Thiazolidinones: An Ultrasonic study in DMF solutions

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ABSTRACT

Some new thiazolidinone derivatives are synthesized and their acoustical properties are studied in dimethylformamide at 298.15 K. The evaluated properties are interpreted in terms of molecular interactions occurring in solutions. It is observed that in DMF, for all the derivatives, solute-solvent interactions dominate.

1. INTRODUCTION

In recent years, ultrasonic has become the subject of extensive research in wide range of applications in different fields like chemical industries, consumer industries, medical field, process industries, food industry, physics, chemistry and biology etc [1-10]. As it is a non-destructive technique, it attracts more attention.

In chemistry, ultrasound waves have also proven to enhance reaction yields in more convenient reaction conditions [11-14]. Further, it helps to understand the molecular interactions in pure liquids, liquid mixtures and solutions. Literature survey shows that much work has been done in solutions of inorganic salts [15,16], amino acids [17,18], polymers [19-21] etc. However, scanty work has been done for organic compounds [22,23].

Thus, in the present work, acoustical properties of some thiazolidinone derivatives in dimethyl formamide have been studied at 298.15 K.

2. EXPERIMENTAL

Overall, seven thiazolidinone derivatives were synthesized in laboratory. The general structure of these thiazolidinone derivatives is given in Figure 1. The physical constants and different substitutions are reported in Table 1. These compounds were recrystallized before use.

The solvent dimethyl formamide (DMF) used in the present study was purified by standard method [24] and its purity was found to be more than 99.8 %.

The solutions of all the thiazolidinone derivatives were prepared in DMF over the wide range of concentrations. The densities, viscosities and ultrasonic velocities of pure DMF and solutions of different concentration were measured at 298.15 K by using pyknometer, an Ubbelohde suspended level viscometer and ultrasonic interferometer operating at 2 MHz with the uncertainties of 0.0001 g/cm³, ±0.06 % and 0.01% respectively.

3. RESULTS AND DISCUSSION:

The density (ρ), viscosity (η) and sound velocity (U) of pure DMF and solutions are reported in Table 2.

From these measurements, various acoustical parameters like specific acoustical impedance (Z), isentropic compressibility (κs), intermolecular free length (L₀), Rao’s molar sound function (R_m), molar compressibility (W), Vander Waals constant (b), relaxation strength (r), internal pressure (π), solvation number (S_n) etc. were evaluated using the following equations:

Specific acoustical impedance: \( Z = U \rho \)

Isentropic compressibility: \( \kappa_s = 1/U^2 \rho \)
Intermolecular free path length: \( L_f = K_{\text{J}} \kappa_s^{1/2} K_{\text{J}} \) (Jacobson constant) = 2.0965 x 10^{-6}

Rao’s molar sound function: \( R_m = (M/\rho) U^{1/3} \) where \( M \) = molecular weight of solution.

Molar compressibility: \( W = (M/\rho) \kappa_s^{-1/7} \)

Van der Waals Constant: \( b = M/\rho \{1 - (RT/MU^2)^{1/2}\} \sqrt{[1 + (MU^2/3RT) - 1]} \}

where \( R \) is gas constant and \( T \) is the absolute temperature.

Relaxation Strength: \( r = 1 - [U/U_{\infty}]^2 \) where \( U_{\infty} = 1.6 \times 10^5 \text{ cm/s.} \)

Solvation Number: \( S_n = M_2 / \{M_1 [1-\kappa_s/\kappa_{s1}] [(100-X)/X]\} \)

where \( X \) is the number of grams of solute in 100 g. of the solution and \( M_1 \) and \( M_2 \) are the molecular weights of solvent and solute respectively. \( \kappa_{s1} \) and \( \kappa_s \) are the isentropic compressibility of solvent and solution, respectively.

Some of these parameters are given in Table 3. Figure 2 (A) shows the variation of ultrasonic velocity with concentration which is found to increase non-linearly with concentration for all the compounds. Whereas intermolecular free path length \( (L_f) \) decreases with concentration as shown in Figure 2 (B). Thus, ultrasonic velocity is reverse of intermolecular free path length \( (L_f) \).

The increase in ultrasonic velocity and decrease in intermolecular free path length indicates interaction between solvent and compound molecules.

