Section A -Research paper
ISSN 2063-5346

Detection of Ultrasonic Properties on Aspartame and Malic Acid Binary Systems to Ascertain the Existence of Molecular Interaction

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ABSTRACT

Molecular interaction is the interaction between the two nearby molecules that are present in solute and solvent. In order to study about the molecular interaction between the solute aspartame and solvent malic acid, several acoustical parameters are calculated by using basic parameters. Basic parameters such as ultrasonic velocity, density, and viscosity are measured, from which various acoustical parameter are calculated and interpreted. Spectroscopic studies are made to find the functional group and band gap. The results are interpreted and discussed. The applications of the binary mixtures are also interpreted.

Keywords – Ultrasonic velocity, Density, Acoustical parameters, Aspartame, Binary systems.

1. Introduction

Ultrasonics is a sound wave that lies above the hearing range of human that lies vaster than 20KHZ. Due to its property of interacting with molecules, it is used in Non-destructive testing industries, productive industries, pharmaceuticals, etc. [1]. Majorly, it has a vast application in non-destructive methods in order to determine the interaction between molecules, acoustics, and in the field of medicine [2].

The present investigation is about the binary mixture of artificial sweetener aspartame and edible acid malic acid. For various compositions of aspartame and malic acid basic parameters are determined analytically [3]. The basic parameters are ultrasonic velocity, density, and viscosity. Using these basic parameters, various acoustical parameters are calculated and compiled in a tabular column that is given below. Further spectroscopic studies such as FTIR-ATR and Raman spectroscopy are done for endorsement [4].

2. Literature Survey

Diabetes is a one of the serious ailments in which the pancreas could not produce insulin or the body could not use the insulin. According to the survey, more than 400 million people suffering from diabetes [5].

Aspartame ($C_{14}H_{18}N_2O_5$) is the synthesized artificial sweetener of aspartic acid and phenylalanine with the formula mass of 294.307g/mol. The chemical name of aspartame is L-alpha-aspartyl-L-phenylalanine methyl ester [6]. It is white, achromic and deodorized. It is available commercially with the names NutraSweet, Equal, and Canderel in the form of tablet

and powder [7]. It has a sweetness of 180 – 200 times than sucrose. It dissolves completely in water at extreme heat while sparingly dissolves at ambient temperature [8]. It has high solubility at acidic solution. Though it decomposes on heating it has a wide application in the field of food, beverages, and pharmaceutical industries [9].

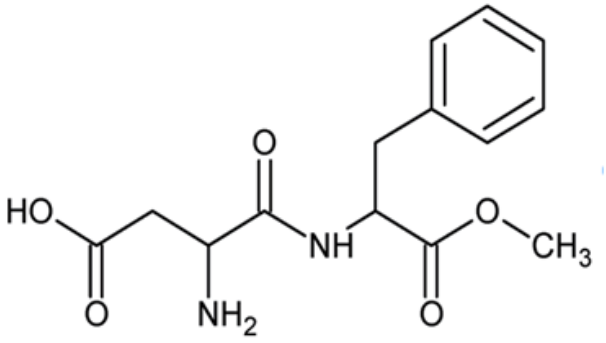

Fig 1: Structure of Aspartame

Malic acid ($C_4H_6O_5$) is one of the edible acids which has the two functional carboxylic acid with the formula mass of 134.09g/mol. The other chemical name of malic acid is cis-butenedioic acid. It is in sour taste of fruit [10]. It is white, achromic and deodized acid. It is commercially available in the form of powder [11]. It is said to found to be the source of the acid is from the stone fruits such as cherries, apricots, peaches, and nectarines and especially found high in apples [12]. It turns into anhydrides at intense heat. It is a used in industries in food industries such as beverages and confectioneries to enrich the taste of the product [13].

