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Ultrasonic investigation on aqueous polysaccharide (starch) at 298.15 K



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Abstract The ultrasonic velocity, density and viscosity at 298.15 K have been measured in the binary system of starch in aqueous medium. The acoustical parameters such as adiabatic compressibility (β), free length (L_f), free volume (V_f), internal pressure (π_i), acoustical impedance (Z), relative association (R_A), Rao's constant (R), Wada's constant (W), classical absorption coefficients (α/f^2), relaxation time (τ) and relaxation strength (r) are calculated. The results are interpreted in terms of molecular interaction between the components of the mixtures.

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1. Introduction

Ultrasonic analysis of biological specimens began at the end of the First World War. There were substantial works on tissue studies in recent past, especially by Floyd Dunn (1976) and his group. Survey of literature (Pholman, 1939; Hueter, 1948) reveals that there have been five broad divisions of bio-acoustical studies of which the present work deals with the Characterization of the specimen using the sound velocity. The magnitude of density as well as the velocity of sound in human body fluids or constituents is of vital importance for carrying out acoustical analysis of human system or organs (Ludwig, 1950; Jasvir Singh and Bhatti, 1998; Singh and Behari, 1994;

Kirti Ghandhi Bhatia et al., 2002; Palaniappan and Velusamy, 2004) since sudden excess or reduction of velocity of the wave indicates some abnormality (Jerie et al., 2004; Panday et al., 2004). The Carbohydrate (starch) splitting enzymes must break down the linkages in order to form simple products (Carl et al., 1998), these are mostly α -amylases (or) by hydrolysis, found both in the salivary and in the pancreatic juice (Chakrabarthy et al., 1972). It is also activated by chloride with the help of Ca^{2+} ions. Another type of amylase recognized as β amylase, acts only at the terminal reducing end of a polyglucan chain found in plants. Animal amylases including those present in human tissues are α -amylases. They attack α -1, 4 linkages in a random manner anywhere along the polyglucan chain (Jain, 1998). But, this present work deals only with hydrolysis.

2. Sample preparation and experimental techniques

A 1–6% standard solution of amylase, in steps of 1% was prepared initially. All the solutions are left for 2 h and complete solubility is found (Walter Moore, 1962). The ultrasonic veloc-

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Nomenclature

kT	temperature dependent constant	β	adiabatic compressibility
k	temperature independent constant	L_f	free length
M_{eff}, M	effective molecular weight	V_f	free volume
x	mole fraction	π_i	internal pressure
i	component	T	temperature
m	molality	R	Universal gas constant
m	molecular weight	b	atomic scaling factor

ity (U) in the liquid mixtures have been measured using an Ultrasonic interferometer (Mittal type – 82, New Delhi, India) working at 2 MHz frequency with accuracy $\pm 0.1 \text{ ms}^{-1}$. The density (ρ) and viscosity (η) are measured using a Pycknometer and an Ostwald's viscometer of accuracy of $\pm 0.1 \text{ kg m}^{-3}$ and $\pm 0.001 \text{ mN s m}^{-2}$ respectively. Using the measured data, the acoustical parameters such as adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i), acoustical impedance (Z), relative association (R_A), Rao's constant (R), Wada's constant (W), classical absorption coefficients (α/f^2), relaxation time (τ) and relaxation strength (r) have been calculated using the following expressions (1)–(11).

$$\beta = 1/U^2 \rho \quad (1)$$

$$L_f = kT(\beta)^{1/2} \quad (2)$$

$$V_f = (M_{eff}U/\eta k)^{3/2} \quad (3)$$

$$\pi_i = bRT(k\eta/U)^{1/2}/(\rho^{2/3}/M^{7/6}) \quad (4)$$

where b is the atomic cubic factor = 2.

$$Z = U_\rho \quad (5)$$

$$R_A = \rho/\rho_0(U_0/U)^{1/3} \quad (6)$$

$$R = U^{1/3} V \quad (7)$$

$$W = \beta^{1/7} V \quad (8)$$

$$(\alpha/f^2) = (8\pi^2\eta/3\rho U^3) \quad (9)$$

$$\tau = (4\eta s/3\rho U^2) \quad (10)$$

and

$$r = 1 - (U/U_\alpha)^2 \quad (11)$$

where $U_\alpha = 1600 \text{ ms}^{-1}$.

The starch, supplied by S.D. fine Chem. has been taken in the forms of solutions. Double distilled water is used throughout the work.

3. Results and discussion

Table 1 lists the measured values of various percentages (1–6%) of starch solution having the same clusters of maltose and glucose molecules. As the molecular weight of these polysaccharides are in order of lakhs of units (1,000,00) and their solubility in water is relatively very low (Jain, 1998), percentage composition is preferred along with the procedure given in standard preparation techniques of starch solution (Kim et al., 2001).

