

# Reduction of Crystal Size & Shape & Stability of DL-Valine: Effect of Surfactant

Asmita Sah<sup>1</sup> Dr. Kushan Parikh<sup>2</sup>

<sup>1,2</sup>Department of Industrial Chemistry

<sup>1,2</sup>Parul Institute of Applied Sciences, Parul University, Vadodara, India

**Abstract** — Amino acid; DL-Valine, has been crystallized in the presence of different ionic surfactants (Cationic CTAB, Anionic SDS) in the aqueous solution. A Crystal size and shape has been characterized by UV spectrophotometer and FT-IR and observed through optical microscope at room temperature. Crystal size alterations of DL-Valine were found due to nature of surfactant. Surfactant charge plays an important role to reduce the agglomeration of crystals by electrostatic reaction. The study shows that with the help of CTAB micellar solution; DL-Valine has lower crystal size and uniform shape.

**Keywords:** Amino Acid. Surfactant. Surfactant-Amino Acid Interaction. Critical Micellar Concentration. Crystallization

## I. INTRODUCTION

The human body relies heavily on amino acids for building amino acids and for metabolizing nutrients. Aspartic acid, Glutamic acid, and Arginine are examples of amino acids with electrically charged side chains, and Serine, Threonine, Asparagine, and Glutamine are some of the amino acids with polar uncharged side chains; Alanine, Valine, Isoleucine, Leucine, Methionine, Phenylalanine, Tyrosine, and Tryptophan have hydrophobic side chains; Cysteine is a special case; because it contains a highly reactive sulphhydryl group on its side chain.

Valine, an essential amino acid, is hydrophobic, and as expected, is usually found in the interior of proteins. Valine is often referred to as one of the amino acids with hydrocarbon side chains, or as a branched chain amino acid. Valine is an  $\alpha$ -amino acid that is found in most proteins and is essential in the human diet. It is similar to leucine and isoleucine in being a branched-chain amino acid and whose build up in the blood and urine, due to a particular enzyme deficiency, causes the serious metabolic disorder maple syrup urine disease.

DL-Valine is a non-polar aliphatic chiral compound that contains  $\text{NH}_2$  group and a  $\text{COOH}$  group with an isopropyl group attached to its side chain. It is found in foods that contains amino acids such as pulses, meat, dairy products etc. DL-amino acids contain both L- and D-amino acids, and are also called racemic mixtures.

On addition of DL-Valine; crystallization phenomena and processes are also greatly littered that plays a vital role in nucleation and growth dynamics of the surfactant and might well modify each habit and size distribution of crystal product.

As conventional methods for crystallization of amino acid, there have been several methods for crystallization which comprises i) Concentrating an aqueous solution of amino acid under reduced pressure, ii) Neutralization for crystallization, iii) A method which comprises crystallization with a solvent while adding a lower alcohol or a ketone to the aqueous solution in large quantities.

As anionic surfactants, fatty acid salt type, sulfate salt type, alkylalylsulfonate type and phosphate salt type; that includes sodium oleate, sodium lauryl sulfate, sodium dodecyl benzenesulfonate, lecithin. As cationic surfactants, quaternary ammonium salt type, aliphatic amine type and pyridinium type; that includes SANISOL, laurylamine, lauryl hydrogensulfatepyridinium, etc. As nonionic surfactants, polyoxyethylene ether type, sorbitan alkyl ester type, esters of polyvalent alcohols and fatty acids and fatty acid ethanolamide type; that includes Tween, glycerol monostearate have been used.

In this research work; we have worked & studied the various aspects on the crystallisation effect; size & shape alterations on the structure of DL-Valine amino acid by the addition of surfactant; ie SDS & CTAB using UV spectrophotometer & FTIR spectrometer.

## II. EXPERIMENTAL SECTION

### A. Materials

Sisco Research Laboratories (SRL) DL-Valine (98%) amino acid. As surfactants, LR grade Sodium Dodecyl Sulphate (>97%) and Cetyltrimethylammonium Bromide (>98%) from Tokyo Chemical Industry (TCI). As solvent; distilled water was used throughout the study.

### B. Method

#### 1) Preparation of Supersaturated DL-Valine solution

In a beaker; 10 ml distilled water was taken and DL-Valine amino acid was added until the solution turned supersaturated. The solution was allowed to settle and then the crystals were observed under an optical microscope.

#### 2) Preparation of CTAB & SDS micellar solution

Cetyl Trimethyl Ammonium Bromide was dissolved in Distilled water to make up the micellar concentrated solution of 4 mM. This was done under constant agitation in volumetric flask in room temperature until the micellar solution was formed.

