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# Molecular interactions by ultrasonic velocity, viscosity and density measurements in binary mixtures at 298.15 K

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## ABSTRACT

*The ultrasonic velocity (U), viscosity ($\eta$) and density ($\rho$) at 298.15 K have been measured in the binary mixture of methanol and ethanol with p-anisaldehyde over entire range of mole fraction.  From the experimental data, various acoustical parameters such as acoustic impedance (Z), relative association ($R_A$), internal pressure ( $_{int}$), intermolecular free length ($L_F$), adiabatic compressibility ($K_s$), and apparent molar volume (V ).  The results were interpreted in terms of molecular interaction between the components of the mixtures.*

**Keywords**: Density, Viscosity, Ultrasonic velocity, acoustic properties, molecular interaction.

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## INTRODUCTION

The ultrasonic velocities (U), viscosity ($\eta$) and Density ($\rho$) measurements find wide applications in characterizing the physico-chemical behaviour of the binary liquid mixtures.[1-3]  These studies find extensive application in chemical engineering design, process simulation, solution theory and molecular dynamics [4-7].  These properties are extensively used to estimate the thermodynamics properties and predict the intermolecular interactions.  P-anisaldehyde is chemically known as 4-methoxy benzaldehyde and used in perfume and pharmaceutical industries. These physico-chemical analyses are used to handle the mixtures of alcohols, aldehyde, ketones, hydrocarbons etc.

The study of molecular association in binary liquid mixture having 1-alkanol group as one of component is of particular interest since alcohols are strongly self associated liquids having three dimensional network of hydrogen bonding and can be associated with any other group having some degree of polar attraction.[8-11]  p-anisaldehyde is aprotic solvent, strongly associated due to highly polar C = 0 group in the molecule and large dipole moment.  The variation in ultrasonic velocity gives information about the bonding between molecules and formation of complexes at various concentration and temperature through molecular interactions.[12-15]

In view of the importance mentioned, an attempt has been made to elucidate the molecular interactions in the mixtures of methanol and ethanol with p-anisaldehyde respectively at 298.15 K with regards to adiabatic compressibility ($K_s$), intermolecular free length ($L_f$), acoustic impedance (z), relative association ($R_A$), internal pressure ($\pi_{int}$) and apparent molar volume ($\phi_v$), from ultrasonic measurements.

## MATERIALS AND METHODS

The chemicals methanol, ethanol and p-anisaldehyde used were of analytical grade (AR) and spectroscopic reagent (SR) grades of minimum assay of 99.9 % obtained from Hi-media and Sd fine chemicals, India, which are used as

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such without further purification. The densities of pure components and binary mixtures were measured by using a Bi-capillary pycometer. The purities of the above chemicals were checked by density determination at 298.15 K, the uncertainty is less than $\pm\ 1 \times 10^{-4}$ gcm$^{-3}$. The binary liquid mixtures of different known concentrations were prepared in stopper measuring flasks. The weight of the sample was measured using electronic digital balance with an accuracy of $\pm\ 0.1$ mg. An Ubbelohde viscometer (20 ml) was used in the viscosity measurement and efflux time was determined using a digital clock to within $\pm\ 0.015$. The ultrasonic velocity (U) in liquid mixtures have been measured at 298.15 K using an ultrasonic interferometer (Mittal type, model f-83) working at 2 MHz frequency. The accuracy of sound velocity was $\pm\ 0.1$ ms$^{-1}$. An electronically digital double walled measuring cell made up of steel containing the experimental solution at the desired temperature with accuracy of $\pm\ 0.01$ K.

