Available online at www.elixirpublishers.com (Elixir International Journal)

Condensed Matter

Elixir Condensed Matter 100 (2016) 43822-43826

ISSN: 2229-712X

Study of molecular interactions in ternary aqueous solutions of SDS with dye and enzyme in the presence of sodium sulphate

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ARTICLE INFO

Article history:

Received: 17 September 2016;
Received in revised form:
17 November 2016;
Accepted: 28 November 2016;

Keywords

SDS,
Lipase,
Methylene blue,
Hydration number,
Internal pressure.

ABSTRACT

Surfactants are basic cleaning agents in soaps and detergents. Most surfactants are less toxic to aquatic organisms due to their surface activity which will react with the biological membranes of the organisms. The study of surfactant materials along with the other additive compounds seeks more attention because of their increasing industrial and domestic applications. Dyes and enzymes which are the important ingredient in detergents have their own cleaning properties. Nowdays, lipases stand amongst the most important biocatalysts carrying out novel reactions in both aqueous and non-aqueous media. They also possess massive applications in various areas of industrial microbiology and biotechnology. This statement is well documented by the enormous number of research investigations undertaken in the last one and a half decades. Lipases show immense versatility regarding their catalytic behaviour. Therefore, there is a lot of scope to search for newer lipases with desired selectivity and substrate tolerance. The present study is an attempt to investigate the thermodynamic properties like internal pressure, free volume, $\Delta\pi_i$, molar and molal hydration numbers of anionic surfactant SDS with sodium sulphate in the presence of dye (methylene blue) and an enzyme (lipase) at 303K, 313K and 323K temperatures. The determination of the above properties has thrown light into the various types of molecular interactions existing in aqueous ternary solutions.

Introduction

Physicochemical behaviour and molecular interactions occurring in a variety of liquid mixtures and solutions can be studied with the help of ultrasonic velocity. There has been an increasing interest in the study of molecular interactions and a number of experimental techniques have been used to investigate the same in binary solutions, since data on sound velocity offers a convenient method for determining certain thermodynamical properties of liquids and solutions, which are not obtained by other methods[1]. By reducing the surface tension of water, surfactants improve the cleaning performance by enabling the solution to wet a surface quickly and effectively, and hence the soil can be readily loosened and removed. SDS is highly effective anionic surfactant and used in any task requiring removal of oily stains and residues. Detergent filler like sodium sulphate is added to surfactants to improve the detergency. The addition of fillers helps in lowering the production of foam thereby making the presence of detergents in waste water less obvious. Sodium sulphate is a very cheap material used in powdered home laundry detergents, consuming approximately 50% of world production[2]. It helps in "levelling", reducing negative charges on fibres so that dyes can penetrate evenly. Unlike the alternative sodium chloride, it does not corrode the stainless steel vessels used in dyeing. Methylene blue is a basic dye which is positively charged and water soluter. They are largely used to dye acrylic fibres. They owe their substantivity to the electrostatic attraction between the dye and the anions formed from acid groups on the polymer chains of the fiber. Enzymes used in detergent formulations are stable at high pH and temperature which removes protein and lipid stains. Lipase used detergent become biodegradable, leaves no harmful residues, have no negative impact on sewage treatment processes and do not have risk for aquatic life[3]. They can reduce the environmental load of detergent products because they save energy by enabling a lower wash temperature. To the best of our knowledge, this is the first attempt to study the thermodynamic properties of SDS added with dye and lipase.

Materials and Methods

Analar grade samples of Sodium dodeyl sulphate, sodium sulphate, methylene blue and lipase were used for the present investigation. Ternary solutions of sodium dodecyl sulphate (10 mM) with dye (0.05mM), enzyme (0.004mM) added with filler sodium sulphate of different concentrations (2 mm to 14 mm) were prepared.

Ultrasonic velocity measurement

Ultrasonic velocity was measured using ultrasonic interferometer of fixed frequency 2MHz (Model F-81, Mittal enterprises, New Delhi). The measuring cell of interferometer is a specially designed double walled vessel with provision for maintaining temperature constant. A digital constant temperature bath operating in the temperature range 10C to 90C with an accuracy of $\pm$ 0.1°C has been used to circulate water through the outer jacket of double walled measuring cell containing the experimental liquid/ solution.

Density measurement

The density of surfactant solutions are measured using 10ml of specific gravity bottle. The specific gravity bottle with experimental solution is immersed in a temperature controlled water bath. The density was measured using this formula,

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$\rho = (m_2-m)/(m_1-m) \times \rho_0$.