After the micellar solution was prepared; 10 ml of it was taken into a beaker & agitated with the continuous addition of DL-Valine amino acid until the solution turns supersaturated. Precipitates were observed as the solution turned supersaturated and were allowed to settle. The crystals formed were then seen using an optical microscope.

Sodium Dodecyl Sulphate was dissolved in Distilled water to make up the micellar concentrated solution of 10 mM. After the micellar solution was prepared; 10 ml of it was taken into beaker & agitated with the continuous addition of DL-Valine amino acid until the solution turns supersaturated. Precipitates were observed as the solution turned supersaturated and were allowed to settle. The crystals formed were then seen using an optical microscope.

### 3) UV Spectrophotometer

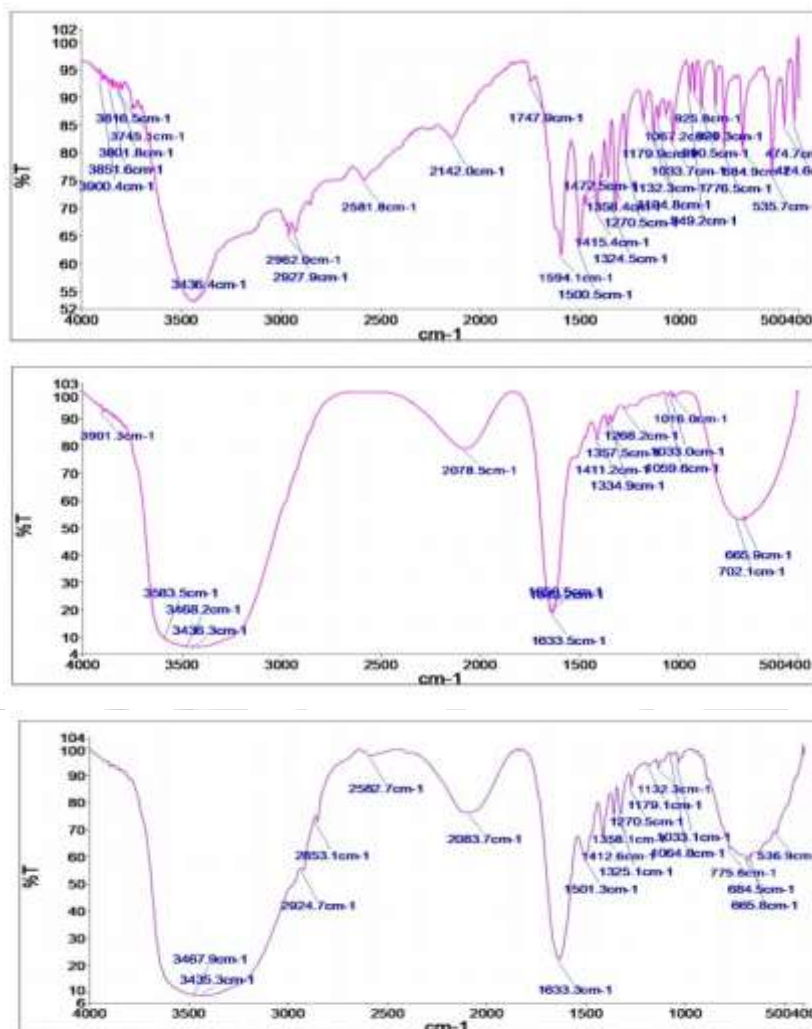
Absorbance of Amino acid was characterized by the help of UV-Visible Double beam Spectrometer (200-760nm). Distilled water was kept as reference inside the cuvettes in UV-Spectrometer during the analysis, to determine how much amino acid is absorb by the solution of surfactant.

### 4) FTIR Spectrometer

To determine the presence of functional group & its effect on the size & shape of crystal; a comparative study of IR Spectra of DL-Valine, Cetyl Trimethyl Ammonium Bromide & Sodium Dodecyl Sulphate ( $400\text{cm}^{-1}$  to  $4000\text{cm}^{-1}$ ) range was done.

## III. RESULT & DISCUSSION

### A. FTIR Analysis



#### 1) FTIR Chromatogram of Pure DL-Valine supersaturated solution

Figure 1 shows the IR spectra of Pure DL-Valine in the region between  $4000\text{-}400\text{ cm}^{-1}$ . DL-Valine exhibits bands due to symmetric C-H & asymmetric C-H stretching & deformation of the methylene chain at  $2927.9$  &  $2142.0\text{ cm}^{-1}$  respectively.

#### 2) FTIR Chromatogram of 4mm CTAB micellar solution at $384.2\text{nm}$

Figure 2 shows the IR spectra of 4mm CTAB micellar solution in the region between  $4000\text{-}400\text{ cm}^{-1}$ . In the presence of CTAB surfactant, the symmetric & asymmetric C-H stretching bands shifted to lower frequencies, i.e.  $2924.7$  &  $2083.7\text{ cm}^{-1}$  respectively.

