# NOTE

# Some Physicochemical Measurements of Chitosan Polymer in Acetic Acid–Water Mixtures at Different Temperatures

**Mahaveer D. Kurkuri,[1] Anandrao R. Kulkarni,[2] Tejraj M. Aminabhavi[1]**

[1]*Center of Excellence in Polymer Science, Karnatak University, Dharwad 580 003, India*
[2]*KLE's College of Pharmacy, Vidyanagar, Hubli 580 031, India*

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## INTRODUCTION

Chitin, a naturally occurring polymer, is the second most abundant organic resource on the earth next to cellulose.[1] It is an exoskeleton of crustaceans, cuticle of insects, and cell wall of fungi. Because of its biodegradability, it is frequently used as a membrane material to develop drug-loaded controlled-release formulations[2] as well as a membrane in the pervaporation separation of water–acetic acid mixtures.[3] Deacetylation of chitin yields chitosan, which is relatively reactive. It is important to know its physicochemical properties at lower concentrations of acetic acid in aqueous media because the degree of acetylation of chitosan varies depending on the number of acetyl groups present. This need prompted us to measure density, $\rho$, viscosity, $\eta$, refractive index for the sodium–D line, $n_D$, and speed of sound, $\mu$, in 0.05 to 0.20 mass % of chitosan in acetic acid–water mixtures ranging in mole fraction from 1.6 to $9.4 \times 10^{-3}$. At higher amounts of acetic acid, chitosan is insoluble, making the measurements difficult. Therefore, the properties have been measured in aqueous acetic acid mixtures at lower concentration of acetic acid. To the best of our knowledge, no such data on chitosan are available in the literature.

## EXPERIMENTAL

### Materials and methods

Medium molecular weight chitosan [product batch #9012-76-4] with 75–85 % deacetylated chitosan was purchased from Aldrich, Milwaukee, WI. Acetic acid [product batch #S-0994-494-138931] was purchased from s.d. fine Chemicals Ltd., Mumbai, India. The acetic acid purity, as assayed by gas chromatography, was 99.7 mol %, and its density was 1.0490 $g/cm^3$ at 293.15 K. Double-distilled deionized water was used throughout the research.

Acetic acid–water mixtures were prepared by mass within an uncertainty of $\pm$0.01 mg using an electronic single pan Mettler balance (AE 240, Switzerland). Four chitosan concentrations, expressed in 0.05, 0.10, 0.15, and 0.20 mass % units, were prepared in different compositions of acetic acid–water mixtures. The reproducibility in mole fraction of acetic acid–water mixtures was within $\pm$ 0.0002 units.

Solution densities were measured within an uncertainty of $\pm 0.0005\ g \cdot cm^{-3}$ with a pycnometer having a bulb volume of 10 $cm^3$ and a capillary bore with an internal diameter of 1 mm. Speeds of sound values were measured within an uncertainty of $\pm 2\ m \cdot s^{-1}$ with a variable path single crystal interferometer (Mittal Enterprises, Model M-84, New Delhi). The data were collected at a frequency of 1 MHz, and the instrument was calibrated with water and benzene.[4,5]

Refractive indices for the sodium D-line were measured to an uncertainty of $\pm$0.0001 units with a thermostatically controlled Abbe Refractometer (Atago 3T, made in Japan). The calibration procedure of the refractometer is the same as given earlier.[6]

The molecular mass of chitosan was calculated by measuring the viscosity (uncertainty, $\pm 0.001\ mPa \cdot s$) of 0.05, 0.10, 0.15, and 0.20 mass % solutions of chitosan in 2% aqueous acetic acid at 303.15 K with the Scott Gerate viscometer (AVS 320, Germany) as per the detailed procedure published earlier.[7] The intrinsic viscosity ($\eta$) was calculated from the reduced viscosity versus concentration plot shown in Figure 1. Then, by using the Mark–Houwink–Sakurada

