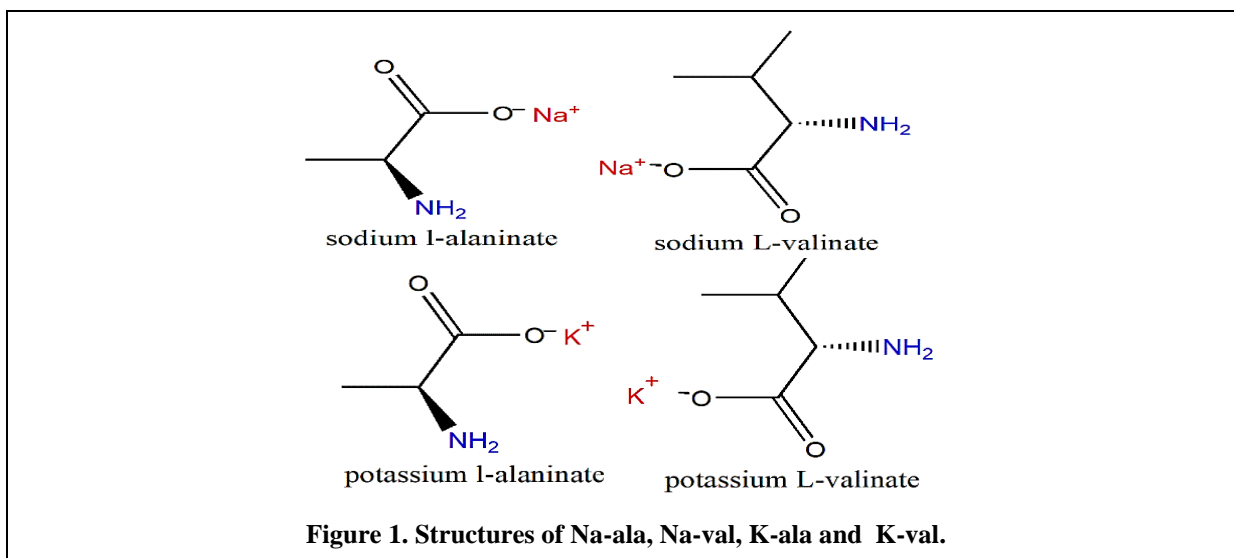
I. INTRODUCTION

Carbon dioxide (CO₂) as a major greenhouse gas is held responsible for the observed global warming over the four decades and the concerns for related climate change and its possible effect on mankind. Therefore, removal of CO₂ from a process gas is an important step in many industrial processes. CO₂ capture technologies comprise ways to separate CO₂ from flue gas, before the flue gas is released into the atmosphere. The amino acid salt solution is developing into an CO₂ capture absorbent and various researchers have studied their reactions with CO₂¹⁻³. Their physical parameters, optimized geometrical parameters and molecular properties (Global Reactivity Descriptors) could be helpful for their evaluation and characterization as a CO₂ capturing absorbent and for other industrial applications.

Such properties have not yet been reported in the open literature sodium L-alaninate(Na-ala), sodium L-valinate(Na-val), potassium L-alaninate(K-ala), and potassium L-valinate(K-val). Thus, in the present work, we presented new data on the optimized geometrical parameters like bond lengths; L_{O-M} and bond angle; O-C=O of -COOM group(M=Na/k), molecular properties including Chemical hardness (η), Softness (S), chemical potential (μ) and electronegativity (χ) and physical parameters like hydration free energies(HFE), total dipole moment, HOMO/LUMO band gap energy, C=O vibration of COOH group, bond lengths and bond angles in Na-ala, Na-val, K-ala, K-val and K-leu.

II. METHODS

Gaussian 09 Software was used for computational work. In the present work hydration free energies and other optimized parameters of sodium L-alaninate(Na-ala), sodium L-valinate(Na-val), potassium L-alaninate(K-ala), and potassium L-valinate(K-val) were calculated in the gas phases well as in the aqueous phase. To calculate the various parameters and hydration free energy, geometry of salt of amino acid (SAA) was fully optimized and the frequencies were calculated by using Density Functional Theory (DFT) B3LYP method at 6-31++G (d, p) basis set⁴ using PCM (Polarizable Continuum Model) solvation Model.