The shift increased with the continuous addition of the DL-Valine in the CTAB micellar solution.

#### 3) FTIR Chromatogram of 10mm SDS micellar solution at $384.9\text{nm}$

Figure 3 shows the IR spectra of 10mm SDS micellar solution in the region between  $4000\text{-}400\text{ cm}^{-1}$ . The symmetric S=O & asymmetric S=O stretching bands of SDS were observed at  $1059$  &  $1268.2\text{ cm}^{-1}$  respectively due to the stretching of sulfate groups.

The symmetric S=O stretching bands of SDS shifts from  $1059.6$  to  $1016.0\text{ cm}^{-1}$  with the continuous addition of DL-Valine in the SDS micellar solution which resulted in the decrease in the frequency.

B. Microscopic Analysis

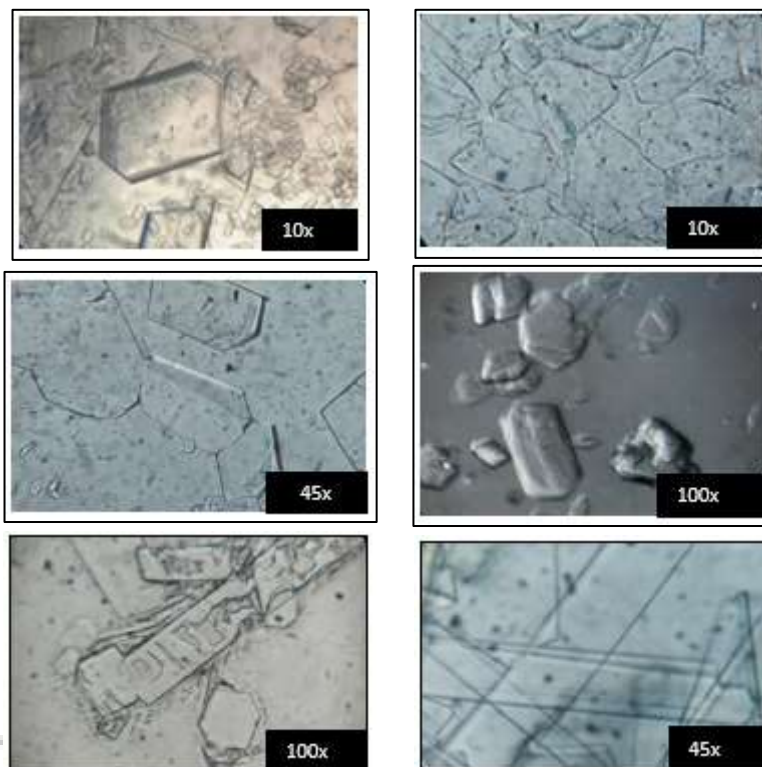


Figure i, ii, iii Representative microscopic image of Pure DL-Valine concentrated solution at 10x, Representative microscopic image of CTAB Micellar solution at 45x & 100x respectively, Representative microscopic image of SDS Micellar solution at 100x & 45x respectively.

Crystals of Figure(i) represents that due to the presence of high C-H stretching molecules, the crystals of amino acids have assumed to be found on the most outer layer of micellar formation i.e. Gouy Chapman layer whereas the Crystals of Figure(ii) represents that due to the presence of symmetric and asymmetric C-H low stretching bonds, the crystals are found in the inner micellar core, i.e. Hydrophobic core. Figure(iii) represents that due to the presence of S=O stretching bands, the crystals are found in the middle layer of micelle; i.e. Stern layer.

Sr. No	Surfactant/ Amino acid	Shape	Zoom	Main crystal faces
i	SDS	Long hexagonal	45 & 100x	{101}
ii	CTAB	Hexagonal	45 & 100x	{110}
iii	DL-Valine	Agglomeration of hexagonal crystals	10x	{110} & {111}

Table 3.2.1: Details of microscopic analysis

IV. CONCLUSION

Consideration of impact of two ionic surfactant on the crystallisation of DL-Valine has been studied. Comparative study between the supersaturated DL-Valine solution, Sodium Dodecyl Sulphate & Cetyltrimethylammonium

Bromide micellar solutions concluded that the effect of surfactant reduced the agglomeration of crystals & played an important role in the nucleation & growth kinetics.

From the FTIR analysis & observation from microscopic images; it is assumed that in the CTAB micellar solution, the stretching of the molecules is least i.e. 2078.5 cm<sup>-1</sup> & thereby the crystals formed are of the least dimension.