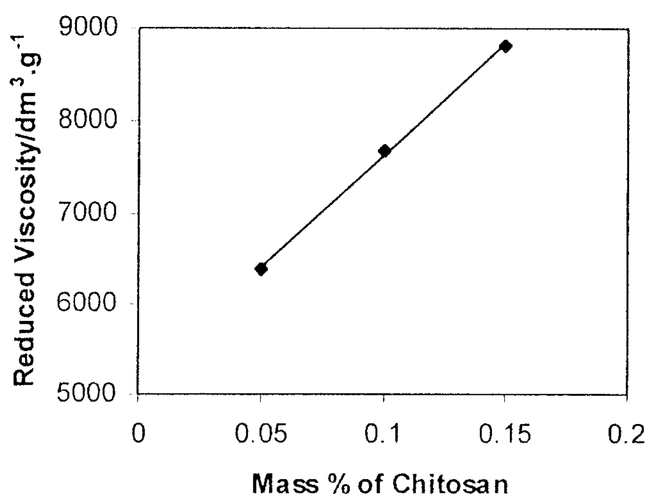


**Figure 1** Reduced viscosity versus concentration of chitosan in acetic acid at 303.15 K.

*Correspondence to:* T.M. Aminabhavi (rrist@bgl.vsnl.net.in; cc to aminabhavi@yahoo.com).

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**TABLE I**
**Experimental Values of Density, $\rho$, Refractive Index, $n_D$, Viscosity, $\eta$, and Speed of Sound, $u$, of Different Mass % Chitosan Solutions in Acetic Acid (1) + Water (2) Mixtures at Different Temperatures**

