Solution Thermodynamics and Preferential Salvation of Chloro-m-xynol (antiseptic) in Acetone

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Abstract

Ultrasonic velocities in solution of acetone in different concentration of chloro m- xynol were measured at 30°C, 35°C and 40°C atmospheric pressure by using a single-crystal interferometer at a frequency of 2 MHz. The ultrasonic velocity, density, and viscosity were used to calculate adiabatic compressibility (β_s), intermolecular free length (L_f), specific acoustic impedance (Z), apparent molar compressibility (φ_k), solvation number (S_n) and relative association (R_A). The observed variation in these parameters with respect to the molarities of chloro-m-xynol highlights ion-solvent and ion-ion interactions were present, ion-solvent interactions were much pronounced at lower molarities and ion-ion interactions were very apparent at higher molarities of chloro-m-xynol in acetone.

Keywords: Ultrasonic velocity, Chloro-m-xynol (antiseptic), Adiabatic compressibility, Viscosity, Ion-solvent interaction.

1. Introduction

The chloro-m-xynol (antiseptic) organic compounds are essential chemicals for human beings, so emphasized the theoretical interpretation of these compound to discuss the molecular interaction of these compound with solvent medium. The solvents are selected dividing them as non-polar solvents. The solvation of antiseptic electrolyte will be more in polar solvents but less solvolysis takes place in non-polar solvents.

The study of molecular interactions has been a subject of extensive investigations by IR[1, 2], Raman[3], NMR[4, 5] and ultrasonic absorption[6, 7] measurements. Several workers[8-15] have used ultrasonic velocity measurements for studying the ion-solvent interaction and solvation of salts in non-aqueous solvents. The complementary use of adiabatic compressibility and apparent molar compressibility can provide interesting information on ion-solvent interaction.

In the present work ultrasound velocity, density and viscosity measured practically in the laboratory of the solvent and solute solutions in the solvents. The measured ultrasound velocity, density and viscosity were used for the determination of acoustic and thermodynamics properties like Isentropic Compressibility (β_s), Specific Acoustic Impedance (Z), Intermolecular Free Length (L_f), Molar Sound Velocity (R), Relative Association (R_A), Shears Relaxation Time (τ_s), Apparent Molal Compressibility (ϕ_k), Salvation Number (S_n), Viscosity (η), Specific Viscosity (η_{sp}) and Reduced Viscosity have been calculated. The above computed acoustic and thermodynamics parameter will decide nature and extent of interaction between solute and solvent molecules. The solvolysis depends on the interaction of solute molecules with the solvents.

2. Experimental

Density (ρ) and Viscosity (η): The densities of the solvent and solutions were measured with a double walled bi-capillary pyknometer. The viscosity of solvents and solution measured by suspended level canon-ubbelhode type viscometer is of special utility in observing the variation of viscosity with concentration. The viscometer was calibrated against distilled water, benzene and toluene. Viscosity (η) of liquid calculated by using formula

$$\eta_1 = \frac{\pi r^4 t_1 P_1}{8V}$$

and

$$\eta_2 = \frac{\pi r^4 t_2 P_2}{8V}$$

Therefore

$$\frac{\eta_1}{\eta_2} = \frac{t_1 P_1}{t_2 P_2} \qquad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (1)$$

Where η_1 and η_2 is the viscosity of two liquids and P_1 & P_2 are the hydrostatic pressure and t_1 & t_2 is the time flow of liquid in viscometer. We know that the hydrostatic pressure is the proportional to the density. Therefore,

$$\frac{\eta_1}{\eta_2} = \frac{t_1 \rho_1}{t_2 \rho_2} \qquad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2)$$

Where ρ & ρ are the density of liquids and η_2 is the viscosity of water. Specific Viscosity (η_{sp}) and Reduced Viscosity (η_r) were calculated as by following equation-

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta} \qquad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots .. (3)$$

$$\eta_r = \frac{\eta_{sp}}{C} \qquad \dots\dots\dots\dots\dots\dots\dots\dots (4)$$

Where η and η_0 are the viscosity of solution, solvent and C is the concentration of solution.

