Growth, Nucleation Kinetics and Structural Studies on L-Valine Piperazinium Single Crystals

R. ARUNKUMAR^{1,2} and D. BENNY ANBURAJ^{1,3,*}

¹P.G. and Research Department of Physics, Thiru. Vi. Ka. Government Arts College, Thiruvavur-610003, India

²Department of Physics, Sri Sankara Arts and Science College (Autonomous), Enathur, Kanchipuram-631561, India

³P.G. and Research Department of Physics, D.G. Government Arts College (Women), Mayiladuthurai-609001, India

*Corresponding author: E-mail: bennyannburaj@rediffmail.com; arunram85@gmail.com

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A single crystal of L-valine piperazinium was grown by slow growth technique. Structural studies confirm the monoclinic structure with space group $P2_1$. The solubility curve showing high soluble in water and peak shows positive solubility nature. A tiny nucleation formed at 10 °C for room temperature process and it gradually increasing with respect process temperature. Induction period reveals that time period for nucleation at constant temperature and it absorbed that in (10 °C) 500 s for room temperature. The calculated interfacial tension values are greater than one order other amino acid based piperazinium. By using growth parameters bulk L-valine piperazinium crystal were harvested and single crystal XRD confirms that formation of L-valine piperazinium crystals.

Keywords: L-Valine piperazinium, Crystal growth,

INTRODUCTION

A limitation of optical signal broadcast point and heat uprightness were trigger off the tools which plays a key role in photons emits from electron in optoelectronic applications. Insights of crystal growers are fascinated to growing high optical transparent single crystals for optoelectronics application especially for non-linear optical (NLO) properties with high efficiency. The exploration of high efficiency NLO materials have difficult task for current researchers towards up to device fabrication [1,2]. In general, NLO properties exhibits in both organic and inorganic materials, Compare to inorganic nowadays organic materials have higher charge, Ultra fast response, and large flexible so which leads to developed the many optical device fabrications. In organic materials, π -electron is responsible for the NLO response but in inorganic is due to ions [3].

Piperazine consists of a six associated soaked ring and have two nitrogen atoms at opposite positions in the ring. It also known as 1,4-hexahydropyrazine and it exists a small alkaline hydrophilic with a salty flavour. Piperazine has lot of applications in the field of science in recent they used for multi-drugs resistance in malaria and cancer diseases [4-6].

In amino acid, L-valine compound plays major role in the listed acids because it has aliphatic non-polar chains in a material. L-valine is also called as 2-amino-3-methylbutanoic acid which is mainly used for biosynthesis of proteins and some optical applications [7]. In general nature of all amino acids have two groups, L-valine also had two groups first is primary amino group (α -amino group: its protonated $-NH_3^+$ form biological conditions) and second is primary carboxyl group (α -carboxyl acid group: its deprotonated $-COO^-$ form biological and optical conditions) [8]. Till now several hundreds of donor and acceptor substituted delocalized π -electron system have been reported which show NLO properties. In this respect, amino acids are interesting materials for NLO applications [9]. The importance of amino acid for NLO application lies on the fact that almost all amino acids contain an asymmetric carbon atom which makes them optically active and most of them crystallize in non-centrosymmetric space groups [10].

Bulk crystals have a great potential in physical properties, which makes them ideal candidates for nonlinear optical devices. Piperazinium with L-tartrate, L-histidine tartrate, L-proline tartrate, urea L-tartrate, imidazolium L-tartrate with solution growth methods single crystal reports are already available but these crystals are lack in growth aspects as well

as NLO properties [11-13]. To enhancing NLO properties in bulk crystal creates challenging factor for current crystal growers. So crystals of L-valine piperazinium have been subjected to broad exploration by few researchers for their nonlinear optical properties because L-valine have zwitterionic nature and large hyperpolarizability.

In this article, we reports on the various growth parameters such as solubility, metastable zone-width, induction period, interfacial tension, Gibbs free energy change, radius of critical nucleus, nucleation rate and the number of molecules present in the critical nuclei of L-valine piperazinium which are essential parameters for the growth of bulk crystals. In addition, the structural parameters are also discussed.