| Amount of Chitosan in acetic acid–water solution, mass % | Temperature, K | $x_1 10^3$ | $\rho$ (g · cm$^{-3}$) | $n_D$ | $\eta$ (mPa · s) | $u$(m · s$^{-1}$) |
|---|---|---|---|---|---|---|
| 0.05 | 298.15 | 1.6 | 1.0629 | 1.3330 | 4.731 | 1504 |
| | | 3.2 | 1.0638 | 1.3334 | 4.262 | 1506 |
| | | 4.8 | 1.0644 | 1.3338 | 3.716 | 1508 |
| | | 6.4 | 1.0654 | 1.3342 | 3.647 | 1509 |
| | | 7.9 | 1.0663 | 1.3346 | 3.468 | 1511 |
| | | 9.4 | 1.0668 | 1.3352 | 3.269 | 1514 |
| 0.05 | 303.15 | 1.6 | 1.0609 | 1.3328 | 4.191 | |
| | | 3.2 | 1.0619 | 1.3330 | 3.811 | |
| | | 4.8 | 1.0624 | 1.3334 | 3.319 | |
| | | 6.4 | 1.0631 | 1.3338 | 3.264 | |
| | | 7.9 | 1.0640 | 1.3340 | 3.090 | |
| | | 9.4 | 1.0647 | 1.3344 | 2.921 | |
| 0.05 | 308.15 | 1.6 | 1.0595 | 1.3326 | 3.684 | |
| | | 3.2 | 1.0601 | 1.3328 | 3.354 | |
| | | 4.8 | 1.0606 | 1.3330 | 2.974 | |
| | | 6.4 | 1.0612 | 1.3332 | 2.921 | |
| | | 7.9 | 1.0617 | 1.3334 | 2.766 | |
| | | 9.4 | 1.0625 | 1.3336 | 2.613 | |
| 0.1 | 298.15 | 1.6 | 1.0635 | 1.3333 | 9.816 | 1505 |
| | | 3.2 | 1.0642 | 1.3337 | 9.130 | 1507 |
| | | 4.8 | 1.0648 | 1.3340 | 8.650 | 1509 |
| | | 6.4 | 1.0656 | 1.3344 | 7.834 | 1510 |
| | | 7.9 | 1.0664 | 1.3349 | 7.695 | 1512 |
| | | 9.4 | 1.0673 | 1.3354 | 7.222 | 1515 |
| 0.1 | 303.15 | 1.6 | 1.0617 | 1.3330 | 8.536 | |
| | | 3.2 | 1.0624 | 1.3332 | 7.946 | |
| | | 4.8 | 1.0628 | 1.3336 | 7.537 | |
| | | 6.4 | 1.0634 | 1.3340 | 6.797 | |
| | | 7.9 | 1.0643 | 1.3342 | 6.764 | |
| | | 9.4 | 1.0650 | 1.3346 | 6.218 | |
| 0.1 | 308.15 | 1.6 | 1.0599 | 1.3328 | 7.396 | |
| | | 3.2 | 1.0604 | 1.3330 | 6.958 | |
| | | 4.8 | 1.0610 | 1.3332 | 6.613 | |
| | | 6.4 | 1.0617 | 1.3334 | 6.063 | |
| | | 7.9 | 1.0622 | 1.3336 | 6.047 | |
| | | 9.4 | 1.0628 | 1.3338 | 5.540 | |
| 0.15 | 298.15 | 1.6 | 1.0640 | 1.3336 | 14.100 | 1506 |
| | | 3.2 | 1.0645 | 1.3339 | 13.250 | 1508 |
| | | 4.8 | 1.0651 | 1.3344 | 13.152 | 1510 |
| | | 6.4 | 1.0659 | 1.3347 | 12.862 | 1512 |
| | | 7.9 | 1.0668 | 1.3352 | 12.272 | 1513 |
| | | 9.4 | 1.0677 | 1.3356 | 12.161 | 1516 |
| 0.15 | 303.15 | 1.6 | 1.0622 | 1.3332 | 12.248 | |
| | | 3.2 | 1.0628 | 1.3334 | 11.518 | |
| | | 4.8 | 1.0633 | 1.3338 | 11.236 | |
| | | 6.4 | 1.0640 | 1.3342 | 11.084 | |
| | | 7.9 | 1.0647 | 1.3345 | 10.825 | |
| | | 9.4 | 1.0653 | 1.3348 | 10.552 | |
| 0.15 | 308.15 | 1.6 | 1.0603 | 1.3330 | 10.782 | |
| | | 3.2 | 1.0608 | 1.3332 | 9.999 | |
| | | 4.8 | 1.0613 | 1.3334 | 9.938 | |
| | | 6.4 | 1.0621 | 1.3336 | 9.667 | |
| | | 7.9 | 1.0628 | 1.3340 | 9.291 | |
| | | 9.4 | 1.0632 | 1.3342 | 9.232 | |
| 0.2 | 298.15 | 1.6 | 1.0643 | 1.3339 | 20.317 | 1507 |
| | | 3.2 | 1.0648 | 1.3342 | 19.760 | 1508 |
| | | 4.8 | 1.0654 | 1.3346 | 18.446 | 1511 |
| | | 6.4 | 1.0662 | 1.3349 | 17.850 | 1513 |
| | | 7.9 | 1.0670 | 1.3354 | 17.715 | 1515 |
| | | 9.4 | 1.0679 | 1.3358 | 17.190 | 1517 |
| 0.2 | 303.15 | 1.6 | 1.0628 | 1.3334 | 17.483 | |
| | | 3.2 | 1.0633 | 1.3336 | 16.963 | |
| | | 4.8 | 1.0637 | 1.3340 | 15.905 | |
| | | 6.4 | 1.0643 | 1.3344 | 15.524 | |
| | | 7.9 | 1.0648 | 1.3348 | 15.064 | |
| | | 9.4 | 1.0657 | 1.3350 | 14.978 | |
| 0.2 | 308.15 | 1.6 | 1.0607 | 1.3332 | 15.257 | |
| | | 3.2 | 1.0611 | 1.3334 | 14.689 | |
| | | 4.8 | 1.0617 | 1.3336 | 13.959 | |
| | | 6.4 | 1.0623 | 1.3338 | 13.416 | |
| | | 7.9 | 1.0630 | 1.3342 | 13.223 | |
| | | 9.4 | 1.0636 | 1.3346 | 13.149 | |