III. RESULT AND DISCUSSION

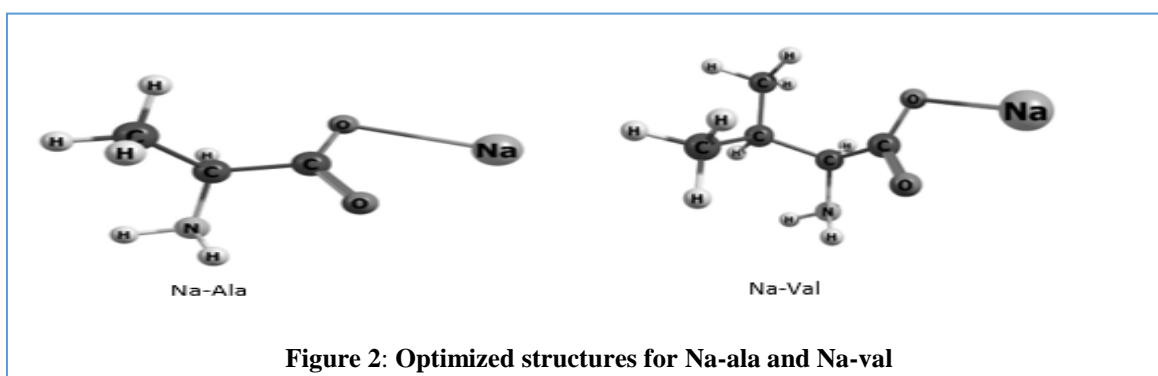
3.1. Optimized geometrical parameters (bond length (L) in Å and angle (A) in Degrees)

The optimized geometrical parameters such as bond length; L_{O-M} and bond angle $O-C=O$ of $-COOM$ group ($M=Na/k$) were computed⁵ for Na-ala, Na-val, K-ala, and K-val are placed in Table 1. The O-M bond length increases from Na-SAA to K-SAA this is probably due to increase in the radius of the metal ion. Similar trend is observed as we move from gas phase to aqueous phase, the O-M bond length increases for both $M = Na$ and $M = K$. The $O-C=O$ bond angle increases from Na-SAA to K-SAA in both phases and the value is higher for alanine salts compare to valine salt. This $O-C=O$ bond angle increase is also observed from gas to aqueous phase. This trend is observed for all studied SAA. Figure 2 presents the optimized structures for Na-SAA and Figure 3 presents the optimized structures for k-SAA.

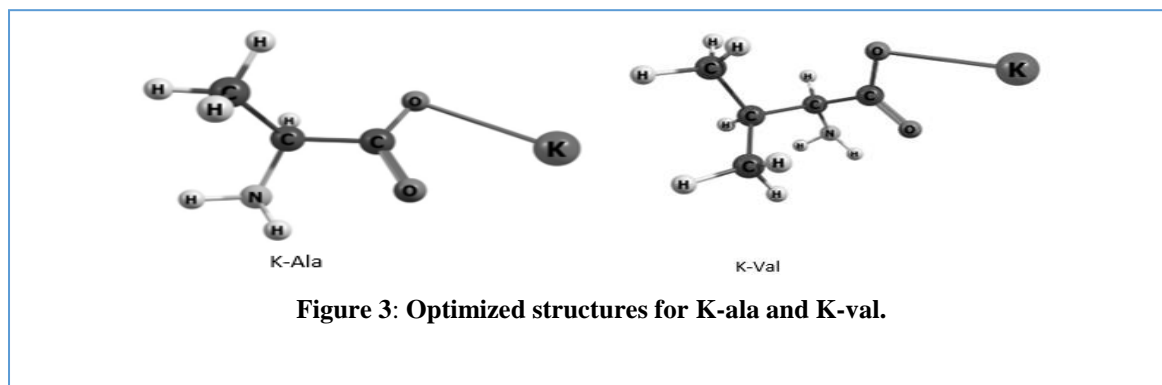
3.2. Molecular properties (Global Reactivity Descriptors)

The eigenvalues of the highest-occupied molecular orbitals (HOMO), lowest-unoccupied molecular orbitals(LUMO), the HOMO-LUMO gap, electronegativity, and chemical hardness are the most well-known of these parameters (Global Reactivity Descriptors) that are based on the DFT^{6,7}. The 1930s-era Koopmans theorem⁸ provides a different method for predicting the ionization energy and electron affinities of chemical species and serves as a link between conceptual density functional theory and molecular orbital theory.