Ultrasonic Velocity: The ultrasonic velocity measurements were recorded on an ultrasonic interferometer (F-81, Mittal Enterprises, New Delhi) at 40.0 + 0.05 C using a crystal of 2 MHz frequency. Quartz crystal have different frequency of about 0.05%, the uncertainty of velocity measurements is 0.2%. The various acoustic parameters such as Isentropic Compressibility (β_s), Specific Acoustic Impedance (Z), Intermolecular Free Length (L_f), Molar Sound Velocity (R), Relative Association (R_A), Shears Relaxation Time (τ_s), Apparent Molal Compressibility (ϕ_k) and Salvation Number (S_n), have been calculated by using following relationship:

Isentropic Compressibility (β_s): The relation between the sound velocity and βs were written as

$$\beta_s = \frac{1}{V^2\rho} \qquad \dots\dots\dots\dots\dots\dots\dots\dots. (5)$$

Where V is the ultrasound velocity and ρ is the density of liquid mixtures.

Intermolecular Free Length (L_f): Jacobson gave the empirical formula for the L_f as

$$L_f = K\sqrt{\beta_s} \qquad \dots\dots\dots\dots\dots\dots\dots\dots (6)$$

Where is the temperature dependent constant which known as Jacobson's constant. The temperature dependent value of K at different temperature are given below

Temp (°C)	0	10	20	25	30	35	40	45
Value of K	588	604	618	625	631	636.5	642	652

Molar Sound Velocity (R): R may be expressed by this equation

$$R = \frac{\overline{M}}{\rho}V^{\frac{1}{3}} \qquad \dots\dots\dots\dots\dots\dots\dots\dots (7)$$

Where $\overline{M}$ is the effective molecular weight which determined by following equation as

$$\overline{M} = \frac{n_1 M_1 + n_2 M_2}{n_1 + n_2} \qquad \dots\dots\dots\dots\dots\dots\dots (8)$$

Where n_1 and n_2 are the number of mole of solvent and solute, M_1 and M_2 are the molecular weight of solvent and solute.

Relative Association (R_A): R_A may be expressed by this equation

$$R_A = \left(\frac{\rho}{\rho_0}\right)\left(\frac{V_0}{V}\right)^{1/3} \qquad \dots\dots\dots\dots\dots\dots \ (9)$$

Where ρ and ρ_0 are the density and V and V_0 are the ultrasonic velocity of solutions and solvent.

Shears Relaxation Time (τ_s): τ_s derived by this equation

$$\tau_S = \frac{4}{3}\eta\,\beta_S \qquad\qquad \dots\dots\dots\dots\dots\dots\dots.. \ (10)$$

Where η is the viscosity of solution.

Apparent Molal Compressibility (ϕ_k): ϕ_k expressed by this equation

$$\emptyset_K = \frac{1000}{C \times \rho_0}\left(\rho_0\beta_S - \beta_{S0}\rho\right) + \beta_{SO}\frac{M}{\rho_0} \quad \dots\dots \ (11)$$

Where ρ, ρ_0 & β_S, β_{S0}, are the density and adiabatic compressibility of solutions and solvent respectively.

Apparent Molar Volume ($\emptyset_V$): The $\emptyset_V$ is calculated by the following expression

$$\emptyset_V = \frac{1000}{C \times \rho}\left(\rho_0 - \rho\right) + \frac{M}{\rho_0} \qquad \dots\dots\dots.. \ (12)$$

Where M is the molecular weight of solute, C is the concentration.

Salvation Number (S_n): The expression used for calculation of S_n is due to passynsky

$$S_n = \frac{n_1}{n_2}\left(1 - \frac{\beta_S}{\beta_{S0}}\right) \qquad \dots\dots\dots\dots\dots.. \ (13)$$

Specific Acoustic Impedance (Z): It is defined as unit area Acoustic Impedance of a sound on a given surface and its value calculated by using formula

$$Z = V \times \rho \qquad \dots\dots\dots\dots\dots\dots\dots\dots\dots.. \ (14)$$

3. Results and Discussion

The measured parameters viz. ultrasonic velocity (V), density (ρ), viscosity (η) are given in the Table (1-3) at different temperatures. The table shows these three parameters increase with concentration of chloro-m-xynol -acetone. This indicates that strong interaction observed at higher concentrations of chloro-m-xynol -acetone and suggests more association between solute and solvent molecules in the system.