**Theory :**
From these experimental values, $K_s$, $L_f$, $Z$, $R_A$, $\pi_{int}$, and $V_{\phi,1}$ have been calculated using the following equations -

$$K_s \qquad = \frac{1}{PU^2} \qquad\qquad\qquad\qquad ----\ (1)$$

$$L_f \qquad = K.\left(K_s\right)^{1/2} \qquad\qquad\qquad ----\ (2)$$

where    K is a Jacoben's constant.

$$Z \qquad = P.\ U \qquad\qquad\qquad\qquad ----\ (3)$$

$$R_A \qquad = \left(\frac{L_f}{L_f^{'}}\right)^3 \qquad\qquad\qquad ----\ (4)$$

$L_f^{'}$ is the free length of the ideal mixture.

$$\therefore \qquad \pi_{int_{12}} \qquad = bRT\left(\frac{K\eta_{1/2}}{U_{12}}\right)^{1/2} \Big/ M_{12}^{7/6} \qquad ----\ (5)$$

where    'b' is a constant, 'k' is an absolute temperature in Kelvin
$\eta_{12}$ is viscosity in Nsm$^{-2}$, '$U_{12}$' is the ultrasonic velocity in m/s and
$M_{12}$ is the mean molecular weight of mixture

$M_{12}$ is given by
$$M_{12} \qquad = X_1\ M_1 + X_2\ M_2 \qquad\qquad ----\ (6)$$

$X_1$ and $X_1$ mole fraction of solute (1) and solvent (2)
$M_1$ and $M_2$ - Molecular weight of solute (1) and solvent (2)

$$V_{,1} \qquad = \frac{X_2\ M_2\ (P_2 - P_{12})}{X_1\ P_2\ P_{12}} + \frac{M_1}{P_{12}} \qquad ----\ (7)$$

where,    $X_1$ and $X_2$ are the mole fractions of component (1) and (2)
$P_2$ and $P_{12}$ are the densities (2) and liquid mixtures
$M_1$ and $M_2$ are the molecular weights of components (1) and (2) respectively.

## RESULTS AND DISCUSSION

The measured parameters viz. density ($\rho$), viscosity ($\eta$) and ultrasonic velocity (U) and calculated parameters such as adiabatic compressibility ($K_s$), intermolecular free length ($L_f$), acoustic impedance (z), relative association ($R_A$), internal pressure ($\pi_{int}$) and apparent molar volume ($V_{,1}$) for the System 1 : methanol (1) + p-anisaldehyde (2) at 298.15 K are given n Table 1 and 2, for the System 2 : Ethanol (1) + p-anisaldehyde (2) at 298.15 K are given in Table 3 and 4.From the Table 1 and Table 3, it is observed that both the system (I) and (II), ultrasonic velocity decreases with concentration of methanol (1) and ethanol (1) in p-anisaldehyde. This indicates that, strong interaction observed at lower concentration of alcohols. The density values also have the same trends with velocity in the system (I) system (II). Density decreases due to the decreased electrostriction in that solution. This less electrostriction increases the volume and hence decreases in the density.[16] Viscosity decreases in system I and system II, suggesting thereby more association between solute and solvent molecules.[17] From the Table 1 and Table 3, it is observed that, adiabatic compressibility (Ks) increases with increase in the concentration of methanol

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(1) and ethanol (1) in p-anisaldehyde (2). This increase in structural disorder of p-anisaldehyde may be result in less cohesion, and leads to a increase in $K_s$. The increase in $K_s$ results in an decrease in the value of U.[18]

The parameter, the free length ($L_f$) is calculated from the ultrasonic velocity (U) and adiabatic compressibility ($K_s$). It is observed that $L_f$, increases with the concentration of methanol (1), and ethanol (1) in p-anisaldehyde (2). Increase in intermolecular free length leads to negative deviation in sound velocity and positive deviation in compressibility. This indicates that the molecules are away from each other in the both system.

The computed other parameters like acoustic impedance (z), relative association ($R_A$), internal pressure ($\pi_{int}$) and apparent molar volume ($V_{\phi,1}$) of system (I) and system (II) are given in Table 2 and Table 4 respectively. Acoustic impedance (z) found to be almost reciprocal of $K_s$. The acoustic impedance decreases with increase adiabatic compressibility ($K_s$) with increase in concentration of methanol (1) and ethanol (1) in p-anisaldehyde (2). The decrease in z with concentration can be explained on the basis of hydrophobic interaction between solute and solvent molecules [19-21] which increases the intermolecular distance making relative wider gap between the molecules.