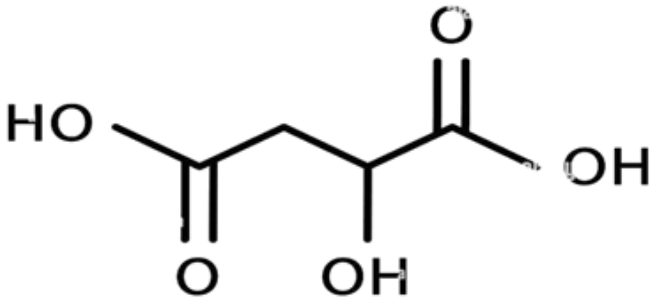

Fig 2: Structure of Malic acid

Acoustical parameter gives concrete information about the molecular interaction between solute and solvent. It provides information about the length of the bond, nature of the interaction and physicochemical properties of the resulted solution. These acoustical parameters are determined with the help of ultrasonic [14]. The basic parameters such as ultrasonic velocity (u), density (ρ) and viscosity (η). Using basic parameters various acoustical parameter are determined [15]. Such as, adiabatic compressibility, acoustic impedance, molar volume, free volume, relaxation time, internal pressure, Gibb's free energy, Rao's constant and Wada's constant [16].

3. Acoustical Parameters

3.1. Adiabatic compressibility

Adiabatic compressibility is a work done to generate the heat due to the structural change of the interacting molecules in a liquid mixture. It is definite by using the values of velocity and density with the formula of:

$$(\beta) = \frac{1}{U^2\rho}$$

3.2. Acoustic impedance

Acoustic impedance is the tendency of the sample to oppose the movement of ultrasonic waves between the molecules of the sample.

$$Z = U\rho$$

3.3. Molar Volume

Molar Volume is defined as the proportion between the mass of the sample to the volume of the substance that is occupied. It is calculated by the values of mole fraction and molecular weight.

$$V_m = \frac{\sum_{i=1}^{n} x_i M_i}{\rho}$$

3.4. Intermolecular free length

Intermolecular free length is elucidated as the length between surfaces of one molecule to another neighbouring molecule.

$$L_f = K_T \beta_{ad}^{1/2}$$

3.5. Molar volume

Molar volume is defined as the space occupied by one mole at a particular temperature and pressure. It is denotes by V_m.

$$V_m = \frac{\sum_{i=1}^{n} x_i M_i}{\rho}$$

3.6. Free volume

Free volume elucidated as the closeness and strength of the bonding between the molecules. It is formulated as

$$V_f = \left(\frac{M_{eff} U}{\eta K}\right)^{3/2}$$

$$M_{eff} = \sum_{i=1}^{n} x_i M_i$$

3.7. Internal Pressure

Internal pressure is intermolecular forces between the solute and solvent. It is expressed as

$$\pi_i = bRT\left(\frac{K\eta}{U}\right)^{1/2}\left(\frac{\rho^{2/3}}{M^{7/6}}\right)$$

3.8. Relaxation time

Relaxation time is a time delay between the two consecutive strikes of molecules. It can be calculated by using the formula,

$$(T) = \frac{4\eta}{3\rho U^2}$$

3.9. Gibb's Free energy

Gibb's free energy is a quantity utmost work done during thermal behaviour at standard temperature and pressure. It can be measure by using the formula,

$$(\Delta G) = KT2.303\log_{10}\frac{KT\eta}{h}$$

3.10. Rao' constant

Rao's constant is a rely on concentration of the sample. It increases with the concentration of the sample.

$$(\mathrm{R}) = (\frac{\mathrm{M_{eff}}}{\mathrm{d_S}})\mathrm{v}^{1/3}$$

4. Stability Constant

Stability Constant is a gauge of how strongly the chemicals interacting to generate the complex interact with one another [17]. Calculating the concentration(s) of the complex in solution requires knowledge of the stability constant(s) as shown in Table 1. It is ascertained by using the values of ultrasonic using the formula as:

$$\mathrm{K} = 2\sqrt{\mathrm{k}}\left[\frac{\sqrt{\mathrm{k}}(\mathrm{C}+\mathrm{C}^1)-(\mathrm{C}+\mathrm{kC}^1)}{(\mathrm{C}-\mathrm{kC}^1)^2}\right]$$

5. Excess Parameter

Excess Parameter is the difference between the experimental and the value of ideal mixtures of all acoustical parameters values [18]. It can be formulated as

$$A^E = A_{mix} - \left(\sum_{i=1}^{n} x_i A_i\right)$$

6. Methodology

6.1. Spectroscopic Study

Fourier Transform Infrared spectroscopy is a spectroscopic study in which infrared spectrum of a sample is obtained. An interferogram is measured of a sample is measured using an interferometer. Then, a Fourier transform is carried out for the interferogram. It is used to determine the functional group and information about bonding between two molecules of solute and solvent.