The ultrasonic velocity and various acoustical parameters for chloro-m-xynol -acetone have been evaluated (Table 1-3) at different temperatures. The variation of ultrasonic velocity (V), with chloro-m-xynol concentration C, can be expressed in terms of concentration derivatives of density ρ and adiabatic compressibility β, by the following relationship

$$\frac{dV}{dC} = -\frac{V}{2}[\frac{1}{\rho} \times \frac{d\rho}{dC} + \frac{1}{\beta_s} \times \frac{d\beta_s}{dC}]$$

The results indicate that the density increases while the adiabatic compressibility decreases with increasing chloro-m-xynol concentration. Therefore, the quantity $d\rho/dC$ (concentration derivative of density) is positive while the quantity $d\beta_s/dC$ (concentration derivative of compressibility), is negative. Since the values of $1/\beta_s \times d\beta_s/dC$ a9re larger than the values of $1/\rho \times d\rho/dC$ for these chloro-m-xynol solutions, the concentration derivative of velocity, (dV/dC) will be positive and so the velocity increases with increasing chloro-m-xynol concentration. This is an agreement with the result of several workers reported for electrolytic solutions[16-18]. The isentropic compressibility, β_s for the solution of chloro-m-xynol decrease with increase in solute concentration (Table 1-3). The decrease in isentropic compressibility is attributed to the fact that the solute molecules, in dilute solution ionize in simple cations and anions. These solutions are surrounded by a layer of solvent molecules, firmly bound, and oriented towards the ions. The orientation of solvent molecules around the ions is attributed to the influence of electrostatic field of ions and thus the internal pressure increases, which lowers the compressibility of solution i.e. the solutions become harder to compress[19]. The intermolecular free length (L_f), which is expected to decrease as a result of mixing of the two components, decreases with the increase in solute concentration. Rise in temperature generally increases the internal energy of the system by distorting the local structure, resulting in an increase in intermolecular free length and subsequently decreasing the ultrasonic velocity. In the present study, the elevation of temperature from 30°C, 35°C and 40°C shows the same trend.

The intermolecular free length (L_f) decrease while specific acoustic impedance (Z) increase with increase in solute concentration (Table-1-3), which can be explained on the basis of lyophobic interaction between the solute and solvent molecule which increases the inter molecular distance leaving relatively wider gaps between the molecules and thus becoming the main cause impediment to the propagation of ultrasound waves[20] and affects the structural arrangement. The specific acoustic impedance, a product of the density of the solution and the velocity, has shown the reverse trends to that of inter molecular free length. Thus the fact that increase of velocity, decrease of isentropic compressibility, decrease of intermolecular free length and increase of specific acoustic impedance with increase in molar concentration at all temperatures is an indicative of the increase in intermolecular forces with the addition of solute forming aggregates

of solvent molecules around solute ions and supports the strong solute-solvent interactions, due to which structural arrangement is affected.

Relative association (R_A) is influence by two factors[21] (i) the breaking up of the solvent molecules on addition of electrolyte to it and (ii) the solvation of ion that are simultaneously present; the former resulting in a decrease and later increase of relative association .In the present investigation, it has been observed that relative association value increases with increase in concentration. Similar results have been reported in literature[22, 23]. Solvation number (Sn) is calculated using Passynsky[24] equation and are listed in Table (1-3). The Sn values are found to increase with the increase in solute, which also suggested close association between solute and solvent.

The values of apparent molar compressibility (φ_k) are found to be negative and it increases negatively with increasing concentration of chloro-m-xynol . It is also found that molar compressibility varies linearly as the square root of molar concentration graph of φ_k *Vs* $\sqrt{C}$. The density, Shears Relaxation Time (τ_s) and ultrasound velocity of the solutions of chloro-m-xynol in foresaid solvent increases an increasing concentration of chloro-m-xynol solutions. The viscosity (η), specific viscosity (η_{sp}), and reduced viscosity (η_{red}) has been calculated for chloro-m-xynol -acetone system at different temperature (Table 1-3) is obvious that the value of η, η_{sp} and η_{red} increases with increase in molar concentration and density of the solution. The increases in viscosity may be due to increases tendency of chloro-m-xynol molecules to form aggregates with the increase in the chloro-m-xynol concentration in solution.

