

## Acoustical Properties of Oxalic Acid-Tartaric Acid-Water Solutions

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The paper reports the acoustical properties of multi component solutions (oxalic acid-tartaric acid-citric acid-water) at 40°C. The ultrasonic velocities of solutions have been measured and the values of ultrasonic velocity have been utilized to calculate other acoustical parameters such as the adiabatic compressibility, acoustic impedance, apparent molar compressibility, molar sound velocity and molar sound compressibility. The ultrasonic velocities of solutions increase with the increase in the concentration of its any individual component.

### INTRODUCTION

Knowledge of acoustical properties of any solution provides information about the interactions occurring in the solution. References on acoustical properties show that most of the works are concerned with the solutions having one or two components. However in chemical industries and physiological processes of body fluids, solutions with more than two components are seen. With this view we have selected: oxalic acid-tartaric acid-citric acid-water solutions for our study.

### EXPERIMENTAL

Oxalic acid, citric acid, tartaric acid, KCl, KBr, KI and glucose (all BDH) were used without further purification and their solutions were prepared in conductivity water having sp. conductance  $0.21 \times 10^{-5}$  mhos  $\text{cm}^{-1}$  at 35°C. Densities were measured at constant temperature with the help of a double capillary pycnometer (25 ml capacity). Ultrasonic velocity of the solution was measured with the help of a single crystal ultrasonic interferometer working at a fixed frequency of 2 MHz. Water from a thermostat fixed at the desired temperature was passed through the ultrasonic cell.

### RESULTS AND DISCUSSION

#### Part 1

(A) Following three systems:

System I O.A. (Ci)—Tt.A (0.1 M)—C.A. (0.1 M)—H<sub>2</sub>O

System II O.A. (0.1 M)—Tt.A (Ci)—C.A. (0.1 M)—H<sub>2</sub>O

System III O.A. (0.1 M)—Tt.A (0.1 M)—C.A. (Ci)—H<sub>2</sub>O

were prepared. The concentration of the component whose concentration is changed has been represented by  $C_i$ . The value of  $C_i$  varies from 0.1 M to 0.2 M. Ultrasonic velocity of each solution was measured at 40°C and the values obtained have been recorded in Table 1.

TABLE 1  
ULTRASONIC VELOCITIES OF SOLUTIONS OF SYSTEM I  
SYSTEM II AND SYSTEM III

| $C_i$<br>(mol. lit <sup>-1</sup> ) | Ultrasonic velocities (V) at 40°C in cm sec <sup>-1</sup> |                      |                      |
|------------------------------------|---|----------------------|----------------------|
|                                    | System I  | System II            | System III           |
| 0.10                               | $1.5078 \times 10^5$                                      | $1.5078 \times 10^5$ | $1.5078 \times 10^5$ |
| 0.12                               | $1.5164 \times 10^5$                                      | $1.518 \times 10^5$  | $1.5200 \times 10^5$ |
| 0.14                               | $1.5180 \times 10^5$                                      | $1.5229 \times 10^5$ | $1.5269 \times 10^5$ |
| 0.18                               | $1.520 \times 10^5$                                       | $1.5380 \times 10^5$ | $1.5457 \times 10^5$ |
| 0.20                               | $1.534 \times 10^5$                                       | $1.547 \times 10^5$  | $1.550 \times 10^5$  |

These values of ultrasonic velocity have been utilized to evaluate acoustical parameters such as specific acoustic impedance ( $Z$ ), adiabatic compressibility ( $\beta$ ), inter-molecular free length ( $L_f$ ), apparent molal compressibility ( $\phi_k$ ), molar sound velocity ( $R$ ) and molar compressibility ( $W$ ) for each system at different concentrations using following equations:

$$Z = \rho v \quad (1)$$

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

$$\phi_k = \frac{1000(\beta \rho_0 - \beta_0 \rho)}{\rho \cdot \rho_0} + \frac{\bar{M}}{\rho} \quad (3)$$