The predominance of a particular interaction in a particular solution can also be decided by isentropic compressibility, which is shown in Figure 3 (A) for all the Thiazolidinones in DMF. It is observed that isentropic compressibility decreases with increase in concentration for all the compounds. When there is strong interaction between solvent and compound molecules, compressibility decreases as observed in the present case. This is further supported by decrease in relaxation strength \( (r) \) as given in Table 3. However, acoustic impedance \( (Z) \) shows reverse nature. The increase in \( Z \) and decrease in \( \kappa_s \) and \( r \) again proves the existence of solute-solvent interactions in DMF.

It is obvious from Table 3 that Rao’s molar function \( (R_m) \), molar compressibility \( (W) \) and Vander Waal’s constant \( (b) \) increase linearly with concentration for all the thiazolidinones in DMF. This suggests the absence of complex formation in these solutions.

The predominance of solute-solvent interactions is again confirmed by solvation number \( (S_n) \). The solvation number \( (S_n) \) is a measure of structure forming or structure breaking tendency of solute in a solution. The increase in \( S_n \) values indicates the structure-forming tendency of solute or vice versa. Figure 3 (B) shows the variation of \( S_n \) with concentration in DMF. It is observed that solvation number increases with concentration for all the compounds indicating thereby structure-forming tendency of compounds in DMF which is due to solute-solvent interactions.

Thus, it is concluded that in DMF solutions, for the studied compounds, solute-solvent interactions dominate.

**Table 1. Physical constants of synthesized Thiazolidinone derivatives**

| Compound Code | R          | M.F.               | M. Wt. g | M.P. | % Yield | \( R_f \) Value |
|---------------|------------|--------------------|----------|------|---------|-----------------|
| SS-1          | 4-OCH\(_3\)-C\(_6\)H\(_4\)- | C\(_{17}\)H\(_{15}\)NO\(_4\)S | 329.29   | 202  | 54      | 0.60            |
| SS-2          | -CH=CH-C\(_6\)H\(_4\)-       | C\(_{18}\)H\(_{16}\)NO\(_3\)S | 325.38   | 221  | 52      | 0.61            |
| SS-3          | 4-CH\(_3\)-C\(_6\)H\(_4\)-   | C\(_{17}\)H\(_{16}\)NO\(_3\)S | 313.37   | 235  | 58      | 0.57            |
| SS-4          | 4-Cl-C\(_6\)H\(_4\)-         | C\(_{18}\)H\(_{15}\)ClNO\(_3\)S | 333.78   | 215  | 60      | 0.49            |
| SS-5          | 3-Cl-C\(_6\)H\(_4\)-         | C\(_{18}\)H\(_{15}\)ClNO\(_3\)S | 333.79   | 213  | 57      | 0.42            |
| SS-6          | 3-NO\(_2\)-C\(_6\)H\(_4\)-   | C\(_{16}\)H\(_{15}\)NO\(_2\)S | 344.34   | 248  | 62      | 0.55            |
| SS-7          | 2-OH-C\(_6\)H\(_4\)-         | C\(_{16}\)H\(_{13}\)NO\(_3\)S | 315.14   | 240  | 59      | 0.39            |

* Ethyl acetate : Hexane: - 3:7
Table 2. The density ($\rho$), ultrasonic velocity ($U$) and viscosity ($\eta$) of thiazolidinones in DMF