The perusal of **Table 1** clearly shows that all the measured parameters, sound velocity (U), density (ρ) and viscosity (η) increases with increase in % of starch. The increase in starch molecules makes the medium to be denser. This leads to less compressibility and hence sound velocity also increases. Further, the increase in the number of particles simply increases the cohesion between the layers of the medium and so the co-efficient of viscosity increases. Thus, the existence of particle-particle interaction is suspected and this observation is further supported by the non-linear increase in the trend of the measured parameters.

A clear look at the **Table 1** suggests that the range of sound velocity variation with percentage composition is almost same for all percentages of starch. Considering the density variation, for a given % composition, the maximum densities are recorded for 6% and lower for 1%. The same trend is obtained for viscosity variation and seems this is to be % dependent of the solute.

All these structural variations are reflected in the observed trend. From the same **Table 1**, the co-efficient of viscosity of the liquid is one of the peculiar properties that determine the inner nature of the medium. Starch has a higher viscosity at higher concentration, i.e., the molecules of starch have a highly cohesive nature.

As regards the surface area of the starch the number of glucose units is large, it may lead to a notion that the effective

Table 1 Measured values of ultrasonic velocity (U), density (ρ) and viscosity (η), some calculated values of adiabatic compressibility (β), free length (L_f), free volume (V_f), internal pressure (π_i), for various percentages (%) of starch in water at 298.15 K.

%	U (m s ⁻¹)	ρ (kg m ⁻³)	$\eta \times 10^3$ N s m ⁻²	$\beta \times 10^{10}$ N ⁻¹ m ²	$L_f \times 10^{11}$ m	$V_f \times 10^8$ m ³ mol ⁻¹	$\pi_i \times 10^{-9}$ N m ⁻²
1	1517.8	1001.3	0.981	4.335	4.154	1.685	2.798
2	1521.2	1006.8	1.000	4.292	4.134	1.666	2.800
3	1524.3	1012.3	1.026	4.252	4.114	1.632	2.812
4	1528.7	1018.2	1.051	4.202	4.090	1.604	2.821
5	1531.2	1021.8	1.870	4.174	4.077	0.688	3.726
6	1533.7	1027.5	2.550	4.137	4.058	0.439	4.316

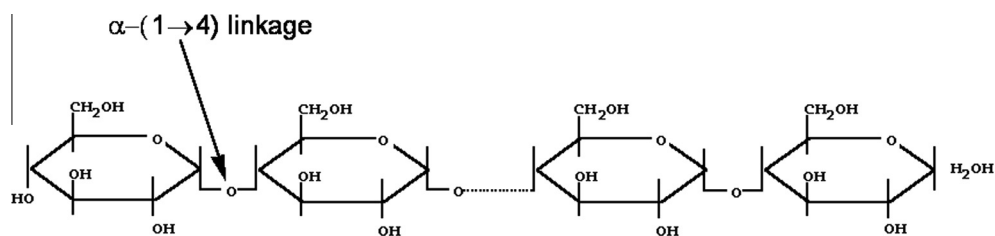


Figure 1 Structure of amylose.

surface area of starch molecules. However, it is to be noted that, starch has both straight chain (Fig. 1) [amylose] and branched chain (Fig. 2) [amylopectin] component (Satyanarayana, 2000). The straight chain components relatively occupy a very low area than the branched chain and hence, it should be noted that the effective surface area per molecule of starch is higher for amylose than amylopectin. These are reflected in the viscosity variations and observed more time of flow for starch. However, as percentage increases, the number of molecules increases and so the viscosity gradually shifts to maximum limit with percentage of starch. Furthermore, the indication of inter particle and intraparticle cohesion is suspected in starch.

To search the nature and type of existing interactions some thermoacoustical parameters have been determined and their trends are analysed in the light of existing structural variations. The derived values of the chosen thermoacoustical properties are presented in Table 2. Referring to the Table 2, it is observed that the adiabatic compressibility in general decreases with increasing percentage for all solutes.

The intermolecular free length (L_f) is another important factor in determining the existence of interactions among the components of the solution. On analysing the above referred Table 2, it is noticed that the free length reflects the similar trend as that of adiabatic compressibility (Nithiyantham and Palaniappan, 2005, 2006).

In each of the solutions, the medium is having only one solute, whose structure depends on the number of basic molecules (glucose). The basic molecule is always bonded with the neighbour by oxygen. As the percentage of starch increases, the β and L_f values are in decreasing trend indicating the medium is getting denser. This may be taken as the splitting of starch into maltose (Fig. 3) and glucose (Fig. 4).