This hypothesis states that a molecule's ionization energy and electron affinity are approximately equivalent to the negative values of its HOMO and LUMO orbital energies. A key factor in determining the molecule electrical transport capabilities is the energy difference between the HOMO and LUMO states⁹. HOMO and LUMO energy values for a molecule have been used to define the global chemical reactivity descriptors¹⁰, of molecules such as chemical hardness(η), chemical potential(μ), softness(S), and



electronegativity(χ)¹¹⁻¹³. On the basis of HOMO and LUMO energy values, for closed-shell molecules using Koopmans's theorem¹⁴ the hardness(η), chemical potential (μ) and electronegativity(χ) and softness (S) are defined as follows.



$$\eta = \frac{I - A}{2}$$

$$\mu = -\frac{I + A}{2}$$

$$\chi = \frac{I + A}{2}$$

$$S = \frac{1}{\eta}$$

where I is the ionization potential and A is the electron affinity of the molecule. I and A can be expressed through HOMO and LUMO orbital energies as $I = -E_{\text{HOMO}}$ and $A = -E_{\text{LUMO}}$ ¹⁵.

Chemical hardness is a measure of the resistance of a chemical species to changes in its electronic configuration¹⁶⁻¹⁸. It also has some important applications in topics like complex stability, chemical reactivity¹⁹, estimation of formed products in a reaction and solubility of molecules²⁰. All the calculated values of ionization potential, electron affinity, hardness, potential, and softness for Na-ala, Na-val, K-ala and K-val are presented in Table 2. The stability of the molecule can also be related to hardness and softness²¹. The chemical hardness and electronegativity values of K-salts are slightly less than that of corresponding Na-SAA in both gas and aqueous phase. In gas phase both χ and η values of Na-ala are highest among studied Na and K salts respectively. But in aqueous phase, for K-SAA the trend was observed, as number of carbon increases in alkyl group, the χ and η values goes on decreasing and found lowest χ and η values of K-val. Ongoing from gaseous medium to aqueous medium the chemical hardness and chemical potential increases while the electronegativity decreases for all studied SAA.

The collective molecular properties data for, Na-ala, Na-val, K-ala and K-val suggest that

1. The chemical hardness and chemical potential values are higher in aqueous phase compare to gas phase while the softness and electronegativity shows lower values for all studied structures.
2. Observed trend of chemical hardness (η), and electronegativity (χ) of Na-SAA and K-SAA of an amino acids is as follows

$$\eta (\text{Na-SAA}) > \eta (\text{K-SAA})$$

$$\eta (\text{Na-ala}) > \eta (\text{Na-val})$$

$$\chi (\text{Na-SAA}) > \chi (\text{K-SAA})$$

3.3. Calculated physical parameters for all studied SAA molecules including total dipole moment (TDM), HOMO/LUMO band gap energy (ΔE) and the C=O vibration of carboxyl group.

The Total Dipole Moment(TDM) values, HOMO/LUMO band gap energy(ΔE), and C=O vibration of carboxylic group of studied SAA in both gas and water phase were also computed. The two physical parameters TDM and ΔE measures the reactivity^{22,23} and stability²⁴ of a given compound with their surrounding molecules. High total dipole moment and a low band gap energy is an indication of reactive compounds²⁵. TDM is increased and band gap energy is slightly decreased from Na-SAA to K-SAA for both amino acids.

$$(\Delta E) \text{ Na-salt} > (\Delta E) \text{ K-salt,}$$

$$(\text{TDM}) \text{ Na-salt} < (\text{TDM}) \text{ K-salt,}$$

$$\text{Aqueous phase}(\text{TDM and } \Delta E) > \text{Gas phase} (\text{TDM and } \Delta E)$$

Trend of total dipole moment (TDM) in aqueous phase for SAA as shown below

$$(\text{TDM}) \text{ K-ala} > (\text{TDM}) \text{ K-val}$$

$$(\text{TDM}) \text{ Na-ala} > (\text{TDM}) \text{ Na-val,}$$

Trend of HOMO/LUMO band gap energy(ΔE) in aqueous phase for SAA as:

$$\begin{aligned} (\Delta E) \text{ K-ala} &> (\Delta E) \text{ K-val,} \\ (\Delta E) \text{ Na-ala} &> (\Delta E) \text{ Na-val} \end{aligned}$$

From the aforementioned trend, it is evident that the TDM and ΔE values decrease in aqueous solutions for K-SAA as one carbon increases (increase in molar mass) in the alkyl group of amino acid. Comparison of ΔE and TDM of Na-SAA and K-SAA, respectively, is shown graphically in Figures 4 and 5. Na-val was found to be having lowest ΔE values in both phases.

The C=O vibrational characteristic band of carboxyl group was shifted toward higher wavenumber from Na-SAA to K-SAA as a result of increase in the ionic radius of the metal ion, this was considerable for all the studied SAA. According to observations, it is higher for K-ala/val compare to Na-ala/val.