$$L_f = K \sqrt{\beta} \quad (4)$$

$$R = \left( \frac{M}{\rho} \right) v^{1/3} \quad (5)$$

$$W = \left( \frac{M}{\rho} \right) \beta^{-1/7} \quad (6)$$

where  $\rho_0$  and  $\beta_0$  are the density and the adiabatic compressibility of the solvent.  $\rho$  is the density of the solution and  $K$  is the temperature dependent Jacobson's constant.  $\bar{M}$  and  $M$  are average molecular weight of the solutes and solution respectively  $\bar{M}$  and  $M$  are calculated by the equation:

$$\bar{M} = \sum_{j=1}^{j=n} X_j M_j \quad (7)$$

$$M = \sum_{j=0}^{j=n} X_j M_j \quad (8)$$

where  $n$  is the no. of solutes present in the solution and  $X_j$  is the molal weighing factor  $\left( = \frac{m_j}{m_T} \right)$  where  $m_j$  = molarity of the  $j$ th component and  $m_T$  is the total molarity given as  $m_T = \sum m_j \cdot M_j$  is the molecular weight of the  $j$ th component and  $M_0$  is the molecular weight of the solvent.

Acoustical parameters calculated from these equations have been recorded in Table 2.

TABLE 2  
ACOUSTICAL PARAMETERS OF SOLUTIONS OF SYSTEM I,  
SYSTEM II AND SYSTEM III

| Systems    | Ci<br>mol<br>lit <sup>-1</sup> | $\rho$ | $\beta \times 10^{11}$<br>cm <sup>2</sup><br>dyne <sup>-1</sup> | $L_r$   | $Z \times 10^{-5}$<br>gm cm <sup>-2</sup><br>sec <sup>-1</sup> | $\phi_k \times 10^9$ | R<br>c.g.s.<br>unit | W<br>c.g.s.<br>unit |
|------------|--------------------------------|--------|---|---------|--|----------------------|---------------------|---------------------|
| System I   | 0.10                           | 1.0134 | 4.3400  | 0.42290 | 1.5280   | 3.368                | 981.811             | 557.780             |
|            | 0.12                           | 1.0135 | 4.2900  | 0.42040 | 1.5369   | 2.662                | 985.255             | 559.535             |
|            | 0.14                           | 1.0136 | 4.2810  | 0.42000 | 1.5386   | 2.430                | 986.900             | 560.413             |
|            | 0.18                           | 1.0139 | 4.2689  | 0.41946 | 1.5412   | 2.069                | 989.985             | 562.137             |
|            | 0.20                           | 1.0140 | 4.1559  | 0.41559 | 1.5560   | 1.096                | 994.288             | 564.352             |
| System II  | 0.1                            | 1.0134 | 4.340   | 0.4229  | 1.5280   | 3.368                | 981.811             | 557.780             |
|            | 0.12                           | 1.0137 | 4.281   | 0.4200  | 1.5387   | 2.710                | 986.579             | 560.228             |
|            | 0.14                           | 1.0141 | 4.251   | 0.4185  | 1.5443   | 2.366                | 989.924             | 562.083             |
|            | 0.18                           | 1.0146 | 4.166   | 0.4143  | 1.5604   | 1.407                | 998.050             | 560.467             |
| System III | 0.1                            | 1.0134 | 4.340   | 0.42290 | 1.5280   | 3.3680               | 981.811             | 557.780             |
|            | 0.12                           | 1.0139 | 4.2689  | 0.41940 | 1.5411   | 2.6700               | 987.617             | 560.792             |
|            | 0.14                           | 1.0143 | 4.2287  | 0.41740 | 1.5487   | 2.3116               | 992.305             | 563.367             |
|            | 0.18                           | 1.0154 | 4.1220  | 0.4121  | 1.5695   | 1.2326               | 1002.411            | 568.860             |
|            | 0.20                           | 1.0157 | 4.0716  | 0.4096  | 1.5794   | 0.7220               | 1007.747            | 571.748             |