Whereas; in the DL-Valine solution; the stretching of the molecules is highest i.e. 2142.0 cm<sup>-1</sup> & thereby the crystals formed are of the highest dimension. The stretching & shape size order is DL-Valine > SDS > CTAB.

ACKNOWLEDGEMENT

The author is thankful to the Parul Institute of Applied Science for financial support to carry out this work. The author is also grateful & acknowledge for the use of research facilities provided by Lab Assistants, Department of Industrial Chemistry, Parul Institute of Applied Sciences, Parul University, Vadodara.

REFERENCES

[1] PA, Kabirud D, Ismail K. Micellization and thermodynamic parameters of butanediyl-1, 4-bis (tetradecyltrimethylammonium bromide) Gemini surfactant at different temperatures: effect of the addition of 2-methoxyethanol. Journal of Solution Chemistry 2012; 41:1271-1281.

[2] Goronja J, Pejić N, JankovicLežaić A, Stanisavljev D, Malenović A. Using a Combination of Experimental and Mathematical Method to Explore Critical Micelle

- Concentration of a Cationic Surfactant. *Journal of Chemical Education* 2016; 93:1277-1281.
- [3] Scholz N, Behnke T, Resch-Genger U. Determination of the Critical Micelle Concentration of Neutral and Ionic Surfactants with Fluorometry, Conductometry, and Surface Tension-A Method Comparison. *Journal of Fluorescence* 2018; 28:465-476.
- [4] Chatterjee A, Moulik SP, Sanyal SK, Mishra BK, Puri PM. Thermodynamics of Micelle Formation of Ionic Surfactants: A Critical Assessment for Sodium Dodecyl Sulphate, Cetylpyridinium Chloride and Dioctyl Sulfosuccinate (Na Salt) by Microcalorimetric, Conductometric, and Tensiometric Measurements. *The Journal of Physical Chemistry B* 2001; 105:12823-12831
- [5] Chauhan S, Sharma K. Effect of temperature and additives on the critical micelle concentration and thermodynamics of micelle formation of sodium dodecyl benzene sulfonate and dodecyl trimethylammonium bromide in aqueous solution: A conductometric study. *The Journal of Chemical Thermodynamics* 2014; 71:205-211.
- [6] Quagliotto P, Barbero N, Barolo C, Costabello K, Marchese L, Coluccia S, et al. Characterization of monomeric and Gemini cationic amphiphilic molecules by fluorescence intensity and anisotropy. *Dyes and Pigments* 2009; 82:124-129.
- [7] Carpena P, Aguiar J, Bernaola-Galván P, Carnero Ruiz C. Problems Associated with the Treatment of Conductivity-Concentration Data in Surfactant Solutions: Simulations and Experiments. *Langmuir* 2002; 18:6054-6058.
- [8] Quagliotto P, Viscardi G, Barolo C, Barni E, Bellinva S, Fisicaro E, et al. Gemini Pyridinium Surfactants: Synthesis and Conductometric Study of a Novel Class of Amphiphiles1. *The Journal of Organic Chemistry* 2003; 68:7651-7660.
- [9] Tikariha D, Kumar B, Singh N, Ghosh KK, Quagliotto P. Micellization Behavior of Cationic Gemini Surfactants in Aqueous-Ethylene Glycol Solution. *Journal of Surfactants and Detergents* 2011; 14:555-562.
- [10] Bakshi MS. Micelle formation by sodium dodecyl sulphate in water-additive systems. *Bulletin Chemical Society of Japan* 1996; 69:2723-2729.
- [11] Chauhan S, Jyoti J, Sharma K, Kumar K. A conductance study to analyse the effect of organic solvents on micellization behaviour of carbohydrate-surfactant system at variable temperatures. *Fluid Phase Equilibria* 2014; 375:286-292.
- [12] Ali A, Alam M, Farooq U, Uzair S. Effect of the nature of counterion on the micellar properties of cationic surfactants: a conductometric study. *Physics and Chemistry of Liquids* 2018; 56:528-543.
- [13] Hoque MA, Alam MM, Molla MR, Rana S, Rub MA, Halim MA, et al. Interaction of cetyltrimethylammonium bromide with drug in aqueous/electrolyte solution: A combined conductometric and molecular dynamics method study. *Chinese Journal of Chemical Engineering* 2018; 26:159-167.
- [14] Naorem H, Devi SD. Conductometric and surface tension studies on the micellization of some cationic surfactants in water-organic solvent mixed media. *Journal of Surface Science and Technology* 2006; 22:89-94.
- [15] Das S, Naskar B, Ghosh S. Influence of temperature and organic solvents (isopropanol and 1, 4-dioxane) on the micellization of cationic gemini surfactant (14-4-14). *Soft Matter* 2014; 10:2863-2875.