3.4. Calculated Hydration Free Energies for all studied SAA molecules.

A key idea in comprehending chemistry in solutions is the free energy of solvation, which is the energy involved in a molecule transitioning from the gas phase to solution. The solvation free energy is referred to as the hydration free energy when the solvent is water. The stability of the hydrated ion in comparison to the stability of its anhydrate state is determined by the HFE²⁶. DFT B3LYP method at 6-31++G (d, p) basis set was used for calculating Hydration free energy(HFE). It is the work required to transfer a molecule from the gas phase into the solution phase. The following equation is used to compute HFE

$$\Delta G_{\text{Hydr}}^{\circ} = \Delta G_{\text{s}}^{\circ} - \Delta G_{\text{g}}^{\circ}$$

where $\Delta G_{\text{g}}^{\circ}$ and $\Delta G_{\text{s}}^{\circ}$ represents the standard free energy of solute in the gas phase and in the solvent respectively, and G_{Hydr}° refers to HFE. Comparison of HFE of interested SAA is shown in Table 4 and Figure 6. HFE for all studied SAA are negative indicative of strong solute(SAA)-solvent interaction. The HFE values of Na-salts are higher than the correspond K-salt of amino acid. Na-ala were found to be having highest HFE values among all studied SAA.

Table 1: Optimized geometrical parameters: (bond length (L) in Å and bond angle (A) in Degrees) for all studied SAA molecules obtained at B3LYP/6-311+G (d, p) level.

Optimized geometrical parameters	Na-ala	Na-val	K-ala	K-val
Gas Phase				
L(O-M)	2.1952	2.1969	2.5524	2.5547
A(O-C=O)	123.55	123.30	124.57	124.31
Aqueous Phase				
L(O-M)	2.3547	2.3542	2.7598	2.7598
A(O-C=O)	124.08	123.88	125.00	124.76

Table 2: Molecular properties (Global Reactivity Descriptors) including Chemical hardness (η), Softness (S), chemical potential (μ) and electronegativity (χ).

Molecular Properties	Na-ala	Na-val	K-ala	K-val
Gas Phase				
I	5.9185	5.8431	5.6412	5.5909
A	1.5747	1.5859	1.3965	1.4068
Chemical hardness(η)	2.1719	2.1286	2.1223	2.0920
Softness (S)	0.4604	0.4698	0.4712	0.4780
Chemical potential(μ)	-3.7466	-3.7145	-3.5188	-3.4989
Electronegativity(χ)	3.7466	3.7145	3.5188	3.4989
Aqueous Phase				
I	6.5800	6.4840	6.4921	6.4078
A	0.3518	0.3404	0.3739	0.3660
Chemical hardness(η)	3.1141	3.0718	3.0591	3.0209

Softness (S)	0.3211	0.3255	0.3269	0.3310
Chemical potential(μ)	-3.4659	-3.4122	-3.4330	-3.3869
Electronegativity(χ)	3.4659	3.4122	3.4330	3.3869

Table 3: Calculated physical parameters for all studied SAA molecules including HOMO/LUMO band gap energy (ΔE),

Molecular Properties	Na-ala	Na-val	K-ala	K-val
Gas Phase				
ΔE (eV)	4.3438	4.2573	4.2447	4.1841
TDM (D)	6.0884	6.1270	8.2997	8.2177
C=O vibration	1584.40	1580.58	1591.84	1588.21
Aqueous Phase				
ΔE (eV)	6.2282	6.1436	6.1182	6.0418
TDM (D)	7.6616	7.6555	10.3979	10.1040
C=O vibration	1570.40	1569.27	1574.10	1572.37

Table 4: Calculated Hydration Free Energies for all studied SAA molecules.

Molecular Properties	Na-ala	Na-val	K-ala	K-val
Free Energy in Gas Phase (a.u.)	-485.530471	-564.163031	-923.141328	-1001.773711
Free Energy in Water Phase (a.u.)	-485.581098	-564.212785	-923.186234	-1001.817544
Hydration Free Energy (Kcal/mol)	-31.77	-31.22	-28.18	-27.51

IV. CONCLUSIONS

The geometry of the studied amino acid salt is changed as the C-O and C=O bond length decreases while the O-M bond length increases from Na-SAA to K-SAA with a change in the (C-O=C) bond angle. In aqueous phase, Na-ala possesses higher chemical hardness as well as electronegativity value among all studied SAA. Therefore, we can interpret that it is least reactive. K-val in both phases, with lowest η is found to be more reactive in all studied SAA.