6.1.1. Instrumentation

FTIR uses an interferometer consists of source, beam splitter, two mirrors, a laser and a detector. A beam from the source is allowed to incident on a beam splitter. Then it is splitted into two beams. One beam is allowed to transmit to the moving mirror and the other beam is reflected using fixed mirror. The moving mirror moves to and fro which is controlled by calibrating laser's response. These two beams recombined to form interference pattern and it is sent to detector. Detector generates a signal. After that, the FT function is used to this signal to produce a spectrum.

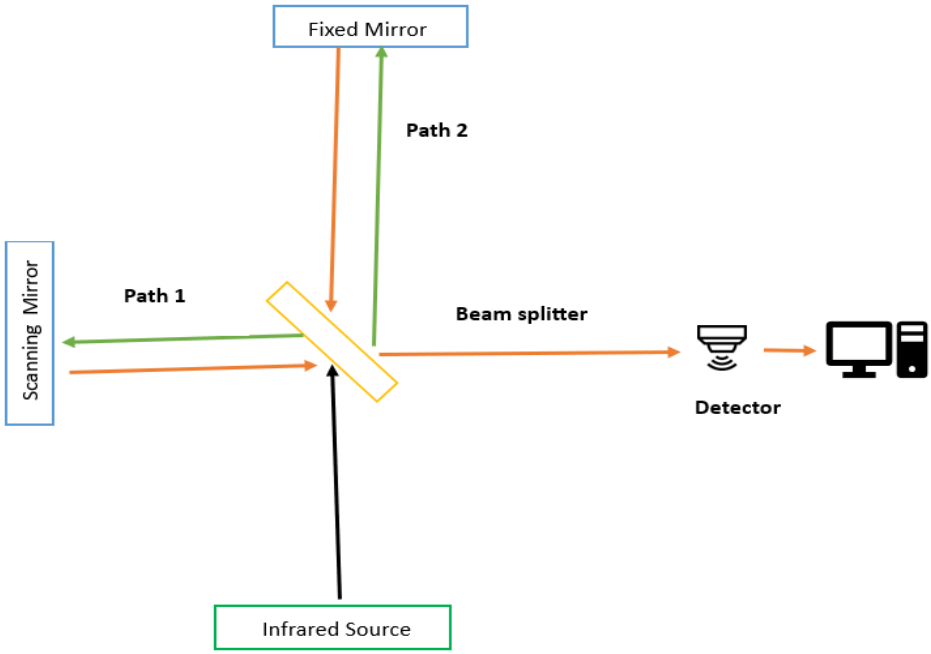

Fig 3: Schematic Representation of FTIR Spectroscopy

6.1.2. Raman Spectroscopy

One spectroscopic method used to identify the vibrational, rotational, and other low frequency modes in a system is Raman spectroscopy. In this method a radiation is allowed to fall on the sample. Then according to the wavelength absorbed by the sample, beam scattered

accordingly. This scattering of radiation gives information about the structure of the molecules.

Instrumentation and Working

Lasers are used as source for Raman spectroscopy as it has high intensity because Raman scattering varies with the fourth power of the frequency. Argon and krypton are the sources of Raman spectroscopy. The benefit of argon and krypton ion sources over competing sources is that they emit in the blue and green portions of the spectrum. It determines the molecular bond in a molecule. Sample is placed inside sample chamber which allows the laser to incident on the sample. Laser from the sample chamber it is passed through the filters. Filters are used for separating the Raman scattered light and Rayleigh scattered light for high quality Raman spectra. In recent Raman spectrometers LCD is used as detectors. These are enhanced such a way to detect the signals with different wavelengths and with low signals. Then the detected signal is allowed to pass to a computer in order to draw a Raman spectrum of a sample.