| Conc. (M) | $\rho$ (g.cm$^{-3}$) | $U \cdot 10^{-5}$ (cm.s$^{-1}$) | $\eta \cdot 10^3$ (poise) | $\rho$ (g.cm$^{-3}$) | $U \cdot 10^{-5}$ (cm.s$^{-1}$) | $\eta \cdot 10^3$ (poise) |
|-----------|---------------------|-------------------------------|---------------------------|---------------------|-------------------------------|---------------------------|
| SS - 1    |                     |                               |                           | SS - 5              |                               |                           |
| 0.00      | 0.9433              | 1.4624                        | 7.1940                    | 0.9433              | 1.4624                        | 7.1940                    |
| 0.01      | 0.9460              | 1.4636                        | 7.3042                    | 0.951               | 1.4701                        | 8.0163                    |
| 0.02      | 0.9472              | 1.4644                        | 7.4256                    | 0.9525              | 1.4708                        | 8.0763                    |
| 0.04      | 0.9484              | 1.4656                        | 7.5406                    | 0.9539              | 1.4721                        | 8.1627                    |
| 0.06      | 0.9505              | 1.4680                        | 7.6609                    | 0.956               | 1.4728                        | 8.3671                    |
| 0.08      | 0.9512              | 1.4692                        | 7.7882                    | 0.9594              | 1.4736                        | 8.5234                    |
| 0.10      | 0.9529              | 1.4716                        | 7.9239                    | 0.9632              | 1.4764                        | 8.7898                    |
| SS - 2    |                     |                               |                           | SS - 6              |                               |                           |
| 0.01      | 0.9461              | 1.4902                        | 7.3095                    | 0.9511              | 1.4700                        | 8.0163                    |
| 0.02      | 0.9473              | 1.4908                        | 7.3973                    | 0.9525              | 1.4708                        | 8.0763                    |
| 0.04      | 0.9480              | 1.4924                        | 7.5374                    | 0.9539              | 1.4722                        | 8.1627                    |
| 0.06      | 0.9495              | 1.4936                        | 7.6528                    | 0.956               | 1.4728                        | 8.3671                    |
| 0.08      | 0.9512              | 1.4956                        | 7.7769                    | 0.9594              | 1.4736                        | 8.5234                    |
| 0.10      | 0.9529              | 1.5008                        | 7.9239                    | 0.9632              | 1.4764                        | 8.7898                    |
| SS - 3    |                     |                               |                           | SS - 7              |                               |                           |
| 0.01      | 0.9437              | 1.4784                        | 7.9491                    | 0.9504              | 1.4644                        | 7.5498                    |
| 0.02      | 0.9504              | 1.4792                        | 8.0022                    | 0.9511              | 1.4652                        | 7.6927                    |
| 0.04      | 0.9515              | 1.4801                        | 8.0836                    | 0.9517              | 1.4668                        | 7.781                     |
| 0.06      | 0.9525              | 1.4821                        | 8.1778                    | 0.9525              | 1.4682                        | 7.875                     |
| 0.08      | 0.9534              | 1.4836                        | 8.3572                    | 0.9536              | 1.4692                        | 7.9727                    |
| 0.10      | 0.9542              | 1.4868                        | 8.5337                    | 0.9552              | 1.4724                        | 8.0992                    |
| SS - 4    |                     |                               |                           |                     |                               |                           |
| 0.01      | 0.9523              | 1.4700                        | 7.9348                    |                     |                               |                           |
| 0.02      | 0.9535              | 1.4708                        | 8.0306                    |                     |                               |                           |
| 0.04      | 0.9556              | 1.4716                        | 8.1682                    |                     |                               |                           |
| 0.06      | 0.9583              | 1.4728                        | 8.3661                    |                     |                               |                           |
| 0.08      | 0.9613              | 1.4756                        | 8.6495                    |                     |                               |                           |
| 0.10      | 0.9628              | 1.4792                        | 8.9389                    |                     |                               |                           |

Table 3. Variation of acoustical parameters with concentration of thiazolidinones in DMF.