EXPERIMENTAL

The raw materials of L-valine and piperazinium chemicals were purchased 4n purity in Alfa-Aser Company. The 1:1 stoichiometric ratio of L-valine and piperazinium were dissolved in deionized water and stirred for 24 h to formulate the homogeneous solution and maintains solution throughout reaction in 5.35 pH at room temperature. The high quality single crystal was harvested within 32 days. The growth parameters were investigated using by constant water bath with accuracy of $\pm 0.01^\circ\text{C}$. The solubility was evaluated gravimetrically for various temperatures such as 35, 40, 45 and 50°C . Metastable zone-width was measured by polythermal method and based on the solubility data the nucleation was done. The structural data were recorded for L-valine piperazinium (LVP) crystals using XRD, FTIR, NMR techniques.

RESULTS AND DISCUSSION

Solubility: The solubility of L-valine piperazinium (LVP) crystals were determined using deionized water as solvent at various temperature range varying from room temperature to 50°C with the interval of 5°C . The complete reaction was carried out in a constant temperature water bath with accuracy of $\pm 0.01^\circ\text{C}$. Initially 100 mL of deionised water taken in beaker and it maintains at 30°C . The synthesized powder of LVP was pour slowly into the beaker and continuously stirred using immiscible magnetic stirrer up to saturated level. After reaches the saturation, the equilibrium concentration of the solution was analyzed gravimetrically. The same process was repeated up to 50°C with the interval of 5°C to determine the solubility. The variation of solubility with different temperature is shown in Fig. 1.

Metastable zone width: The metastable zone width indicates that stability of the mixture solution with respect to difference in saturated and nucleation temperature [14-16]. It plays major role in bulk crystal growth and it was calculated by using conventional polythermal method [17,18]. The nucleation temperatures (Fig. 2) was measured from supersaturated solution to lowering the temperature ($0.05^\circ\text{C}/2\text{ h}$) up to small tiny particle absorbed in the solute medium and repeat the procedure for all temperature in saturated solutions.

Induction period: Isothermal technique was used to find out the induction period of LVP crystals. The induction period were recorded for different super-saturation ratio (s) from

Fig. 1. Solubility curve of L-valine piperazinium crystals

Fig. 2. Nucleation period of L-valine piperazinium crystals

1 to 2 with the interval of 0.2 at different temperatures (30, 35, 40, 45, and 50°C). The induction period (τ) is the time taken between the attainment of supersaturation and the appearance of a bright sparkling particle in a supersaturated solution [19,20]. For experimental purpose, repeat the sequence 5 times and get accurate induction time period (Fig. 3).

Fig. 3. Induction period of L-valine piperazinium crystals

Interfacial tension: Interfacial tension of solid-solute interface is an important parameter involved in crystal growth and kinetics. Interfacial tension was evaluated from the experimentally determined induction period values. The evaluated values are tabulated (Table-1) and compared with other amino acid determined values. Due to the hydration number variation as the results temperature increase the concentration of the solution also increases. So, super-saturated region will be decreased, which leads to decrease the nucleation rate and interfacial tension goes too inversely [21,22].

By using the interfacial tension the radius of critical nuclei (r^*), change in Gibbs free energy (ΔG^*), the number of molecules present in the nucleus (i^*) and nucleation rate (J) have been evaluated as the super-saturation increases the change in Gibbs free energy (ΔG^*), the number of molecules present in the nucleus (i^*) and nucleation rate (J) decreases [23-27]. The interfacial tension which was calculated experimentally from the measured induction period values and compared with the amino acid based piperazinium values (Table-1).

Bulk growth of L-valine piperazinium (LVP): Using the growth parameters, L-valine piperazinium bulk single crystal (Fig. 4) was grown by slow evaporation method. After 32 days from the constant temperature bath at 50 °C, the good quality L-valine piperazinium crystal was harvested.