Where, ρ_0 is the density of water at particular temperature, m_1 and m_2 are the mass of the distilled water and experimental solution.

Viscosity measurement

The viscosities of the solutions are measured using Ostwald's viscometer with the experimental solution is immersed in a temperature controlled water bath. The time of flow was measured using a stop watch with an accuracy of 0.1sec. The viscosity was determined using the relation,

$$\eta_s = \eta_w \frac{\rho_s t_s}{\rho_w t_w}$$

where, η_s and ρ_s are the viscosity and density of solution respectively. η_w and ρ_w are the corresponding values for water. The viscosity of water at various temperatures has been taken from literature.

Theoretical formulations

Using the measured data of velocity, density and viscosity values, the following thermodynamical parameters have been calculated using the standard relations,

Internal pressure

$$\pi_i = bRT\left(\frac{k\eta}{U}\right)^{\frac{1}{2}}\left(\frac{\rho^{\frac{2}{3}}}{M^{\frac{7}{6}}}\right) \text{Nm}^{-2}$$

Free volume

$$V_f = \left(\frac{MU}{k\eta}\right)^{\frac{3}{2}} \text{m}^3\,\text{mol}^{-1}$$

Change in internal pressure

$$\Delta\pi_i = \pi_i - \pi_0$$

Molar hydration number

$$n_h = (1/n_2)\left[n_1 - \frac{\beta}{\beta_0}N\right]$$

Molal hydration number

$$n_h' = \frac{n_1}{n_2}\left(1 - \frac{\beta}{\beta_o}\right)$$

where, U = ultrasonic velocity (m/s), ρ = density (Kg/m^3), η = viscosity (Nsm^{-2}), M_{eff} = effective molecular weight, b = packing factor, R = gas constant, T = temperature (K), k = temperature independent constant, K = Boltzmann's constant, n_h = molar hydration number, n_h' = molal hydration number, n_1 = number of solvent molecules, n_2 = number of solute molecules, β & β_0 = compressibility (Kg^{-1}ms^2) of the solution and solvent respectively.

The concept for coefficients of internal pressure and free volume with respect to concentration is initiated by Suryanarayana and Kuppusamy[4]. They conferred the general equation for them as,

$$\pi_i = \pi_o + Am^2 + Bm$$

where π_o is the internal pressure of the solvent, m the molality, A and B are constants, holds good for electrolytes and non electrolytes. A similar relation holds for the free volume,

$$V_f = V_{f(0)} + Cm^2 + Dm$$

The $V_{f(0)}$ is the free volume of solvent and C, D are constants.

Results and Discussions

In this study, the internal pressure (π_i), free volume (V_f), $\Delta\pi$i and molar, molal hydration numbers for the two ternary systems viz., sodium sulphate in aqueous mixture of SDS-dye and SDS-lipase were computed from the measured values of ultrasonic velocity, density and viscosity at various temperatures are represented in table -1 & 2 respectively. The values of A, B coefficients of internal pressure and C, D coefficients of free volume were presented in table - 3. From the variations of the values with the concentration and temperatures of the solutions the interaction occurring in the ternary surfactant solutions were studied.

The measurement of internal pressure is important in the study of the thermodynamic properties of liquids. The internal pressure is the cohesive force, which is a resultant of forces of attraction and forces of repulsion between the molecules[5-6]. The internal pressure increases with the increase in concentration and decreases with respect to temperature in both the systems. This increase in internal pressure indicates the incline in cohesive forces with the rise in forces of attraction. It is also attributed to the association of solute-solvent molecules through hydrogen bonding. The decrease of internal pressure with temperature may be due to breaking up of hydrogen bond in the solvent medium and contact ion paring may reduce the association between ion and solvent.

The free volume value decreases with increase in concentration in both the ternary systems studied. The decrease in free volume with increase of concentration is due to the presence of tightly packed solvent molecules around the ions. This indicates a significant interaction between the ions and solvent molecules. The free volume shows the reverse trend of internal pressure. Its value rises with the increase in temperature. When the temperature is increased there is a tendency for the ions to move away from each other reducing the possibility for interaction, which may further reduces the cohesive forces. This weakening of molecular association leads to a larger free volume available for molecular motion with temperature. The variation of internal pressure for SDS with methylene blue and SDS with lipase with varying concentration of sodium sulphate at different temperatures is depicted in figures – 1 & 2.