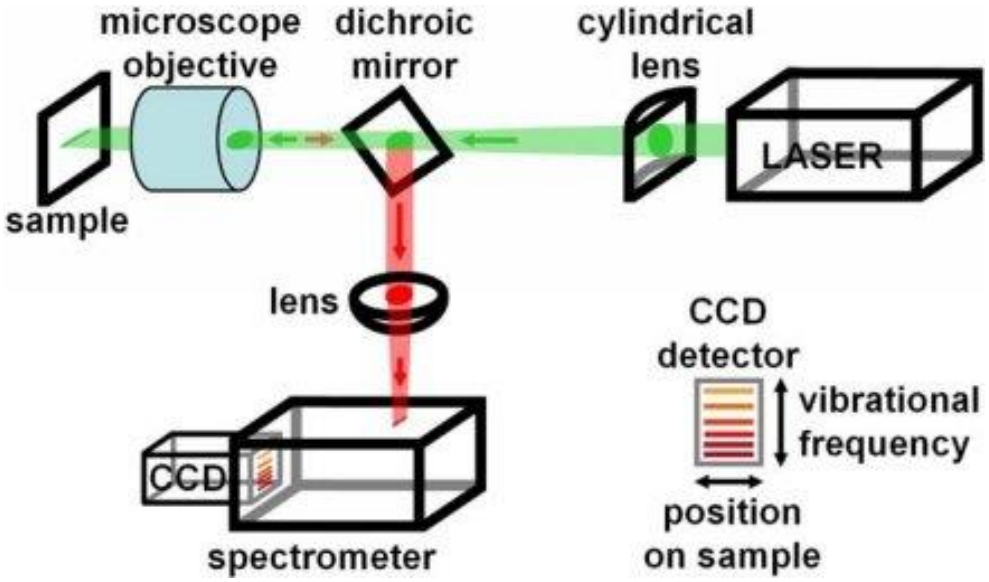

Fig 4: Block diagram of Raman Spectroscopy

7. Results and Discussions

7.1. Sample Preparation

Malic acid and aspartame is purchased from a local market. Then malic acid and aspartame are amalgamated in 40ml of distilled water in a definite ratio. Initially a specified amount of malic acid is allowed to dissolve in 40ml of water completely using a magnetic stirrer. Then powder aspartame is added to liquify with the solution. The resultant solution is subjected to determine ultrasonic velocity (u), Density (ρ) and viscosity (η). These are determined by using ultrasonic interferometer, specific gravity bottle and Ostwald viscometer.

7.2. Ultrasonic Investigation

Ultrasonic waves are one of the mechanical waves in which the frequency lies between 20 Hz and 20 KHz. It is a type of electromagnetic radiation. The medium's frequency and

temperature affect the ultrasonic waves' speed. A velocity of ultrasonic waves is determined using the ultrasonic interferometer as shown in Table 2.

Table 1. Ultrasonic velocity, density and viscosity

Mole fraction (xi)	Mole fraction of Malic acid (x2)	Ultrasonic velocity (m/s)	Density Kg/m3	Viscosity Nms-1×10^{-3}
0.01	0.99	1502	1007.6	0.912
0.02	0.98	1530.5	1015.3	0.98
0.04	0.96	1535.6	1017.6	0.99
0.05	0.95	1542.2	1018.4	0.992
0.06	0.94	1558.7	1025.3	0.1017

Table 2. Intermolecular free length, molar volume, free volume

Mole fraction (xi)	Mole fraction of Malic acid (x2)	Intermolecular free length (Lf) × 10-11 (m)	Molar volume m^3 mol^{-1}	Free volume m^3 mol^{-1}
0.01	0.99	4.1789	0.133	1.2508
0.02	0.98	4.0964	0.134	1.1127
0.04	0.96	4.0873	0.1347	1.1107
0.05	0.95	4.06378	0.1355	1.0937
0.06	0.94	4.0268	0.1361	1.0904

Table 3. Adiabatic compressibility and acoustic impedance

Mole fraction (xi)	Mole fraction of citric acid (x2)	Adiabatic compressibility (β) × 10^-10 m^2/N	Acoustic impedance(Z) × 106 kg/m^2s
0.01	0.99	4.3658	1.5249
0.02	0.98	4.1952	1.5532
0.04	0.96	4.1768	1.5574
0.05	0.95	4.1285	1.5705
0.06	0.94	4.0539	1.5825

Molecular interaction is a cohesive, adhesive, and repulsive interaction between two molecules or between two atoms, which are not bonded with each other. Ultrasonic velocity is calculated by utilising ultrasonic interferometer. Along the velocity of ultrasonic waves by using the values of density and viscosity various acoustical parameters. These values give data about molecular interaction between the malic acid and aspartame. Various acoustical

parameters such as intermolecular free length, free volume are tabulated in Table 3 and Table 4, internal pressure, relaxation time, Gibb's free energy and Rao's constant and the values are tabulated in Table 5.