The relative association ($R_A$) decrease with increase in concentration upto $X_1 = 0.4 - 0.5$ and then increases of methanol (1) and ethanol (1) in p-anisaldehyde due to increase in electrostatic attraction. The internal pressure ($\pi_{int}$) increases with increase the concentration of alkanols in p-anisaldehyde in both the systems I and II due to decrease in free volume and close association between solute and solvent. Thus, a progressive decrease in free volume and increase in internal pressure in methanol + p-anisaldehyde than ethanol + p-anisaldehyde mixtures clearly indicates the existence of ion-solvent interaction is more in system I, due to which the structural arrangement is considerably affected[22-23]. The apparent molar volume is the practically available molar volume of the solute. In both the systems, the apparent molar volume increases with increase the concentration of methanol and ethanol (solute) in the p-anisaldehyde [24-25].

**Table 1: Values of density (ρ), viscosity (η), ultrasonic velocity (U), adiabatic compressibility ($K_s$) and intermolecular free length ($L_f$) at different concentrations for binary system of Methanol (1) + p-anisaldehyde (2) at 298.15 K**

| Conc. $X_1$ | Density ρ (kg/m³) | Viscosity η x 10⁻³ (kg/m³) | Ultrasonic velocity U (m/s) | Adiabatic compressibility $K_s$ x 10⁻¹⁰ (Pa⁻¹) | Intermolecular free length $L_f$ x 10⁻¹⁰ (m) |
|---|---|---|---|---|---|
| 0.0000 | 1.1159 | 4.2025 | 1526.8 | 384.42 | 0.3874 |
| 0.1227 | 1.1074 | 3.5601 | 1517.6 | 392.50 | 0.3915 |
| 0.2453 | 1.0972 | 2.9942 | 1508.4 | 400.57 | 0.3955 |
| 0.3312 | 1.0867 | 2.6152 | 1472.5 | 418.07 | 0.4039 |
| 0.4171 | 1.0723 | 2.2846 | 1463.6 | 435.35 | 0.4123 |
| 0.5090 | 1.0517 | 1.9654 | 1441.2 | 469.16 | 0.4280 |
| 0.6600 | 1.0063 | 1.4929 | 1399.2 | 507.59 | 0.4452 |
| 0.7481 | 0.9709 | 1.2309 | 1357.2 | 559.16 | 0.4673 |
| 0.8101 | 0.9402 | 1.0467 | 1315.2 | 614.89 | 0.4850 |
| 0.9185 | 0.8667 | 0.7286 | 1265.2 | 690.83 | 0.5194 |
| 0.9625 | 0.8272 | 0.6162 | 1202.0 | 995.47 | 0.6234 |
| 1.0000 | 0.7864 | 0.5513 | 1098.0 | 1054.76 | 0.6417 |

**Table 2: Calculated values of acoustic impedance (z), relative association ($R_A$), internal pressure ($\pi_{int}$) and apparent molar volume ($V_{\phi,1}$) at different concentrations for binary system of Methanol (1) + p-anisaldehyde (2) at 298.15 K**

| Conc. $X_1$ | Acoustic z x 10⁻³ (kg S⁻¹ m⁻³) | Relative association $R_A$ | Internal pressure $\pi_{int}$ (Pa) | Apparent molar volume $V_{\phi,1}$ x 10⁻³ (m³ mol⁻¹) |
|---|---|---|---|---|
| 0.0000 | 1703.76 | 1.0000 | 58509.01 | |
| 0.1227 | 1687.82 | 0.3349 | 59721.18 | 36.5943 |
| 0.2453 | 1655.02 | 0.3078 | 60933.34 | 35.5824 |
| 0.3312 | 1612.22 | 0.2799 | 62773.64 | 36.1116 |
| 0.4171 | 1569.42 | 0.2521 | 64613.93 | 36.8064 |
| 0.5090 | 1478.96 | 0.2431 | 69851.14 | 37.6464 |
| 0.6600 | 1408.02 | 0.2698 | 73208.28 | 38.6854 |
| 0.7481 | 1317.71 | 0.3145 | 78098.39 | 39.1366 |
| 0.8101 | 1236.55 | 0.3723 | 84032.84 | 39.4248 |
| 0.9185 | 1144.12 | 0.4605 | 90817.33 | 40.0825 |
| 0.9625 | 911.57 | 0.8752 | 103644.8 | 40.307 |
| 1.0000 | 863.47 | 1.0000 | 106789.8 | |