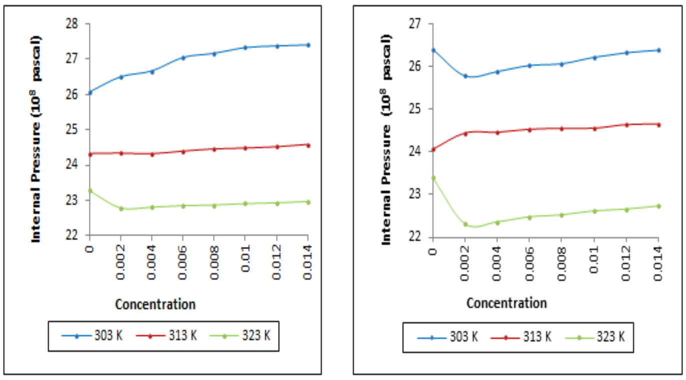

Figure 1 & 2. Internal pressure of ternary solutions of SDS with methylene blue and lipase in the presence of sodium sulphate vs Concentration

The molecules of liquid are not closely packed and as such there is always some free space between them. This free space is known as free volume. It is a significant factor in explaining the free space and its dependent properties have close connection with molecular structure[7] and it may show

Table 1. Values of internal pressure, free volume, change in internal pressure, molar and molal hydration numbers of ternary solutions of sodium dodecyl sulphate combined with methylene blue in the presence of sodium sulphate at different temperatures

Molarity (M)	Internal Pressure (10^8 N/m^2)	Free Volume (10^{-8} m^3 mol^{-1})	$\Delta\pi i$	Molar Hydration number	Molal Hydration number
303K					
0.002	26.5037	2.0920	0.4294	-1816.2	-1718.4
0.004	26.6692	2.0556	0.5949	-734.57	-693.93
0.006	27.0511	1.9715	0.9768	-365.56	-342.70
0.008	27.1689	1.9457	1.0946	-208.25	-190.57
0.010	27.3314	1.9161	1.2571	-114.35	-107.27
0.012	27.3789	1.9081	1.3046	-40.947	-37.406
0.014	27.4083 o	1.9055	1.3340	8.8786	8.3522
313K					
0.002	24.3462	2.9583	0.0148	-1500.0	-1473.8
0.004	24.3627	2.9559	0.0313	-542.68	-537.75
0.006	24.4005	2.9495	0.0691	-311.44	-319.84
0.008	24.4641	2.9314	0.1327	-165.76	-177.45
0.010	24.4859	2.9235	0.1545	-80.825	-89.846
0.012	24.5234	2.9167	0.1920	-8.2569	-20.813
0.014	24.5890	2.8939	0.2576	34.465	23.644
323K					
0.002	22.7913	3.9252	-0.4863	-1794.2	-1706.3
0.004	22.8127	3.9146	-0.4649	-760.40	-717.15
0.006	22.8544	3.8986	-0.4233	-380.62	-358.38
0.008	22.8732	3.8939	-0.4044	-229.48	-217.09
0.010	22.9120	3.8733	-0.3656	-111.57	-100.96
0.012	22.9355	3.8650	-0.3421	-52.248	-45.454
0.014	22.9712	3.8497	-0.3064	-11.221	-6.6463

Table 2. Values of internal pressure, free volume, change in internal pressure, molar and molal hydration numbers of ternary solutions of sodium dodecyl sulphate combined with lipase in the presence of sodium sulphate at different temperatures

Molarity (M)	Internal Pressure (10^8 N/m^2)	Free Volume (10^{-8} m^3 mol^{-1})	$\Delta\pi i$	Molar Hydration number	Molal Hydration number
303K					
0.002	25.7830	2.2685	-0.620	-490.004	-423.523
0.004	25.8848	2.2466	-0.518	-83.8845	-65.2606
0.006	26.0262	2.2127	-0.377	17.1621	24.4939
0.008	26.0676	2.2052	-0.336	77.4741	78.5160
0.010	26.2182	2.1692	-0.185	103.163	101.910
0.012	26.3256	2.1463	-0.078	123.664	119.077
0.014	26.3849	2.1368	-0.018	135.669	127.459
313K					
0.002	24.4452	2.911	0.0238	-222.478	-142.907
0.004	24.4632	2.9034	0.0418	11.1052	53.5960
0.006	24.5341	2.8802	0.1127	85.3547	110.933
0.008	24.5535	2.8766	0.1321	134.051	149.390
0.010	24.5579	2.8762	0.1365	144.649	156.041
0.012	24.6428	2.8522	0.2214	147.405	152.623
0.014	24.6541	2.8512	0.2327	155.192	157.817
323K					
0.002	22.3138	4.1744	-1.079	-111.561	-34.1473
0.004	22.3642	4.1471	-1.029	54.8911	92.3987
0.006	22.4820	4.0946	-0.911	100.637	112.214
0.008	22.5272	4.0743	-0.866	135.556	140.865
0.010	22.6215	4.0269	-0.772	134.445	136.665
0.012	22.6619	4.0120	-0.731	148.520	146.855
0.014	22.7373	3.9770	-0.656	147.064	143.505