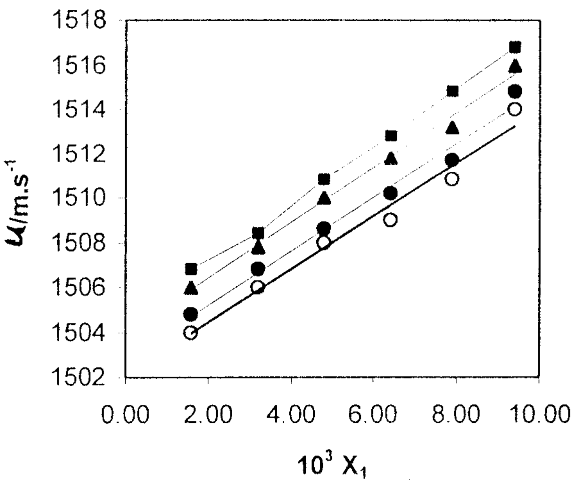


**Figure 2** Speed of sound versus mole fraction of acetic acid for (○) 0.05 mass %, (●) 0.1 mass %, (▲) 0.15 mass %, and (■) 0.2 mass % solutions of chitosan in acetic acid + water mixtures at 298.15 K.

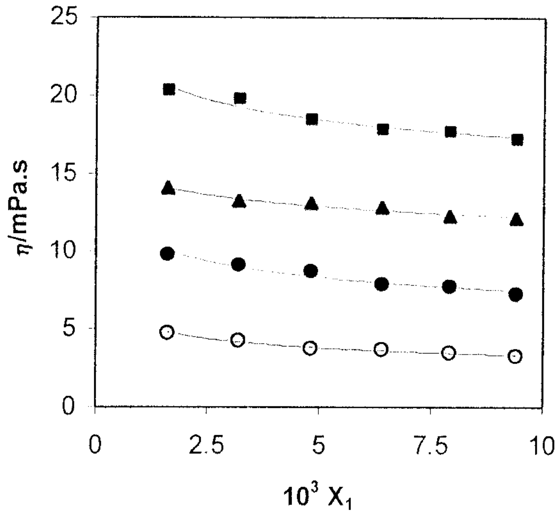


**Figure 4** Viscosity versus mole fraction of acetic acid for (○) 0.05 mass %, (●) 0.1 mass %, (▲) 0.15 mass %, and (■) 0.2 mass % solutions of chitosan in acetic acid + water mixtures at 298.15 K.

(MHS) equation with the MHS constants[8] $k = 1.81 \times 10^{-3}$ and $a = 0.93$, the viscosity average molecular mass of chitosan polymer was calculated as

$$[\eta] = k\overline{M_\eta^a} \quad (1)$$

The molecular mass thus obtained was 8,762,148 Daltons.

In all property measurements, an INSREF, model 016 AP, thermostat was used to control the temperature within an uncertainty of ±0.01 K as seen by a digital temperature display. The results of $\rho$, $\eta$, $n_D$, and $\mu$ presented in Table I are the averages of three independent measurements (< 2–3% uncertainty within each measurement in all the cases) for each mixture composition and temperature.

## RESULTS AND DISCUSSION

The dependence of speed of sound on mole fraction of acetic acid at 298.15 K for different chitosan solutions is shown in Figure 2. The speed of sound values increase linearly with increasing concentration of acetic acid in the mixture. With increasing concentration of chitosan, speed of sound also increases. Speed of sound data at higher temperatures (i.e., at 303.15 and 308.15 K) did not show much variations and hence, we did not attempt to measure these data.

