

Thermo acoustic analysis to study the effect of sunlight on disodium hydrogen citrate

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ABSTRACT

A new thermo acoustic analysis has been used to detect the photochemical reactions in disodium hydrogen citrate, a drug designed to aid in maintaining physiological alkalinity of the blood and urine and to use for peritoneal dialysis. Certain direct and derived acoustic parameters of pure medicine and that exposed to solar radiations have been determined as a function of temperature. Plots of these parameters versus temperature have been made. The nature of variation and the relative shift in the curves for the exposed samples compared with the unexposed ones have been used to study photo-chemical reactions. The results have been explained in the light of existing theories and confirmed using UV absorption spectra of the samples.

Keywords : Thermo-acoustic analysis, non-destructive method, photochemical reaction, disodium hydrogen citrate.

INTRODUCTION

Liquid medicines are usually kept in amber coloured bottles to protect from solar radiations. Direction may be given not to expose the medicine in direct sunlight in order to avoid photochemical reactions. However the UV A (320-400nm) and UV B (290-320nm) radiations from the sun may penetrate into the human body and may cause photo-chemical reactions on the medicine present in the blood circulation¹. So a knowledge of possible reaction of the sunlight on a medicine is helpful in taking necessary precautions during the usage of it. In the present work, thermo-acoustic analysis, a simple and non destructive method compared with expensive and time consuming methods such as chromatographic, spectroscopic and enzymatic techniques, is done to study the photo-degradation of a medicine, disodium hydrogen citrate Fig. 1, commonly used for maintaining physiological alkalinity of the blood and urine and for peritoneal dialysis.

In thermo-acoustic analysis, the acoustical parameters of a liquid are plotted as a function of temperature. A pure liquid (single component or multi component) has a characteristic curve depending on the chemical combination of it. Any deviation from this may be taken as an indication of change in chemical combination due to reaction induced by external agencies. This is the basic principle used in thermo-acoustic analysis. This method has been used successfully to distinguish between fructose and glucose (isomers having the same chemical composition), to detect and quantify the amount of fructose in coconut water² and to detect the adulteration of milk³.

Sunlight is the most universal source of photochemical reactions especially in living organisms and in medicines. But sunlight is not available continuously and the spectral distribution and intensity vary from place to place and time to time. Therefore artificial sources are preferred⁴. Since we are interested only in the effect of solar

radiation on the photochemical changes of the medicine, we used sunlight as the source of photochemical reactions.

MATERIAL AND EXPERIMENTAL METHOD

Three samples were selected for the experiment. Sample A is the pure medicine manufactured by Pfizer Ltd., Mumbai, India. Sample B was prepared by exposing the pure medicine to scattered sunlight entering through the open window of the laboratory for 15 minutes from 12 noon to 12.15 pm on a sunny day. Sample C was prepared simultaneously by exposing the pure medicine to the direct sunlight outside the laboratory on the same day for the same duration. The experiments were carried out immediately after preparing the samples. The density (ρ) and ultrasonic velocity (U) were determined at five different temperatures 298.15, 303.15, 308.15, 313.15 and 318.15 K. The temperature was kept constant using a thermostatically controlled water circulating arrangement with an accuracy of ± 0.1 K. Density measurements were performed using a 12 cm³ double stem pycnometer. Masses were measured using a single pan electronic balance with an accuracy of ± 0.1 mg. Ultrasonic velocities were determined by a single crystal ultrasonic interferometer (Mittal enterprises model No.F81) at a constant frequency of 2 MHz with an accuracy of ± 0.1 m/s. the derived acoustic parameters viz. Rao's specific sound velocity (r), Adiabatic compressibility (β_s) and Specific acoustic impedance (Z_A) were calculated using equations $r = U^{1/3}/\rho$, $\beta_s = 1/U^2\rho$, $Z_A = Ur$

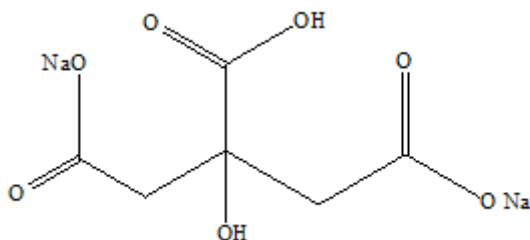


Fig. 1. Disodium hydrogen citrate

The units for r , β_s and Z_A are $\text{Kg}^{-1} \text{m}^{10/3} \text{s}^{-1/3}$, $\text{Kg}^{-1} \text{m} \text{s}^2$ and $\text{Kg} \text{m}^{-2} \text{s}^{-1}$ respectively. The UV absorption spectra of the samples A, B, and C were taken using a computerized UV-Visible spectrophotometer (UV win Lab, Lambda 25 UV/Vis, Perkin-Elmer Ltd, USA).