Table 3. Values of Coefficients of internal pressure and free volume of ternary solutions of sodium dodecyl sulphate combined with methylene blue and lipase in the presence of sodium sulphate at different temperatures

Temperature	Internal Pressure (N/m^2)		Free Volume ($m^3\ mol^{-1}$)	
	$A \times 10^3$	$B \times 10^2$	$C \times 10^3$	$D \times 10^2$
SDS+Methylene blue+Sodium sulphate				
303K	-8.480	2.09	2.70	-0.57
313K	1.270	0.01	-0.18	-0.02
323K	15.59	-2.05	-6.97	0.92
SDS+Lipase+Sodium sulphate				
303K	21.74	-2.55	-16.42	2.20
313K	-10.31	1.63	4.45	-0.68
323K	34.75	-4.55	-26.26	3.54

features about interactions like ion-solvent, dipole-dipole, solute-solvent interactions. The decrease of V_f (increase of π_i) indicates the formation of hard or tight solvation layer around the ion and increase of V_f (decrease of π_i) may be due to the formation of thin or loose solvation layer[8]. With the addition of solute to solvent, the structure of solvent is broken. The available space of solvent in the solution is reduced hence the solution becomes more compressed which decreases free volume with rise in concentration. When the temperature rises, the repulsive force between the solute and solvent is more and the free space availability is also increases. So, free volume increase with increasing temperature. Figures – 3 & 4 show the change in free volume for ternary SDS solutions of dye and lipase with increasing concentration of sodium sulphate. The increase in internal pressure and the decrease in free volume are enhanced and high in SDS + lipase + sodium sulphate than SDS + dye + sodium sulphate indicates that there exists a stronger solute-solvent interaction in lipase system.

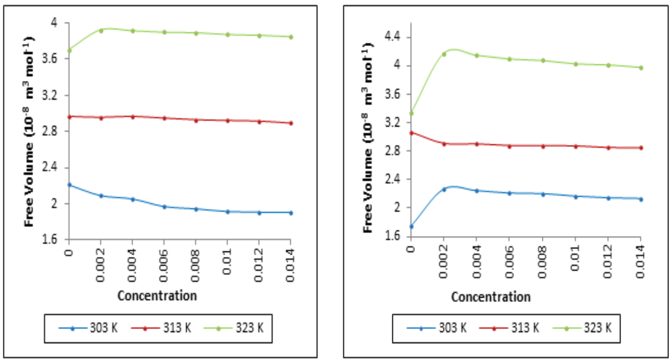

Figure 3 & 4. Free volume of ternary solutions of SDS with methylene blue and lipase in the presence of sodium sulphate vs Concentration

The difference in the internal pressure $\Delta\pi_i = \pi_i - \pi_0$ of the solution and the solvent can be positive or negative depending upon the electrolyte[9]. With the sign of $\Delta\pi_i$, structural making or breaking property of the solute is decided. If $\Delta\pi i$ is positive, the solute has the tendency to enhance the internal pressure of the solvent when added to it and if it is negative the internal pressure value will decrease, which indicates cohesive forces gets loosened with the addition of solute. The changes in $\Delta\pi_i$ values are graphically shown in figures 5 & 6. The $\Delta\pi_i$ value is found to be negative at higher temperature (323K) for dye system but it is negative for lipase system at both 303K and323K except at 313K. This result put on view that this 313K is established to be an optimum temperature for stain removal process in detergent action. However, lipase is said to have superior stain removing action than dye due to the remarkable ability of lipases to carry out a wide variety of chemical transformations.