The density versus mole fraction plots at 298.15 K, presented in Figure 3, show a linear increase in density with increasing composition of acetic acid in the mixture. Because an almost similar dependency of $\rho$ on $x_1$ is observed at

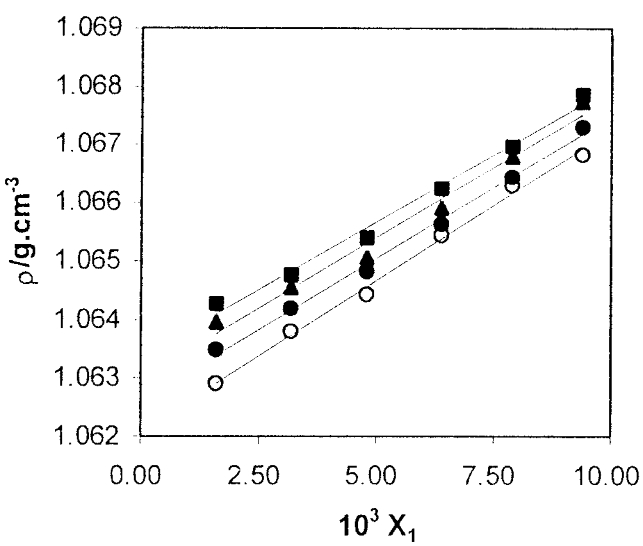


**Figure 3** Density versus mole fraction of acetic acid for (○) 0.05 mass %, (●) 0.1 mass %, (▲) 0.15 mass %, and (■) 0.2 mass % solutions of chitosan in acetic acid + water mixtures at 298.15 K.

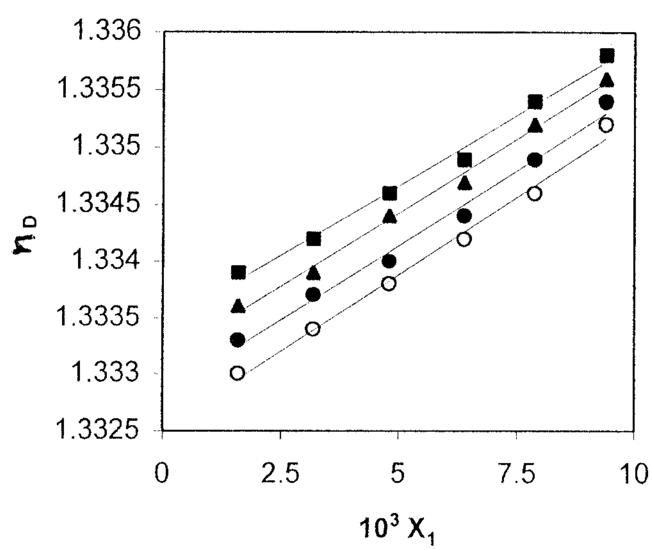


**Figure 5** Refractive index versus mole fraction of acetic acid for (○) 0.05 mass %, (●) 0.1 mass %, (▲) 0.15 mass %, (■) 0.2 mass % solutions of chitosan in acetic acid + water mixtures at 298.15 K.

303.15 and 308.15 K, we have presented the data only at 298.15 K.

Viscosity versus mole fraction plots at 298.15 K, presented in Figure 4, also show an increase with increasing concentration of chitosan. However, as expected, a decrease in solution viscosity with increasing temperature is observed. Viscosity values decrease slightly with increasing concentration of acetic acid in the binary mixture.

The refractive index versus mole fraction plots at 298.15 K, shown in Figure 5, also increase linearly with increasing amount of acetic acid in water. The refractive index values decrease slightly with increasing temperature. To avoid redundancy, the plots at higher temperatures are not presented.

In conclusion, the results of this study may have importance in industrial areas where chitosan is used as a membrane in pervaporative separation of water–acetic acid mixtures. These studies are presently under investigation in our laboratory.

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