XRD analysis: The XRD profile of LVP crystals revealed that the grown crystal have a monoclinic structure with lattice parameters $a = 6.4211 \text{ \AA}$, $b = 9.1272 \text{ \AA}$, $c = 9.3489 \text{ \AA}$. The space group and volume is $P2_1$ and $519.49 \text{ \AA}^3$, respectively. The hydrogen bond geometry (Table-2) represents the two O-O interactions

Fig. 4. L-Valine piperazinium (LVP) single crystal

between the carboxylate moieties (acceptors) and the hydroxyl groups (donors). Fig. 5 shows that each of the carboxylate moiety shows a significant deviation from coplanarity with respect to the adjacent hydroxyl functional group; $O(2)-C(1)-C(2)-O(3)-14.6(2)^\circ$ and $O(4)-C(3)-C(4)-O(5)-8.1(2)^\circ$. Fig. 6 shows the crystal packing diagram of L-valine piperazinium (LVP) molecule with atomic numbering scheme.

FT-IR analysis: The vibration pattern of LVP crystal powder was recorded using FT-IR instrument. The bands at $3500-3000 \text{ cm}^{-1}$ indicates the N-H symmetric stretching vibration present in the titled compound and COO^- stretching mode present in 2136 cm^{-1} it shows the presence of L-valine compound.

TABLE-1
COMPARISON OF INTERFACIAL ENERGY VALUES (mJ/m^2) FOR
DIFFERENT TEMPERATURES OF AMINO ACID BASED PIPERAZINIUM

Temp. ($^\circ\text{C}$)	L-tartrate piperazinium (mJ/m^2)	L-Histadine piperazinium (mJ/m^2)	L-Proline piperazinium (mJ/m^2)	Urea L-tartrate piperazinium (mJ/m^2)	Imidazolium L-tartrate piperazinium (mJ/m^2)	L-Valine piperazinium (mJ/m^2)
30	1.1126	1.1658	1.2458	1.2658	1.3658	1.556
35	1.2763	1.1883	1.2783	1.2883	1.3883	1.583
40	1.3257	1.2108	1.2908	1.3108	1.4108	1.597
45	1.4557	1.2334	1.3334	1.3334	1.4334	1.607
50	1.1126	1.3334	1.3658	1.3755	1.4745	1.676

TABLE-2
SINGLE CRYSTAL BOND LENGTH VALUES OF L-VALINE PIPERAZINIUM SINGLE CRYSTALS

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
C(5)-H(5A)...O(4)#1	0.97	2.45	3.2724(18)	142.0
C(5)-H(5B)...O(4)	0.97	2.51	3.2677(17)	135.2
C(6)-H(6A)...O(1)#2	0.97	2.52	3.3182(18)	139.7
C(6)-H(6B)...O(6)#3	0.97	2.45	3.1665(18)	130.2
C(7)-H(7A)...O(4)	0.97	2.47	3.2402(18)	135.8
C(7)-H(7B)...O(5)#4	0.97	2.47	3.3510(2)	150.6
C(8)-H(8B)...O(3)#5	0.97	2.46	3.2347(18)	137.0
O(3)-H(3A)...O(1)#2	0.82	2.30	2.9823(15)	141.3
O(3)-H(3A)...O(2)	0.82	2.13	2.6226(15)	118.2
O(4)-H(4)...O(1)#6	0.82	2.39	2.9917(14)	130.7
O(4)-H(4)...O(5)	0.82	2.11	2.6048(14)	118.7
N(2)-H(2B)...O(6)#3	0.884(13)	1.925(13)	2.7717(15)	160.0(15)
N(1)-H(1A)...O(2)	0.892(12)	1.881(13)	2.7563(15)	166.3(16)
N(2)-H(2A)...O(1)#6	0.925(13)	1.859(13)	2.7763(15)	170.8(17)
N(2)-H(2A)...O(2)#6	0.925(13)	2.539(17)	3.0860(15)	118.2(13)
N(1)-H(1B)...O(5)#7	0.908(14)	1.822(14)	2.6829(15)	—
N(1)-H(1B)...O(6)#7	0.908(14)	2.619(17)	3.2738(16)	—

Fig. 5. ORTEP diagram of LVP molecule with atomic numbering scheme

Fig. 6. Crystal packing diagram of LVP crystal

The vibrational frequencies of different functional groups of LVP and the frequency assignments are presented in Table-3.