The perusal of the respective Table 2 also reveals that the V_f values are maximum for lower percentage of starch, the inter-

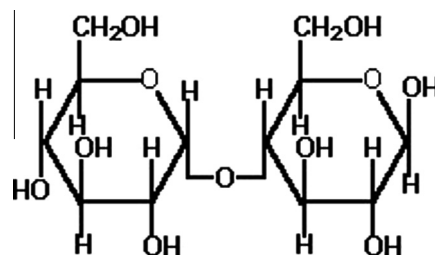


Figure 3 Structure of maltose.

nal pressure exhibits a reverse trend to that of V_f at all given percentages of solutes. This strongly resuggests the previous view that cohesion is unconsiderably maximum for higher percentage of starch, i.e., it implies that the available volume is very low and hence higher numbers of constituents are presented in 5% and 6% and so internal pressure between the particles existing in the solution is higher in this % region.

Starch has large number of free hydrated hydroxyl groups and so their presence in aqueous solutions is supposed not to disturb much of their internal arrangements. Even though solute-solvent interactions are there, it will not disturb the internal symmetry, as the interaction simply replaces one atom by another exactly of same type and nature, large solute-solute interaction arises that predominates the solute-solvent interactions. The structural variations and the rearrangements within the molecule along with the active group participation form the major contribution for the observed trend (Nithiyantham and Palaniappan, 2005, 2006).

The observed trend of Z and R_A for starch increases with increase in percentage. The values of Z and R_A are higher for higher percentage of starch. This indicates that the solute-solute interaction and chances of complexation are en-

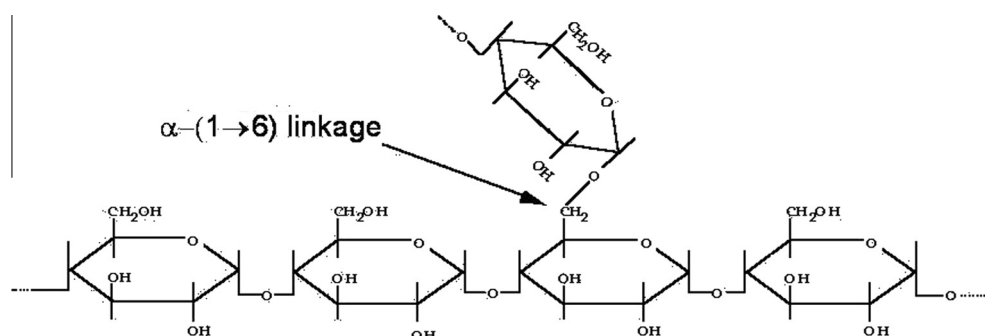


Figure 2 Structure of amylopectin.

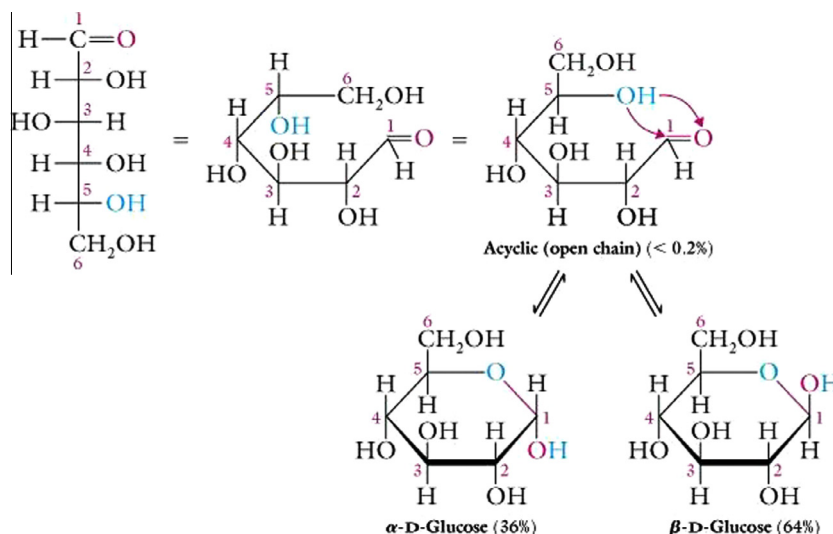


Figure 4 Structure of glucose (in aqueous medium).

Table 2 Some more calculated parameters such as acoustical impedance (Z), relative association (R_A), Rao's constant (R), Wada's constant (W), relaxation amplitude (α/f^2), relaxation time (τ) and relaxation strength (r) for various percentages (%) of starch in water at 298 K.