Table 4. Internal pressure, relaxation time, Gibb's free energy, Rao's constant

Mole fraction (xi)	Mole fraction of Malic acid (x2)	Internal pressure Nm-2	Relaxation time	Gibb's free energy	Rao's constant
0.01	0.99	196.482	4.9887	8.4710	1.5448
0.02	0.98	196.128	5.416	8.4394	1.5375
0.04	0.96	195.311	5.4744	8.4687	1.5499
0.05	0.95	193.948	5.5489	8.4664	1.5568
0.06	0.94	188.323	5.8655	8.4804	1.5595

Table 5. Stability constant

Mole fraction (C)	**Mole fraction (C1)**	**U1**	**U2**	$\mathbf{K = \frac{U_1}{U_2}}$	**Stability constant (K)**
0.01	0.99	1535.26	1536.64	0.999102	0.000917
0.02	0.98	1308	1541.6	0.848469	0.194774
0.04	0.96	1475.2	1562.4	0.944188	0.065426
0.05	0.95	1309.8	1562.4	0.838326	0.227425
0.06	0.94	1131.3	1562.4	0.724078	0.48731

Excess parameter

Excess parameter is one of the key to study about the nature of molecular interaction between the solute and solvent. This can be done by finding the difference between acoustical parameters of experimental and ideal mixtures. It is formulated as

$$A^E = A_{mix}\left(\sum_{i=1}^{n} x_i A_i\right)$$

The values are tabulated in below. The maximum negative value in excess ultrasonic velocity U_E and excess adiabatic compressibility β_E indicates strong interaction between the molecules of mixtures.

Table 6. Excess parameter of ultrasonic velocity

X1 Moles of aspartame	$\mathbf{U_{mix}}$	$\mathbf{X_1U_1}$	$\mathbf{X_2U_2\times10^{+03}}$	$\mathbf{U_E\times10^{+02}}$
0.01	1502	2.24	1.51	-3.45

0.02	1530.5	2.07	1.52	-5.41
0.04	1535.6	2.54	1.49	2.36
0.05	1542.2	2.70	1.53	-1.84
0.06	1558.7	2.57	1.53	1.41

Table 7. Excess parameter of adiabatic compressibility

X1 Moles of aspartame	**$\beta_{mix} \times 10^{-08}$**	**$X_1\beta_1 \times 10^{-12}$**	**$X_2\beta_2 \times 10^{-10}$**	**$\beta_E \times 10^{-11}$**
0.01	4.3658	1.13	4.01	2.39
0.02	4.1952	6.18	4.08	5.12
0.04	4.1768	7.89	4.26	-1.63
0.05	4.1285	9.17	4.12	-9.28
0.06	4.0539	1.70	4.00	-1.19

A graph is plot between ultrasonic velocity and the moles of aspartame. It is observed that the ultrasonic velocity increases with the moles of aspartame. This indicates the melioration of interaction between solute and solvent. Adiabatic compressibility. It is found that the maximum ultrasonic velocity is obtained when the moles of aspartame is at 0.06. This shows that there is a strong interaction between solute and solvent. Adiabatic compressibility is a heat that is released due to the structural changes of interacting molecules that are present in the binary mixture. The maximum adiabatic compressibility is observed at 0.01 moles of aspartame. This proves that maximum heat is generated at 0.01 moles of aspartame. Intermolecular free length is a distance between the two neighbouring molecules. It is found to be decreases as the moles of aspartame increases. This indicates that the distance between two molecules decreases.