TABLE-3
FTIR PEAK AND BAND ASSIGNED OF
L-VALINE PIPERAZINIUM CRYSTALS

Wave number (cm ⁻¹)	Band assignments
3415	N-H symmetric stretching vibration
3373	N-H asymmetric stretching vibration
3246	OH group of amino acid
3024	N-H symmetric stretching vibration
3005,2904	C-H symmetric stretching vibration
2819	C-H asymmetric stretching mode of amino acid
2756	C-N stretching vibration
2139	COO ⁻ stretching mode
1597	CH ₂ deformation
1388	CH ₃ deformation of alcohol group
1228	C-N asymmetric stretching vibration
1190	C-C symmetric stretching mode
1090	C-C asymmetric stretching vibration
1070	C-O vibration
974	C-H out of plane bending vibration
950	C-H bending vibration
740	C-H out of plane bending modes
704, 640, 621, 596	CCN deformation

NMR analysis: In ¹H NMR (Fig. 7), a peak appeared at 3.4 ppm corresponds to CH₂ protons of piperazine moiety. The sharp peak at 4.2 ppm assigned to resonance proton signals of N⁺CH₂COO⁻. The peak identified at 2.08 ppm is attributed to C-H protons of L-valine.

Fig. 7. ¹H NMR spectrum of L-valine piperazinium (LVP) crystals

Conclusion

A single crystal of L-valine piperazinium (LVP) was grown by slow growth technique. Structural studies confirm the monoclinic structure with space group P2₁. The growth parameters were evaluated and showing high solubility in water and peak shows positive solubility nature. The nucleation period were started 10 °C for room temperature saturated solution future increasing temperature nucleation rating also increasing gradually. In induction period (τ) very less time (500 s) the attainment of super-saturation and the appearance of a bright sparkling particle in a supersaturated solution at room temperature. The calculated interfacial tension values are greater than one order other amino acid based piperazinium. By using growth parameters bulk LVP crystal were harvested and single crystal XRD confirms the formation of LVP crystals.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. D.S. Chemla and J. Zyss, *Nonlinear Optical Properties of Organic Molecules and Crystals*, Academic Press: London, vol. 1 (1987).
2. J. Badan, R. Hierle, A. Perigand and J. Zyss, ed.: D.J. Williams: *Non-linear Optical Properties of Organic Molecules and Polymeric Materials* Vol. 233, American Chemical Society, Washington, DC (1993).
3. S. Gunasekaran and B. Anita *Indian J. Pure Appl. Phys.*, **46**, 833 (2008).
4. T. Eicher and S. Hauptmann, *The Chemistry of Hetrocycles*, Thieme: Stuttgart, p. 422 (1995).
5. T. Suzuki, N. Fukazawa, K. San-nohe, W. Sato, O. Yano and T. Tsuruo, *J. Med. Chem.*, **40**, 2047 (1997); <https://doi.org/10.1021/jm960869j>.
6. V. Sasikala, D. Sajan, N. Vijayan, K. Chaitanya, M.S. Babu Raj and B.H. Selin Joy, *Spectrochim. Acta A, Mol. Biomol. Spectrosc.*, **123**, 127 (2014); <https://doi.org/10.1016/j.saa.2013.12.045>.