%	$Z \times 10^{-6} \text{ kg m}^{-2} \text{ s}^{-1}$	R_A	$R \times 10^4 \text{ m}^{10/3} \text{ s}^{-1/3} \text{ mol}^{-1}$	$W \times 10^4 \text{ m}^3 \text{ mol}^{-1} (\text{N/m}^2)^{1/7}$	$(\alpha/f^2) \times 10^{-14} (\text{s}^2/\text{m})$	$\tau \times 10^{-13} \text{ s}$	r
1	1.520	0.9997	2.0865	3.9499	1.1182	5.5908	0.1001
2	1.531	1.0044	2.0973	3.9730	1.1285	5.6426	0.0961
3	1.543	1.0091	2.1078	3.9957	1.1469	5.7345	0.0924
4	1.557	1.0141	2.1179	4.0175	1.1613	5.8066	0.0871
5	1.564	1.0171	2.1320	4.0460	2.0523	1.0261	0.0842
6	1.576	1.0222	2.1414	4.0668	2.774	1.3870	0.0812

hanced with percentage of solutes. Thus, starch exhibits higher interaction due to solute–solute interaction.

From the same Table 2, referring the values of R and W , are in increasing trend with percentage of starch. This indicates that the magnitude of interactions is increased. This indicates the availability of more number of components in a given region and hence leads to a close packing of the medium, thereby increases the interaction between the components (Nithiyantham and Palaniappan, 2005, 2006; Nithiyantham, 2006).

From the same Table 2, the values observed decrease in r and L_r and increase of Z with the concentration of pectin suggest presence of solvent–solute interactions in the mixtures (Shipra baluja and Swati Oza, 2003). In more concentrated solutions direct segment–segment interaction will exist. The interaction giving rise to association between the two types of molecules pectin and water may responsible for the increase in ultrasonic velocity, absorption coefficient and relaxation time (Kalyanansundaram et al., 1997).

4. Conclusions

1. Cohesion plays a key role in deciding the nature and strength of interaction.

2. Solute–solute as well as solute–solvent interactions are existing solutions.
3. Presence of hydrated hydroxyl group has some effect in solute–solvent interaction in starch.

References

- Carl, A.Burtis, Edward, R., Ashwood, 1998. TIETZ, Text book of Clinical Chemistry. Indira Printers, New Delhi, India.
- Chakrabarthi, B.K., Ghosh, H.N., Sahana, S., 1972. Modern Human Physiology, 1st ed. The New Book Stall, Calcutta (India).
- Dunn, F., 1976. Ultrasonic Biophysics (Downden, Hutchinson & Ross Inc.) Stroudsburg Pennsyloanic, USA, Bench Mark Papers in Acoustics, Ser.7.
- Hueter, T.F., 1948. Nature 35, 285.
- Jain, J.L., 1998. Fundamental of Biochemistry. S. Chand & Company, New Delhi, India.
- Jasvir Singh, S., Bhatti, S., 1998. Ind. J. Pure Appl. Phys. 36, 43.
- Jerie, K., Baranowski, A., Przybylski, J., Gliniski, J., 2004. J. Mol. Liqds. 111, 25.
- Kalyanansundaram, S., Natarajan, S., Manuel Stephen, B., 1997. Acta Acoustica 83, 74.
- Kim, O.K., Voit, W., Zapka, W., Bjelke, B., Muhammed, M., Rao, K.V., 2001. Mat. Res. Soc. Symp. Proc. 676, 8321.
- Kirti Ghandhi Bhatia, V.R., Singh, M.C., Bansal, Sanjiv Bhatia, 2002. Ind. J. Pure Appl. Phys. 40, 515.

- Ludwig, G.D., 1950. *J. Acoust. Soc. Am.* 22, 862.
- Nithiyantham, S., Palaniappan, L., 2005. *Acta Cienc. Indica* 31, 533.
- Nithiyantham, S., Palaniappan, L., 2006. *Acta Cienc. Indica* 37, 392.
- Nithiyantham, S. 2006. PhD thesis, Annamalai University, Tamil nadu 608 002, India.
- Pholman, R., 1939. *Physics*, Z 40, 160.
- Palaniappan, L., Velusamy, V., 2004. *Ind. J. Pure Appl. Phys.* 42, 591.
- Panday, J.D., Rajan, Dev, Bhatt, Bishan Datt, 2004. *J. Mol. Liqds* 111, 67.
- Satyanarayana, U., 2000. *Biochemistry*, 6th ed. Book and Allied, Calcutta, India.
- Shipra Baluja, Swati Oza, 2003. *Flu Phase Equilibria* 208, 83.
- Singh, A.K., Behari, J., 1994. *Ind. J. Pure Appl. Phys.* 32, 528.
- Walter Moore, J., 1962. *Physical Chemistry*, 4th ed. Longmans Greens and Co Lts., London.