RESULTS AND DISCUSSION

UV absorption spectra of the above samples are shown in Fig. 2. Graphs plotted with U , ρ , r , β_s and Z_A versus temperature are shown in figures 3 to 7 respectively.

In Fig. 2. the absorbance is taken in the Y-axis and wave length in nm in the X-axis. The pure medicine (sample A) shows peaks at 327.5nm and 384.75nm. These peaks may be due to $n \rightarrow \pi^*$ transition of electrons in the molecular orbits. In sample B (medicine exposed in scattered light) the absorption peaks get amplified without any change in wavelength. In the case of sample C (medicine exposed in direct sunlight), the absorption peaks disappear.

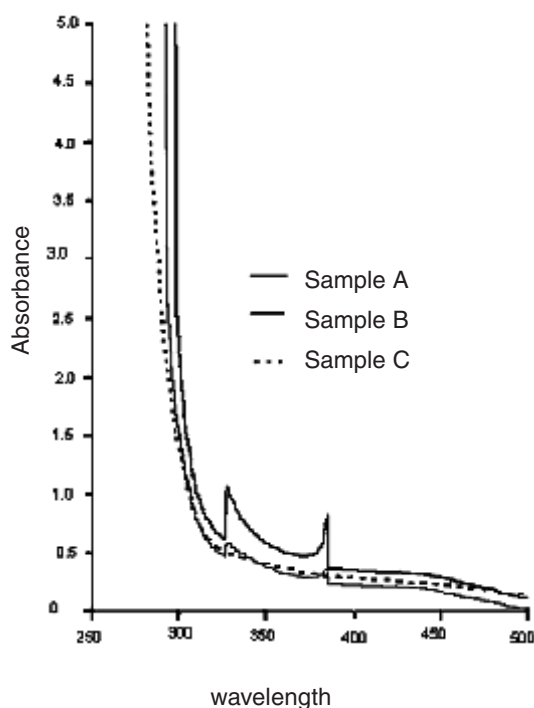
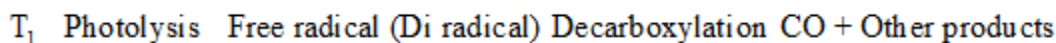
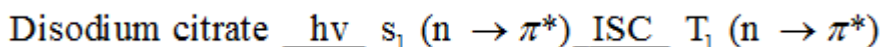


Fig. 2.

When exposed to scattered sunlight, the liquid medicine (sample B) can absorb only the lower frequencies that are available as the higher frequencies were got absorbed by the surrounding objects. There occurs a change in the vibrational and rotational energies of the molecules in the solution. As a result, the molecular association, electric dipole moment, solute solvent interaction etc. may be changed. This is verified by the rapid variation of U , r , β_s and Z_A of the sample B with temperature Figures 3, 5, 6 and 7. Therefore it is to be expected that, when the sample is exposed to scattered sunlight, the population of molecules which undergo the $n \rightarrow \pi^*$ transitions is increased in the solution. This may be the reason for the amplified peaks at 327.5nm and 384.75nm in the UV absorption spectrum of the sample B.

When exposed to direct sunlight, the carboxyl group of the carboxylate absorbs light of wave length from 200-350 nm region. Primary reactions occur from the triplet state (T_1). The final reaction product can be formed after the secondary process of the radiation.

In the primary process a diradical is formed by photolysis and then it is followed by the secondary process, which results in the formation of carbon monoxide. Thus the carbonyl group of the carboxylate is eliminated as carbon monoxide. There is the probability of elimination of carboxylate ion as CO_2 by photolysis as a result of the primary (α – cleavage) and secondary processes.



The UV absorption spectrum for sample exposed to direct sunlight (sample C) shows that the curve becomes a smooth one without absorption peaks at 327.5nm and 384.75nm Fig. 2. This confirms the complete photochemical decarboxylation of disodium hydrogen citrate molecules present in the solution. This may be the reason for the rapidly varying curves of U , ρ , r , β_s and Z_A versus temperature Figure 3-7 for samples A and B, become flat ones for sample C.