7. M. Fanqing, L. Mengkai, Y. Xin, Y. Wentao and W. Yuguo, *Mater. Res. Bull.*, **31**, 1121 (1996);
[https://doi.org/10.1016/0025-5408\(96\)00095-5](https://doi.org/10.1016/0025-5408(96)00095-5).
8. M. Vanier and F. Brisse, *Acta Crystallogr. B*, **38**, 3060 (1982);
<https://doi.org/10.1107/S0567740882010826>.
9. Z. Dega-Szafran, A. Katrusiak and M. Szafran, *J. Mol. Struct.*, **920**, 202 (2009);
<https://doi.org/10.1016/j.molstruc.2008.10.055>.
10. T.R. Jensen, J.E. Jorgensen, R.G. Hazell, H.J. Jakobsen, M.A. Chevallier, L. Jorgensen and A. Wiedermann, *Solid State Sci.*, **9**, 72 (2007);
<https://doi.org/10.1016/j.solidstatesciences.2006.11.004>.
11. C.B. Aakeroy, P.B. Hitchcock and K.R. Seddon, *J. Chem. Soc. Chem. Commun.*, **7**, 553 (1992);
<https://doi.org/10.1039/C39920000553>.
12. V. Subhashini, S. Ponnusamy and C. Muthamizhchelvan, *J. Cryst. Growth*, **363**, 211 (2013);
<https://doi.org/10.1016/j.jcrysgro.2012.10.045>.
13. C.B. Aakeroy, G.S. Bahra and M. Nieuwenhuyzen, *Acta Crystallogr. C*, **52**, 1471 (1996);
<https://doi.org/10.1107/S0108270195016374>.
14. P. Rekha, G. Peramaiyan, R. Mohan Kumar and R. Kanagadurai, *Mater. Lett.*, **129**, 202 (2014);
<https://doi.org/10.1016/j.matlet.2014.05.028>.
15. G.H. Sun, G.H. Zhang, X.Q. Wang, Z.H. Sun and D. Xu, *Mater. Chem. Phys.*, **122**, 524 (2010);
<https://doi.org/10.1016/j.matchemphys.2010.03.038>.
16. J. Nyvlt, O. Sohnel, J.J. Zola and G. Kostesky, *J. Cryst. Growth*, **62**, 543 (1983).
17. N.P. Zaitseva, L.N. Rashkovich and S.V. Bogatyreva, *J. Cryst. Growth*, **148**, 276 (1995);
[https://doi.org/10.1016/0022-0248\(94\)00606-7](https://doi.org/10.1016/0022-0248(94)00606-7).
18. T. Balu, T.R. Rajasekaran and P. Murugakoothan, *Physica B*, **404**, 1813 (2009);
<https://doi.org/10.1016/j.physb.2009.02.034>.
19. A.E. Nielsen and O. Söhnel, *J. Cryst. Growth*, **11**, 233 (1971);
[https://doi.org/10.1016/0022-0248\(71\)90090-X](https://doi.org/10.1016/0022-0248(71)90090-X).
20. J. Christoffersen, E. Rostrup and M.R. Christoffersen, *J. Cryst. Growth*, **113**, 599 (1991);
[https://doi.org/10.1016/0022-0248\(91\)90096-N](https://doi.org/10.1016/0022-0248(91)90096-N).
21. K. Sangwal, *J. Cryst. Growth*, **97**, 393 (1989);
[https://doi.org/10.1016/0022-0248\(89\)90221-2](https://doi.org/10.1016/0022-0248(89)90221-2).
22. A.E. Nielsen and S. Sarig, *J. Cryst. Growth*, **8**, 1 (1971);
[https://doi.org/10.1016/0022-0248\(71\)90014-5](https://doi.org/10.1016/0022-0248(71)90014-5).
23. F. Joseph Kumar, D. Jayaraman, C. Subramanian and P. Ramasamy, *J. Cryst. Growth*, **137**, 535 (1994);
[https://doi.org/10.1016/0022-0248\(94\)90995-4](https://doi.org/10.1016/0022-0248(94)90995-4).
24. N.P. Rajesh, V. Kannan, P. Santhana Raghavan, P. Ramasamy and C.W. Lan, *Mater. Chem. Phys.*, **76**, 181 (2002);
[https://doi.org/10.1016/S0254-0584\(01\)00525-9](https://doi.org/10.1016/S0254-0584(01)00525-9).
25. A.G. Walton, ed.: A. C. Zettlemoyer, *Nucleation*, Marcel Dekker: New York, Chap. 5 (1969).
26. S. Boomadevi, R. Dhanasekaran and P. Ramasamy, *Cryst. Res. Technol.*, **37**, 159 (2002);
[https://doi.org/10.1002/1521-4079\(200202\)37:2/3<159::AID-CRAT159>3.0.CO;2-Y](https://doi.org/10.1002/1521-4079(200202)37:2/3<159::AID-CRAT159>3.0.CO;2-Y).
27. S.K. Kurtz and J.J. Perry, *J. Appl. Phys.*, **39**, 3798 (1968);
<https://doi.org/10.1063/1.1656857>.