Both the total dipole moment and ΔE are changed as a result of increased size of metal ion and the alkyl part of studied amino acid. Lower ΔE and higher TDM values are the indicative of greater reactivity of K-SAA compare to Na-SAA. K-val has lowest ΔE among all studied SAA in both phases. The change in the geometrical parameters are followed with a shift in the characteristic band of carboxyl group that shift the C=O toward lower wavenumbers. Negative value of the hydration free energy of SAA suggests strong SAA-water interaction.

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REFERENCES

- [1] Z. Zhang, S. Rao, Y. Han, R. Pang, W. W. Ho, J. Memb. Sci. **2021**, 638, 119696.
- [2] M. Liu, G Gadikota, Fuel, **2020**, 275, 117887.
- [3] E. Soroush, M. Mesbah, N. Hajilary, M. Rezakazemi, J. Environ. Chem. Eng. **2019**, 7(1), 102925.
- [4] 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. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian. **2013**, Inc., Wallingford CT.
- [5] K. Tayade, B. Bondhopadhyay, A. Basu, G. K. Chaitanya, S. K. Sahoo, N. Singh, A. Kuwar, *Talanta*. **2014**, 122, 16-22.
- [6] S. Kaya, B. Tüzün, C. Kaya, I. B. Obot, *J Taiwan Inst. Chem. Eng.* **2016**, 58, 528-535.
- [7] A. Valaboju, K. C. Gunturu, B. Kotamarthi, D. Joly, M. Hissler, *Comput. Theor. Chem.* **2017**, 1113, 61-71.
- [8] T. Koopmans, *Physica*. **1933**, 1, 104-113.
- [9] G. Zhang, C. B. Musgrave, *J. Phys. Chem. A*. **2007**, 111(8), 1554-1561.
- [10] S. Erdogan, Z. S. Safi, S. Kaya, D. O. Isin, L. Guo, C. Kaya, *J. Mol. Struct.* **2017**, 1134, 751-761.
- [11] M. Miar, A. Shiroudi, K. Pourshamsian, A. R. Oliay, F. Hatamjafari, *J. Chem. Res.* **2021**, 45(1-2), 147-158.
- [12] V. Choudhary, A. Bhatt, D. Dash, N. Sharma, *J. Comput. Chem.* **2019**, 40(27), 2354-2363.
- [13] S. A. Khan, K. Rizwan, S. Shahid, M. A. Noamaan, T. Rasheed, H. Amjad, *Applied Organometallic Chemistry*. **2020**, 34(3), e5444.
- [14] R. G. Pearson, Weinheim: Wiley-VCH. **1997**, 10, 3527606173.
- [15] F. N. M. Lucio, J. E. da Silva, E. M. Marinho, F. R. D. S. Mendes, M. M. Marinho, E. S. Marinho, *Int J. Res.* **2020**, 8(1), 221-36.
- [16] M. Ibrahim, *J. Comput. Theor. Nanosci.* **2009**, 6(3), 682-685.
- [17] N. Abad, M. Hajji, Y. Ramli, M. Belkhiria, H. Moftah, S. A. Elmgirhi, M. Habib, E. M. Essassi, *J. Phys. Org. Chem.* **2020**, 33(6), e4055.
- [18] D. Chakraborty, P. K. Chattaraj, *Chemical Science*. **2021**, 12(18), 6264-6279.
- [19] C. A. Mebi, *J. Chem. Sci.* **2011**, 123(5), 727-731.
- [20] G. Makov, *J. Phys. Chem.* **1995**, 99(23), 9337-9339.
- [21] S. Dheivamalar, K. B. Banu, *Heliyon*. **2019**, 5(12), e02903.
- [22] M. Ibrahim, A. A. Mahmoud, *J. Comput. Theor. Nanosci.* **2009**, 6(7), 1523-1526.
- [23] H. A. Ezzat, M. A. Hegazy, N. A. Nada, M. A. Ibrahim, *Biointerface Res. Appl. Chem.* **2019**, 9, 4143-4149.
- [24] J. S. Singh, *Res. Chem. Intermed.* **2020**, 46(5), 2457-2479.
- [25] M. Miar, A. Shiroudi, K. Pourshamsian, A. R. Oliay, F. Hatamjafari, *J. Chem. Res.* **2021**, 45(1-2), 147-158.
- [26] B. Tansel, *Separation and purification technology*. **2012**, 86, 119-12