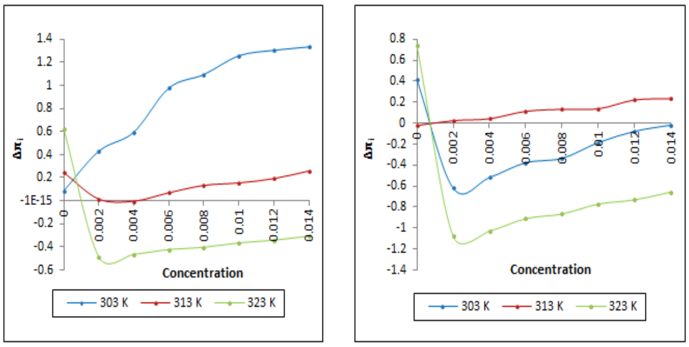

Figure 5 & 6. Change in internal pressure of ternary solutions of SDS with methylene blue and lipase in the presence of sodium sulphate vs Concentration

The values of coefficients of internal pressure and free volume of ternary solutions of sodium dodecyl sulphate combined with methylene blue and lipase in the presence of sodium sulphate at different temperatures are given in table -3. The temperature dependence of A, B, C and D for the ternary SDS solutions are studied. From the tabulation it is clear that the variation of C and D are opposite to that of A and B. Internal pressure is being the resultant of the attractive and repulsive forces in the system. Co-efficient A refers to the attractive component and B to the repulsive component. Thus, the effect of repulsive forces or cohesive forces in ion-solvent interaction is very well understood by $\Delta\pi_i$. In ternary surfactant solutions of methylene blue, A is found to be positive at all temperatures except at 303K. The coefficient B is found to be positive at all temperatures except at 323K. The coefficient B determines the sign of $\Delta\pi_i$. In the case of ternary lipase solutions, the coefficient A is positive except at 313K and B is negative except at 313K. This values are in accordance with the structural nature obtained by the $\Delta\pi i$ values. These consequences show the structure making nature and enhanced detergent action of enzyme lipase solutions at the optimum temperature 313K, whereas dye methylene blue functions only at high temperatures.

When a solute is dissolved in water, there is a volume contraction and a decrease in compressibility due to solute-solvent interaction. These interactions result from the splitting up of the solute into ions which are surrounded by a definite number of water molecules, which is described in terms of hydration.

The hydration number is a measure of number of solvent molecules that get attached with each ion of solute at a time during the process of interaction. While comparing the two systems, both molar and molal hydration numbers shows a negative value at all three temperatures of ternary solutions of SDS+dye, whereas it has a positive value for SDS+lipase solutions at all temperatures except at lower concentrations. Negative hydration number observed in ternary solutions of SDS+dye indicates that solvation is lesser due to the lack of solute molecules that tends to attached with solvent molecules. Hence, the solution has greater compressibility than that of solvent.

The positive value for SDS+lipase solutions indicates an appreciable solvation of solutes. This is an added support not only for the structure promoting nature of solute but also for the presence of a substantial dipole-dipole interaction of lipase and sodium sulphate molecules with solvent. This also suggests that the compressibility of the solution is less than that of the solvent. As a result solutes will gain mobility and have more probability of contacting solvent molecules[10]. This may enhance the interaction between solute and solvent ions[11].

The increasing values of hydration number shows the strength of interaction gets strengthened between solute and solvent molecules[11]. This increasing trend with the increase of concentration may be due to the excess availability of solvent molecules surrounding the ions or occurrence of ion pairing in these solutions. The molar and molal hydration numbers are graphically shown in figures 7 to 10. From the magnitude of molar and molal hydration numbers, it can be concluded that there is a stronger molecular association is found in SDS+lipase system than SDS+dye ternary solutions.

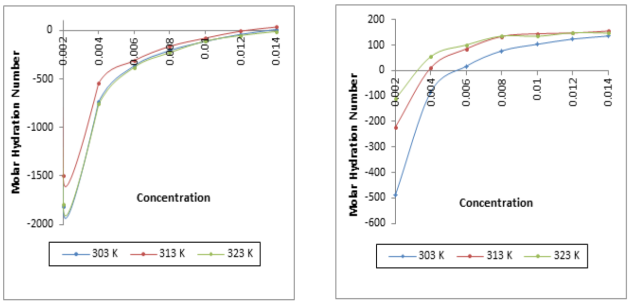

Figure 7 & 8. Molar hydration number of ternary solutions of SDS with methylene blue and lipase in the presence of sodium sulphate vs Concentration