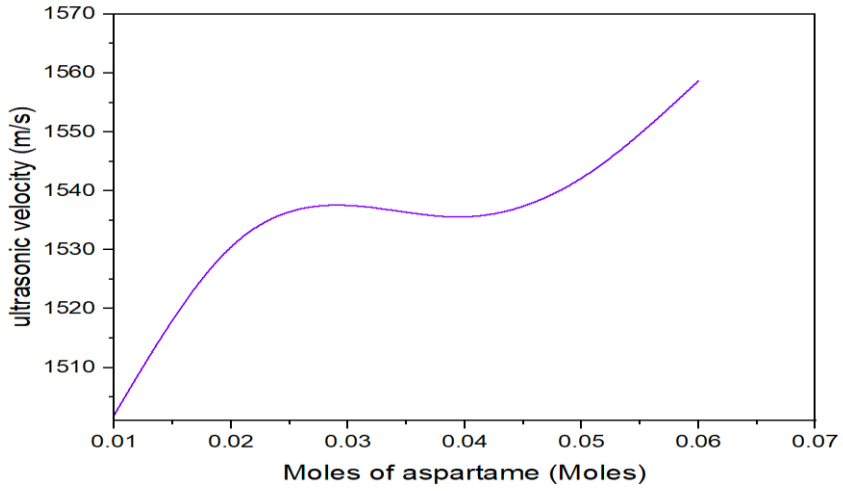

Fig 5: Graphical Representation of Moles of Aspartame Vs Ultrasonic Velocity

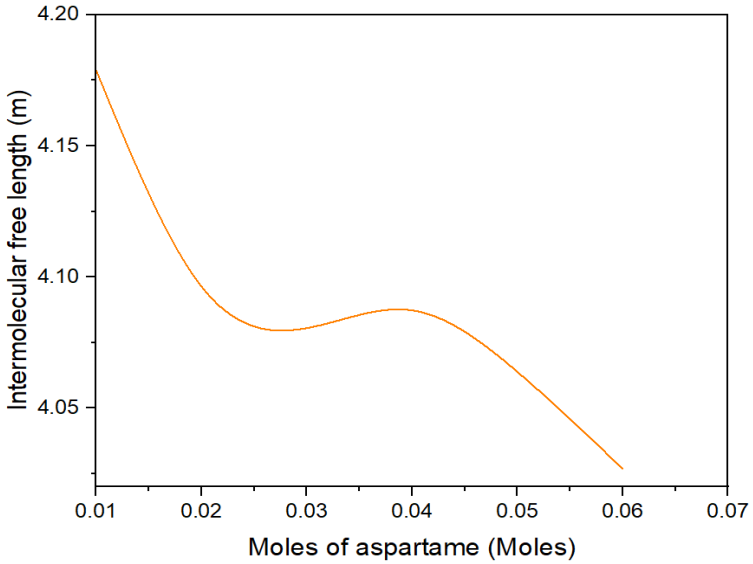

Fig 6: Graphical Representation of Moles of Aspartame vs Intermolecular Free Length

7.3. Spectroscopic Interpretation

FTIR is carried out at ATR mode to determine the functional group that are present in the binary mixture. Absorption spectra is procured and it is shown in figure. The absorption spectra at 2987cm^{-1} indicates the presence of OH functional group in stretching mode with compound class carboxylic acid. The isothiocyanate molecule must be present in group N=C=S with stretching, according to the spectra at 2025cm-1. Absorption spectra at 1077 stipulates the presence of functional group amine with C-N stretching

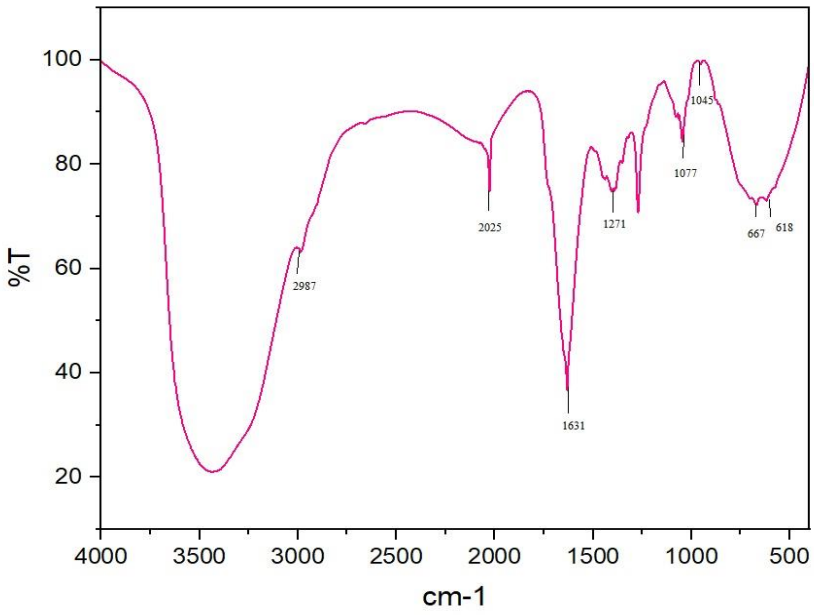

Fig 7: FTIR – ATR Spectra

Table 8. Functional group of FTIR

Region	Absorption	Appearance	Group	Compound class
Single bond	2987	strong, broad	O-H stretching	carboxylic acid
	2025	strong	N=C=S stretching	isothiocyanate
Double bond	1631	strong	C=O stretching	tertiary amide
Finger print	1271	strong	C-O stretching	alkyl aryl ether
	1077	medium	C-N stretching	amine
	1045	strong, broad	CO-O-CO stretching	anhydride
	667	strong	C=C bending	alkene
	618	strong	C-Br stretching	halo compound