| Conc. (M) | $Z \cdot 10^{-5}$ (gm.cm$^2$) | $r$ | $R_{m} \cdot 10^{-3}$ (cm$^{4/3}$ sec$^{-1/3}$) | $W \cdot 10^{-3}$ (cm$^{2}$.dyn$^{-1}$) | $b$ (cm$^{3}$.mol$^{-1}$) |
|-----------|-------------------------------|-----|-----------------------------------------------|----------------------------------------|---------------------------|
| SS-1      |                               |     |                                               |                                        |                           |
| 0.00      | 1.3794                        | 0.1646 | 4.0821                                      | 2.2974                               | 77.4782                   |
| 0.01      | 1.3845                        | 0.1632 | 4.1195                                      | 2.3196                               | 78.1682                   |
| 0.02      | 1.3871                        | 0.1623 | 4.1663                                      | 2.3464                               | 79.0381                   |
| 0.04      | 1.3899                        | 0.1609 | 4.2611                                      | 2.4001                               | 80.8181                   |
| 0.06      | 1.3953                        | 0.1582 | 4.3520                                      | 2.4510                               | 82.4981                   |
| 0.08      | 1.3975                        | 0.1568 | 4.4477                                      | 2.5061                               | 84.2882                   |
| 0.10      | 1.4023                        | 0.1541 | 4.5398                                      | 2.5584                               | 85.9882                   |
| SS-2      |                               |     |                                               |                                        |                           |
| 0.01      | 1.4096                        | 0.1328 | 4.1442                                      | 2.3316                               | 78.1682                   |
| 0.02      | 1.4122                        | 0.1318 | 4.1882                                      | 2.3568                               | 78.9881                   |
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| 0.04 | 1.4148 | 0.1300 | 4.2812 | 2.4101 | 80.7382 |
| 0.06 | 1.4182 | 0.1286 | 4.3746 | 2.4622 | 82.4482 |
| 0.08 | 1.4226 | 0.1282 | 4.4678 | 2.5134 | 84.1681 |
| 0.10 | 1.4301 | 0.1201 | 4.5562 | 2.5653 | 85.7381 |
| SS-3 |   |   |   |   |   |
| 0.01 | 1.4040 | 0.1462 | 4.1133 | 2.3164 | 77.8882 |
| 0.02 | 1.4058 | 0.1453 | 4.1553 | 2.3402 | 78.5682 |
| 0.04 | 1.4082 | 0.1444 | 4.2396 | 2.3888 | 80.0981 |
| 0.06 | 1.4116 | 0.1421 | 4.3225 | 2.4355 | 81.7098 |
| 0.08 | 1.4145 | 0.1402 | 4.3886 | 2.4839 | 82.2881 |
| 0.10 | 1.4187 | 0.1365 | 4.4961 | 2.5329 | 84.1682 |
| SS-4 |   |   |   |   |   |
| 0.01 | 1.3998 | 0.1559 | 4.1012 | 2.3111 | 77.7082 |
| 0.02 | 1.4024 | 0.1550 | 4.1411 | 2.3339 | 78.4482 |
| 0.04 | 1.4053 | 0.1541 | 4.2379 | 2.3892 | 80.2682 |
| 0.06 | 1.4113 | 0.1527 | 4.3277 | 2.4404 | 81.9482 |
| 0.08 | 1.4184 | 0.1495 | 4.4145 | 2.4905 | 83.5382 |
| 0.10 | 1.4242 | 0.1452 | 4.5106 | 2.5451 | 85.2881 |
| SS-5 |   |   |   |   |   |
| 0.01 | 1.3998 | 0.1559 | 4.1012 | 2.3111 | 77.7082 |
| 0.02 | 1.4024 | 0.1550 | 4.1411 | 2.3339 | 78.4482 |
| 0.04 | 1.4053 | 0.1541 | 4.2379 | 2.3892 | 80.2682 |
| 0.06 | 1.4113 | 0.1527 | 4.3277 | 2.4404 | 81.9482 |
| 0.08 | 1.4184 | 0.1495 | 4.4145 | 2.4905 | 83.5382 |
| 0.10 | 1.4242 | 0.1452 | 4.5106 | 2.5451 | 85.2881 |
| SS-6 |   |   |   |   |   |
| 0.01 | 1.3889 | 0.1596 | 4.1225 | 2.3214 | 78.1682 |
| 0.02 | 1.3926 | 0.1587 | 4.1723 | 2.3472 | 79.0982 |
| 0.04 | 1.3952 | 0.1577 | 4.2754 | 2.4081 | 81.0381 |
| 0.06 | 1.4006 | 0.1554 | 4.3761 | 2.4666 | 82.9082 |
| 0.08 | 1.4042 | 0.1527 | 4.4825 | 2.5261 | 84.8781 |
| 0.10 | 1.4048 | 0.1517 | 4.581 | 2.5824 | 86.7281 |
| SS-7 |   |   |   |   |   |
| 0.01 | 1.3918 | 0.1623 | 4.0978 | 2.3078 | 77.6982 |
| 0.02 | 1.3935 | 0.1614 | 4.1364 | 2.3325 | 78.4981 |
| 0.04 | 1.3959 | 0.1596 | 4.2252 | 2.381 | 80.1161 |
| 0.06 | 1.3982 | 0.1582 | 4.3098 | 2.4289 | 81.6981 |
| 0.08 | 1.401 | 0.1568 | 4.3934 | 2.4763 | 83.2581 |
| 0.10 | 1.4064 | 0.1531 | 4.4755 | 2.5228 | 84.7481 |
Figure 1: General structure of synthesized Thiazolidinone derivatives

Figure 2: The variation of ultrasonic velocity (A) and Inter molecular free path length (B) against concentration for thiazolidinones in DMF at 298.15 K.

♦: SS-1; ■: SS-2; ▲: SS-3; ■: SS-4; ♦: SS-5; ●: SS-6; ▲: SS-7.
Figure 3: The variation of isentropic compressibility (A) and solvation number (B) against concentration for thiazolidinones in DMF.

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