The experimental observations in the UV absorption spectra of samples A, B, and C agree well with that of the historic experiment in which there is a gradual disappearance of the absorption peaks of anthracene with exposure to UV radiations in a solution of carbon tetrachloride and anthracene due to the photochemical reaction between them⁵.

Fig-3 shows a plot of ultrasonic velocity U as a function of temperature for samples A, B, and C. For sample A, the rate of fall of U with temperature is rapid up to 308 K and beyond 313 K. From 308 to 313 K, U increases slowly with temperature. In sample B, the curve has large slope and a dip at

303 K and a peak at 313K. It is more or less a magnified version of the curve for sample A. This increased thermal response may be due to the increase in population of molecules which undergo $n \rightarrow \pi^*$ transition. UV absorption spectrum of the sample B shows amplified absorption peaks. This spectrum confirms the increase in the number of active molecules present in the sample B. For sample C, the curve becomes smooth with no dip or peak and the ultrasonic velocity rises slowly with temperature. This inertness in the thermal response may be due to the chemical change taken place due to the photochemical reaction of the medicine. In the UV absorption spectrum, sample C shows no absorption peaks and confirms the chemical change due to the photochemical decarboxylation of the medicine.

In Fig. 4, the density is plotted as a function of temperature for the samples A, B and C. The slope of the curve for the sample A is the greatest from 303 to 313 K. The slope is very small in the regions below 303 K and above 313 K. The exposed samples B and C show an upward shift. At 308 K, the plots

for B and C intersect. The average slope of the curve for sample C is greater than that for sample B. The deviations of the curves for B and C from A suggest photochemical reaction

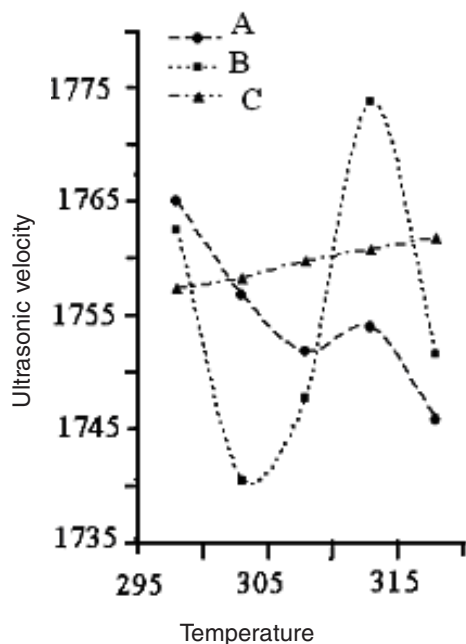


Fig. 3.

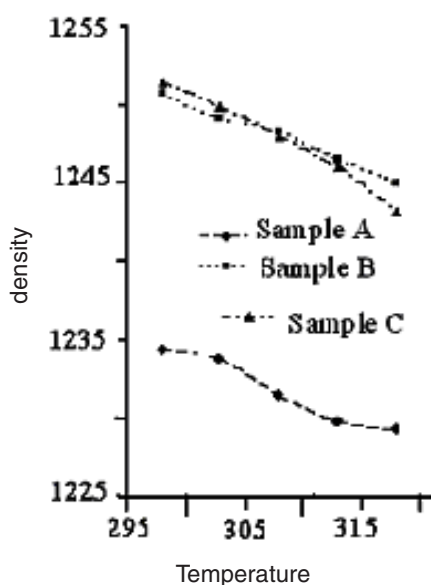


Fig. 4.

In Fig. 5 Rao's specific sound velocity is plotted against temperature. For sample A, Rao's specific sound velocity shows a sinusoidal wave like variation with small amplitude. The samples B and C show a downward shift. For the sample B, the sinusoidal wave like variation has larger amplitude. This is due to the increase in the number of molecules available for $n \rightarrow \pi^*$ transitions. The amplified peaks in the UV absorption spectrum of sample B confirm this fact. For C, the graph becomes almost linear with a positive slope. The inert nature of the thermal response of sample C is due to the chemical changes as a result of photochemical reaction. The disappearance of peaks in the UV absorption spectrum of sample C confirms the chemical change due to photochemical decarboxylation of the medicine.