TABLE (1)

System: Chloro-m-xynol + Acetone at 30°C (Isentropic Compressibility of Acetone = 95.60 × 10^{-12} dyne/cm^2)

Molar Conc. of Chloro-m-xynol (mole/L)	Density ρ (g/mL)	Viscosity η (c.p.)	Sp. Viscosity η_{sp} (c.p.)	Reduced Viscosity η_{red} (c.p.)	Ultrasound velocity (m/sec)	Isentropic Compressibility β_s ($10^{12} \times$ cm^2/dyne)	Lowering Compressibility β_{s0} - β_s ($10^{12} \times$ cm^2/dyne)
0.0352	0.7910	0.3289	0.0428	1.2154	1161	93.79	1.81
0.0705	0.8046	0.3425	0.0859	1.2199	1163	91.89	3.71
0.1057	0.8182	0.3561	0.1291	1.2214	1165	90.05	5.55
0.1409	0.8318	0.3697	0.1722	1.2222	1167	88.28	7.32
0.1761	0.8454	0.3833	0.2154	1.2226	1169	86.56	9.04
0.2114	0.8590	0.3969	0.2585	1.2229	1171	84.90	10.70
0.2466	0. 8726	0.4106	0.3016	1.2231	1173	83.29	12.31
0.2818	0.8862	0.4241	0.3448	1.2233	1175	81.73	13.87

| 0.3171 | 0.8998 | 0.4377 | 0.3879 | 1.2234 | 1177 | 80.22 | 15.38 |
| 0.3523 | 0.9134 | 0.4513 | 0.4310 | 1.2235 | 1179 | 78.76 | 16.84 |

Sp. Acoustic impedance $Z \times 10^{-5}$	Molar sound velocity R (m/sec)	Relative Association R_A	Solvation Number S_n	Inter molecular length L_f (Å)	β_s-β_{s0}/C (10^{12})	Apparent Molar Compressibility (φ_k) $10^2 \times cm^2/dyne$	Shears Relaxation Time τ_s
0.9184	611.25	1.0178	0.1013	0.6111	-51.3640	-80.9158	41.1303
0.9357	622.11	1.0359	0.2078	0.6049	-52.6801	-42.1948	41.9624
0.9532	632.99	1.0540	0.3106	0.5988	-52.5033	-29.2264	42.7562
0.9707	643.88	1.0721	0.4101	0.5929	-51.9804	-22.6985	43.5139
0.9883	654.78	1.0903	0.5062	0.5871	-51.3324	-18.7484	44.2371
1.0059	665.70	1.1084	0.5992	0.5814	-50.6362	-16.0886	44.9276
1.0236	676.62	1.1266	0.6892	0.5759	-49.9229	-14.1671	45.5870
1.0413	687.56	1.1448	0.7764	0.5705	-49.2078	-12.7080	46.2168
1.0591	698.50	1.1631	0.8608	0.5652	-48.4987	-11.5579	46.8184
1.0769	709.46	1.1813	0.9427	0.5600	-47.8000	-10.6246	47.3931

TABLE (2)

System: Chloro-m-xynol + Acetone at 35°C (Isentropic Compressibility of Acetone = 103.24 × 10^{-12} dyne/cm^2)

Molar Conc. of Chloro-m-xynol (mole/L)	Density ρ (g/mL)	Viscosity η (c.p.)	Sp. Viscosity η_{sp} (c.p.)	Reduced Viscosity η_{red} (c.p.)	Ultrasound velocity (m/sec)	Isentropic Compressibility β_s ($10^{12} \times cm^2/dyne$)	Lowering Compressibility β_{s0} - β_s ($10^{12} \times cm^2/dyne$)
0.0352	0.7722	0.2918	0.0485	1.3775	1131	101.24	2.00
0.0705	0.7858	0.3054	0.0974	1.3826	1133	99.14	4.10
0.1057	0.7994	0.3190	0.1463	1.3843	1135	97.11	6.13
0.1409	0.8130	0.3326	0.1952	1.3851	1137	95.15	8.09
0.1761	0.8266	0.3462	0.2441	1.3857	1139	93.25	9.99
0.2114	0.8402	0.3598	0.2930	1.3860	1141	91.42	11.82
0.2466	0.8538	0.3734	0.3418	1.3862	1143	89.65	13.59
0.2818	0.8674	0.3870	0.3907	1.3864	1145	87.94	15.30
0.3171	0.8810	0.4006	0,4396	1.3866	1147	86.28	16.96
0.3523	0.8946	0.4142	0.4885	1.3867	1149	84.67	18.57

Sp. Acoustic impedance $Z \times 10^{-5}$	Molar sound velocity R (m/sec)	Relative Association R_A	Solvation Number S_n	Inter molecular length L_f (Å)	β_s-β_{s0}/C (10^{12})	Apparent Molar Compressibility (φ_k) $10^2 \times cm^2/dyne$	Shears Relaxation Time τ_s
0.8734	0.0352	1.0182	0.1038	0.6404	-56.8203	-117.9500	39.3885
0.8903	0.0705	1.0368	0.2128	0.6337	-58.2596	-60.6091	40.3679
0.9073	0.1057	1.0553	0.3180	0.6272	-58.0450	-41.4342	41.3022