Raman spectroscopy is one of the spectroscopic techniques, which interprets vibrational modes of the sample. Raman shift at 693 stipulate the presence of C-C aliphatic chain with the intensity moderate. The shift at 1005 confirms the presence of functional group toluene with the intensity of mono substituted aromatic ring. The shift that is absorbed at 1143 indicated the presence of 2,2,4- Trimethyl pentane (C_8H_{18}) with intensity of C-C skeletal stretch. Raman shift at 1178 proves the existence of Triethyl amine (C_2H_5)3N) with C-N stretch. The shift that is absorbed at 1593 indicates the strong amide in the binary mixture.

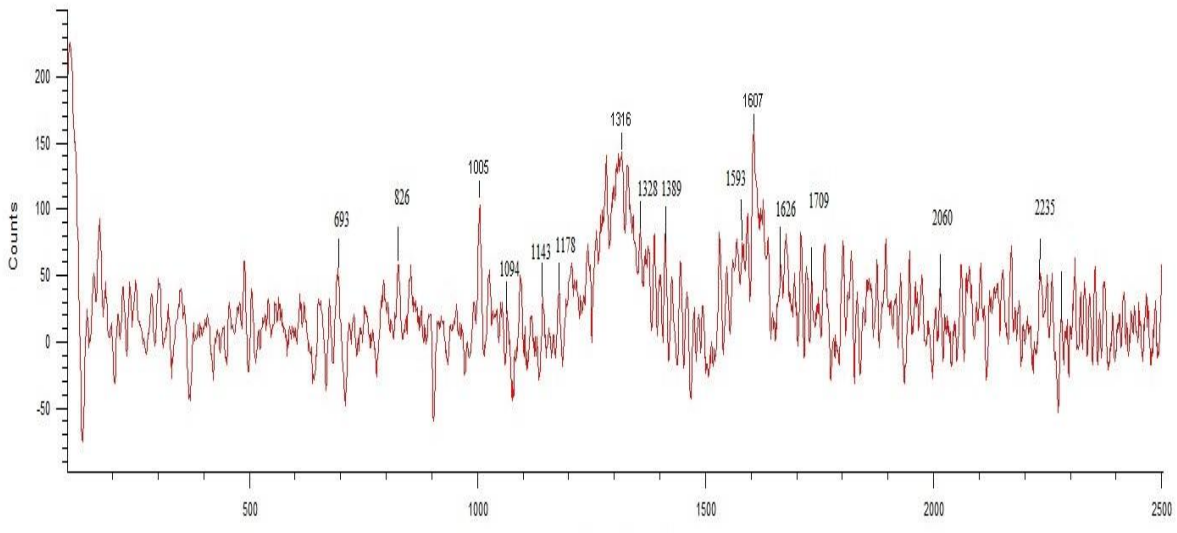

Fig 8: Raman Spectra

Table 9. Raman shift and functional group

Raman shift	Group	Intensity
693	C-C aliphatic chains	Moderate
826	Methyl $tert$-butyl ether (CH3)3COCH3	Symmetrical COC stretch
1005	Toluene (C7H8)	Mono substituted aromatic ring
1094	C=S	Strong
1143	2,2,4- Trimethyl pentane (C8H18)	C-C skeletal stretch
1178	Triethyl amine ((C2H5)3N)	C-N stretch
1317	Carboxylate salt	Moderate
1328	Nitro	Very strong
1389	Aromatic azo	Very strong
1593	Amide	Strong
1626	Carboxylic acid, Acetic acid (CH3COOH)	Dimer C=O stretch
1709	Ketone	Moderate
1762	Anhydride	Moderate
2060	Isothiocyanate	Moderate
2235	Alkyne (3-hexyne)	C≡C stretch
2250	Acetonitrile	C≡N stretch

8. Conclusion

The nature of molecular interaction between the artificial sweetener aspartame and edible acid malic acid has been studied. Various acoustical parameter has been found. From the data it is found that ultrasonic velocity increases with the moles of aspartame and it is tabulated in the table. This shows that there is a strong interaction between the molecules. And the adiabatic compressibility is found to be inversely proportional to moles of aspartame and its is shown in the from the values of stability constant it is found that the values increases with the moles of aspartame show that there is a complex interaction between the surface atoms. To confirm the stronger interaction more, excess values of adiabatic compressibility and intermolecular interaction has been calculated. The functional groups present in the mixture are determined using FTIR in ATR mode and Raman spectroscopy and the tabulated in the table. Thus there is a strong interaction between aspartame and malic acid.