Data of ultrasonic velocities clearly indicate that ultrasonic velocity increases with the increase in the total molarity of the solution. It has also been observed that the ultrasonic velocity depends on the component being added to the solution. Here it is obvious that for the solution of the same total molarity, ultrasonic velocities of various systems follow the order:

$$\text{System I} < \text{System II} < \text{System III}$$

Hence it may be said that the addition of citric acid causes greater increase in the ultrasonic velocity than the addition of tartaric acid and the addition of the later compound causes greater increase than the addition of oxalic acid. This fact may also be observed by comparing

ultrasonic velocities of various solutions in each system to the common solution which is the solution having  $C_i = 0.1$  M

The variation of ultrasonic velocity with concentration is

$$\frac{dV}{dc} = -\frac{V}{2} \left[ \frac{1}{\rho} \left( \frac{d\rho}{dc} \right) + \frac{1}{\beta} \left( \frac{d\beta}{dc} \right) \right] \quad (9)$$

For each system the value of  $dv/dc$  is positive. Other workers have also reported positive values for electrolyte solutions.

The plot of ultrasonic velocity vs. the total molarity of the solution is linear and the variation of ultrasonic velocity with the total molarity of the solution follows the relationship

$$V = V_0 + Gm_T \quad (10)$$

The value of  $V_0$  is obtained by extrapolation of the plots and  $G$  is the slope of the plot. The values of  $V_0$  for system I, system II and system III are  $1.505 \times 10^5$  cm/sec,  $1.504 \times 10^5$  cm/sec and  $1.5035 \times 10^5$  cm/sec respectively, whereas the values of  $G$  for these systems are  $2.692 \times 10^{-4}$  cm mol $^{-1}$  sec $^{-1}$ ,  $3.866 \times 10^{-4}$  cm mol $^{-1}$  sec $^{-1}$  and  $4.761 \times 10^{-4}$  cm mol $^{-1}$  sec $^{-1}$  respectively.

Observation of Table 2 makes it clear that the values of  $\beta$  and  $L_f$  decrease with the increase in ultrasonic velocity which increases with the increase in the total molarity of the solution. The decrease in the values of  $\beta$  and  $L_f$  indicates that there is a significant interaction between the solute and solvent molecules. Data show that the values of  $\beta$  and  $L_f$  of solutions having same molarity follows the order

System I > System II > System III

Hence the addition of citric acid causes the highest interaction between the solute and solvent molecules whereas the addition of oxalic acid causes the lowest. The values were used to examine the Bachem's relationship which is

$$\beta = \beta_0 + AC + BC^{3/2} \quad (11)$$

where  $C$  is the concentration of the solution.  $A$  and  $B$  are constants obtained from the intercept and the slope of the plots of  $\beta - \beta_0/C$  vs.  $\sqrt{C}$ . This relationship has not been found to be followed by these multi-component solutions.

The calculated values of  $\phi_k$  from the equation (3) have been plotted against the total molarity of the solutions. The values of  $\phi_k$  decrease linearly with the increase in the values of  $m_T$  and are best fitted to the equation.

$$\phi_k = \phi_k^0 + S_k \cdot m_T \quad (12)$$

where  $\phi_k^0$  is the apparent molal compressibility at infinite dilution and  $S_k$  is the experimental slope. The values of  $\phi_k^0$  and  $S_k$  have been recorded in Table 3.

TABLE 3  
VALUES OF  $\phi_k^\circ$  AND  $S_k$  FOR SYSTEM I,  
SYSTEM II AND SYSTEM III AT 40°C

| Systems    | $\phi_k^\circ \times 10^9$ | $S_k \times 10^9$ |
|------------|----------------------------|-------------------|
| System I   | 3.552                      | -22.3642          |
| System II  | 3.600                      | -24.1666          |
| System III | 3.630                      | -25.9740          |

The value of molar sound velocity, molar sound compressibility and specific acoustic impedance increases with the increasing total molarity of the solution.

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