0.9244	0.1409	1.0739	0.4196	0.6209	-57.4432	-31.8029	42.1939
0.9415	0.1761	1.0925	0.5178	0.6146	-56.7061	-25.9909	43.0450
0.9587	0.2114	1.1111	0.6127	0.6086	-55.9166	-22.0898	43.8577
0.9759	0.2466	1.1298	0.7045	0.6027	-55.1095	-19.2816	44.6339
0.9932	0.2818	1.1485	0.7933	0.5969	-54.3013	-17.1575	45.3753
1.0105	0.3171	1.1671	0.8793	0.5912	-53.5009	-15.4902	46.0837
1.0279	0.3523	1.1859	0.9627	0.5857	-52.7129	-14.1431	46.7606

TABLE (3)

System: Chloro-m-xynol + Acetone at 40°C (Isentropic Compressibility of Acetone = 107.58 $\times$ 10^{-12} dyne/cm^2)

Molar Conc. of Chloro-m-xynol (mole/L)	Density ρ (g/mL)	Viscosity η (c.p.)	Sp. Viscosity η_{sp} (c.p.)	Reduced Viscosity η_{red} (c.p.)	Ultrasound velocity (m/sec)	Isentropic Compressibility β_s ($10^{12} \times$ cm^2/dyne)	Lowering Compressibility $\beta_{s0} - \beta_s$ ($10^{12} \times$ cm^2/dyne)
0.0352	0.7626	0.2416	0.0592	1.6808	1115	105.48	2.08
0.0705	0.7762	0.2552	0.1189	1.6870	1117	103.26	4.30
0.1057	0.7898	0.2688	0.1785	1.6891	1119	101.12	6.44
0.1409	0.8034	0.2824	0.2382	1.6901	1121	99.05	4.51
0.1761	0.8170	0.2960	0.2978	1.6907	1123	97.05	10.50
0.2114	0.8306	0.3096	0.3575	1.6912	1125	95.13	12.43
0.2466	0.8442	0.3232	0.4171	1.6915	1127	93.26	14.30
0.2818	0.8578	0.3368	0.4768	1.6917	1129	91.46	16.10
0.3171	0.8714	0.3504	0.5364	1.6918	1131	89.71	17.85
0.3523	0.8850	0.3640	0.5961	1.6920	1122	88.02	19.64

Sp. Acoustic impedance $Z \times 10^{-5}$	Molar sound velocity R (m/sec)	Relative Association R_A	Solvation Number S_n	Inter molecular length L_f (Å)	$\beta_s-\beta_{s0}/C$ (10^{12})	Apparent Molar Compressibility (φ_k) $10^2 \times$cm^2/dyne	Shears Relaxation Time τ_s
0.8503	581.41	1.0185	0.1047	0.6593	-59.7265	-106.0609	33.9773
0.8670	592.14	1.0372	0.2151	0.6524	-61.3557	-55.0550	35.1350
0.8838	602.87	1.0560	0.3215	0.6456	-61.1573	-37.9789	36.2402
0.9006	613.62	1.0749	0.4243	0.6389	-60.5302	-29.3880	37.2958
0.9175	624.38	1.0937	0.5236	0.6325	-59.7529	-24.1934	38.3044
0.9344	635.15	1.1126	0.6195	0.6262	-58.9170	-20.6986	39.2684
0.9514	645.93	1.1315	0.7123	0.6200	-58.0608	-18.2631	40.1899
0.9685	656.72	1.1504	0.8020	0.6140	-57.2026	-16.2631	41.0712
0.9856	667.53	1.1693	0.8888	0.6081	-56.3523	-14.7567	41.9141
1.0027	678.34	1.1883	0.9729	0.6023	-55.5151	-13.5359	42.7206

4. Conclusions

The ultrasonic velocity throws light on evaluation of various thermodynamics parameters of chloro-m-xynol in acetone i.e. non-aqueous medium mixture. These results confirm that there is a significant interaction between chloro-m-xynol- acetone molecules in dilute solutions. The observed variation in these param.eters with respect to the molarities of chloro-m-xynol indicated ion-solvent and ion-ion interactions were present, ion-solvent interactions were much observed at lower molarities and ion-ion interactions were very apparent at higher molarities of chloro-m-xynol in acetone.

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