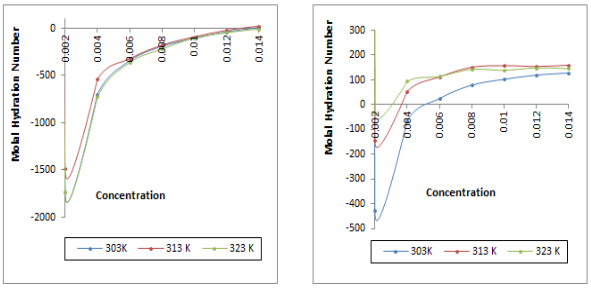

Figure 9 & 10. Molal hydration number of ternary solutions of SDS with methylene blue and lipase in the presence of sodium sulphate vs Concentration

Conclusion

Thermodynamical parameters like internal pressure, free volume and other related parameters were calculated from the measured values of density, viscosity and velocity of surfactant solutions. The variation of these parameters for the above systems provides useful information about the nature of intermolecular interactions existing in the solutions. All the thermodynamical parameters calculated have greater influence in lipase combined ternary surfactant solutions than that of methylene blue. Hence it is concluded that lipase works efficiently and removes stains from clothes and articles quickly and also they are readily biodegradable. Lipases have the following astonishing properties like general ease of handling, high stability towards temperatures and solvents, and convenient commercial availability which made their widespread popularity in detergent industries than methylene blue which are harmful to microbes present in soil.

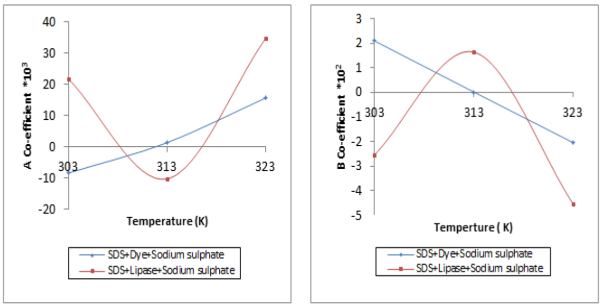

Figure 11 & 12 Internal pressure A & B coefficients of ternary solutions of SDS with methylene blue and lipase in the presence of sodium sulphate vs Temperature

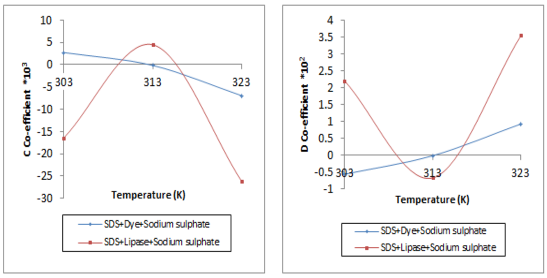

Figure 13 & 14 Free Volume C & D coefficients of ternary solutions of SDS with methylene blue and lipase in the presence of sodium sulphate vs Temperature

References

1. Rajeev Kumar Shukla., Dixitb S N., Pratima Jain., Preeti Mishra and Sweta Sharma., Orbital Electronic Journal of Chemistry, Campo Grande, 2(4), 356-364, (2010).
2. Renuka Devi K and Gomathiyalini A., Journal of Chemical and Pharmaceutical Research, 7(11), 707-714, (2015).
3. Fariha Hasan., Aamer Ali Shah., Sundus Javed and Abdul Hameed., African Journal of Biotechnology, 9(31), 4836-4844, (2010).
4. Suryanarayana C Vand Kuppusamy J., Journal of Acoustical Society of India, 9, 4, (1981).
5. Richards T W., Chemical Review, 2, 315, (1925).
6. Vanderwaals J D., Essay on the Continuity of the Gaseous and Liquid States, London, (1873).
7. Shanmugapriya C., Nithya S., Velraj and Kanappan A N., International Journal of Advanced Science and Technology, 18, (2010).
8. Shende A T., Tabhane P V and Tabhane V A., International Journal of Pharmaceutical, Chemical and Biological Sciences, 2(4), 600-625, (2012).
9. Lalitha V., Ph.D., Thesis, Study of Internal Pressure, free volume and conductivity of Electrolyte solutions and molecular interaction in liquid mixtures, January (1986).
10. Thirumaran S and Mary Christina Gardilya., Recent Research in Science and Technology, 3(8), 56-63, (2011).
11. Palani R., Geetha A., Saravanan A and Vijaya Shanbhag., Rasayan J.Chem., 1(3), 495-502, (2008).