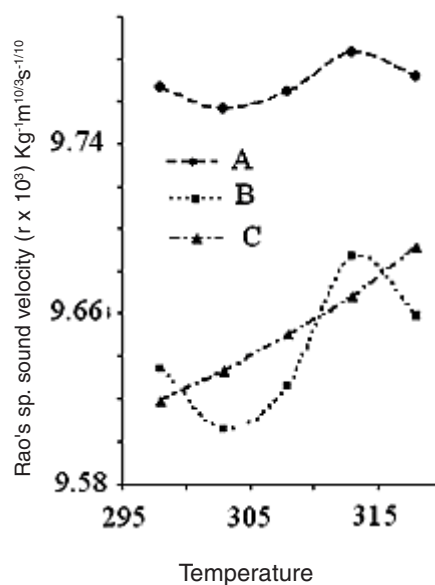


Fig. 5.

In Fig. 6, the adiabatic compressibility β_s is plotted as a function of temperature. For sample A, the curve shows a positive slope with a rapid rise in β_s up to 308 K and beyond 313 K. Between 308 K and 313 K, the slope takes a negative value. There is a peak at 308 K and dip at 313 K. In the case of sample B, the adiabatic compressibility shows a wave like variation with temperature with large

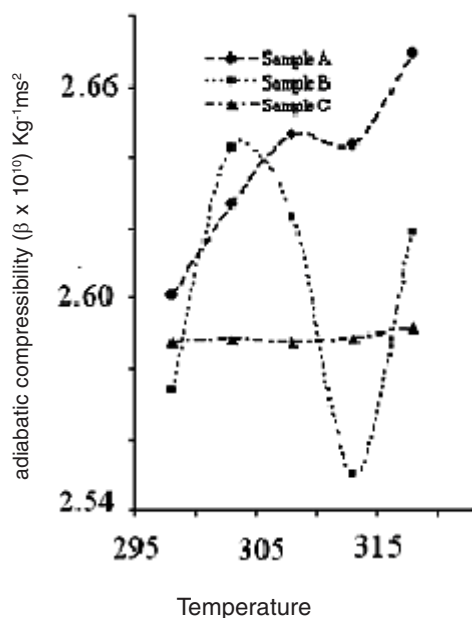


Fig. 6.

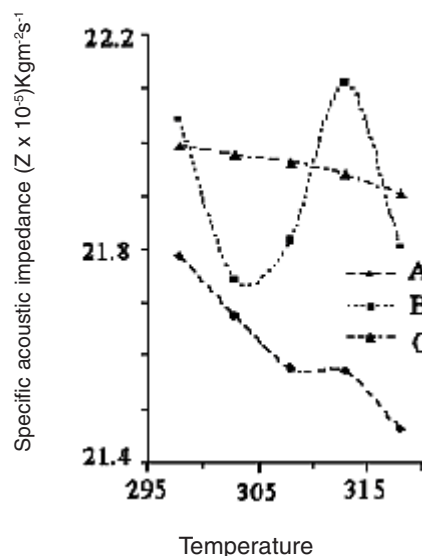


Fig. 7.

amplitude. The peak in the case of sample A is shifted to 303 K but the dip remains at 313 K itself. This is due to the increase in the number of molecules undergoing $n \rightarrow \pi^*$ transitions. This is verified by the magnified absorption peaks in the UV absorption spectrum of sample B. In sample C, a downward shift is observed but no significant variation of β_s . This shows that the medicine has undergone chemical change during photochemical reaction in direct sunlight. This is also verified in the UV absorption spectrum of sample C in which the original absorption peaks are absent.

Fig. 7 shows the variation of Specific acoustic impedance Z_A with temperature. In sample A, the curve shows a rapid fall in Z_A with temperature having a negative slope up to 308 K and beyond 313 K. The slope is zero between 308 and 313 K. the variation of Z_A with temperature for sample B is sinusoidal wave like with a rapid rate of thermal variation of Z_A . A peak is observed at 313 K and a

dip at 303 K. This shows that the number of active molecules which undergo $n \rightarrow \pi^*$ transitions in sample B is greater than that of A. The above result is verified with the magnified absorption peaks of the UV absorption spectrum of sample B. Z_A in the case of sample C shows a linear variation with a very small negative slope with rise in temperature in the whole temperature range of the experiment. This suppressed thermal response is the result of chemical change due to photochemical reaction. This result is in close agreement with the disappearance of the absorption peaks in the UV absorption spectrum of sample C indicating the occurrence of photochemical decarboxylation reaction.

Thus photochemical reaction can be detected by thermo-acoustic method also by considering either the direct parameters (U and ρ) or the derived ones (r , β_s , and Z_A). The results are clear, well defined, accurate and in agreement with that of well established spectrophotometric method.

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