References

[1] Uazman Alam, Omar Asghar, Shazli Azmi, Rayaz A. Malik. Chapter 15 - General aspects of diabetes mellitus, (2014).

[2] Nana Zhang, Xin Yang, Xiaolin Zhu, Bin Zhao, Tianyi Huang and Qiuhe Ji1. Type 2 diabetes mellitus unawareness, prevalence, trends and risk factors: National Health and Nutrition Examination Survey 2017, Vol. 45(2) 594–609.

[3] Michael Fang, Dan Wang, Josef Coresh, Elizabeth Selvin, Trends in Diabetes Treatment and Control in U.S. Adults, 1999–2018.

[4] Garcia-Molina, L., Lewis-Mikhael, AM., Riquelme-Gallego, B. et al. Improving type 2 diabetes mellitus glycaemic control through lifestyle modification implementing diet intervention: a systematic review and meta-analysis. Eur J Nutr 59, 1313–1328 (2020).

[5] Alam, S. Hasan, M.K. Neaz, S. Hussain, N. Hossain, M.F. Rahman, T. Diabetes Mellitus: Insights from Epidemiology, Biochemistry, Risk Factors, Diagnosis, Complications and Comprehensive Management. Diabetology 2021, 2, 36-50.

[6] Kamila Czarnecka, Aleksandra Pilarz, Aleksandra Rogut, Patryk Maj, Joanna Szymanska, Lukasz Olejnik, and Paweł Szymanski. Aspartame—True or False? Narrative Review of Safety Analysis of General Use in Products 2021, 13(6), 1957.

[7] Jennifer L. Kuk jennkuk, Ruth E. Brown. Aspartame intake is associated with greater glucose intolerance in individuals with obesity (2016).

[8] Bernadene A. Magnuson, Ashley Roberts, Earle R. Nestmann, Critical review of the current literature on the safety of sucralose, Food and Chemical Toxicology, Volume 106, (2017).

[9] Landrigan, P.J., Straif, K. Aspartame and cancer – new evidence for causation. Environ Health 20, 42 (2021).

[10] Marina Marinovich a, Corrado L. Galli a, Cristina Bosetti b, Silvano Gallus b, Carlo La Vecchia, Aspartame, low-calorie sweeteners and disease: Regulatory safety and epidemiological issues.

[11] Xiang Zou, Chi Cheng, Jun Feng, Xiaodan Song, Meng Lin, Shang-Tian Yang. (2019) Biosynthesis of polymalic acid in fermentation: advances and prospects for industrial application. Critical Reviews in Biotechnology 39:3, pages 408-421.

[12] Wu, N., Zhang, J., Chen, Y. et al. Recent advances in microbial production of L-malic acid. Appl Microbiol Biotechnol 106, 7973–7992 (2022).

[13] Aline Kovilein, Christin Kubisch, Liyin Cai, Katrin Ochsenreithe, Malic acid production from renewables: a review (2019).

[14] Abigail Raffner Basson, Alexander Rodriguez-Palacios and Fabio Cominelli, Artificial Sweeteners: History and New Concepts on Inflammation (2021).

[15] Satish Khatariya , Khyati Bhagdev , Chintan Tank , Fenil Navadiya , Jayna Gajera, A Review on Artificial Sweeteners: Chemistry, Synthesis and Uses, Volume 8, Issue 3 2021.

[16] Syeda sameena aziz , nikhat unnisa begum, zeenath unnisa begum, artificial sweeteners – a review, Volume 8, Issue 11 2020.

[17] Bernadene A. Magnuson a, Ashley Roberts b, Earle R. NestmannCritical review of the current literature on the safety of sucralose, Volume 106, 2017.

[18] Anushkkaran Periyasamy, Artificial Sweeteners, International Journal of Research & Review Vol. 6, Issue 1, 2019.