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**Table 3: Values of density (ρ), viscosity (η), ultrasonic velocity (U), adiabatic compressibility (Kₛ) and intermolecular free length (L𝒻) at different concentrations for binary system of ethanol (1) + p-anisaldehyde (2) at 298.15 K**

| Conc. $X_1$ | Density ρ (kg/m³) | Viscosity η x 10⁻³ (kg/m³) | Ultrasonic velocity U (m/s) | Adiabatic compressibility $K_s$ x 10⁻¹⁰ (Pa⁻¹) | Intermolecular free length $L_f$ x 10⁻¹⁰ (m) |
|---|---|---|---|---|---|
| 0.0000 | 1.1159 | 4.2025 | 1526.8 | 384.424 | 0.3874 |
| 0.0935 | 1.1052 | 3.7790 | 1518.4 | 392.79 | 0.3916 |
| 0.1869 | 1.0933 | 3.3911 | 1510.0 | 401.15 | 0.3958 |
| 0.3318 | 1.0702 | 2.8220 | 1478.4 | 427.51 | 0.4086 |
| 0.4630 | 1.0416 | 2.3954 | 1434.4 | 466.61 | 0.4268 |
| 0.5799 | 1.0085 | 2.0512 | 1393.2 | 510.85 | 0.4466 |
| 0.6569 | 0.9815 | 1.8611 | 1376.8 | 537.49 | 0.4511 |
| 0.7464 | 0.9443 | 1.6458 | 1335.2 | 594.02 | 0.4816 |
| 0.8324 | 0.9012 | 1.4314 | 1276.0 | 681.52 | 0.5159 |
| 0.8873 | 0.8689 | 1.3194 | 1223.6 | 768.69 | 0.5479 |
| 0.9454 | 0.8283 | 1.1884 | 1201.2 | 836.72 | 0.5716 |
| 1.000 | 0.7851 | 1.0826 | 1173.6 | 924.77 | 0.6009 |

**Table 4: Calculated values of acoustic impedance (z), relative association (R𝐴), internal pressure (π𝒊ₙₜ) and apparent molar volume (V𝜙,₁) at different concentrations for binary system of ethanol (1) + p-anisaldehyde (2) at 298.15 K**

| Conc. $X_1$ | Acoustic z x 10⁻³ (kg $S^{-1}$ m⁻³) | Relative association $R_A$ | Internal pressure $\pi_{int}$ (Pa) | Apparent molar volume $V_{\phi,1}$ x 10⁻³ (m³ mol⁻¹) |
|---|---|---|---|---|
| 0.0000 | 1703.76 | 1.0000 | 58509.01 | |
| 0.6935 | 1677.32 | 0.6409 | 59655.42 | 47.6777 |
| 0.1869 | 1650.88 | 0.5454 | 60801.83 | 47.6058 |
| 0.3318 | 1582.18 | 0.4499 | 63262.79 | 47.9083 |
| 0.4630 | 1494.07 | 0.4334 | 66663.98 | 48.5575 |
| 0.5799 | 1405.04 | 0.4497 | 70313.42 | 49.1509 |
| 0.6569 | 1351.33 | 0.4642 | 73166.22 | 49.5499 |
| 0.7464 | 1260.83 | 0.5216 | 77462.96 | 49.9652 |
| 0.8324 | 1149.93 | 0.6311 | 82326.57 | 50.3164 |
| 0.8873 | 1063.19 | 0.7541 | 86907.81 | 50.5219 |
| 0.9454 | 994.55 | 0.8563 | 90357.16 | 50.8196 |
| 1.0000 | 921.39 | 1.0000 | 94784.34 | |
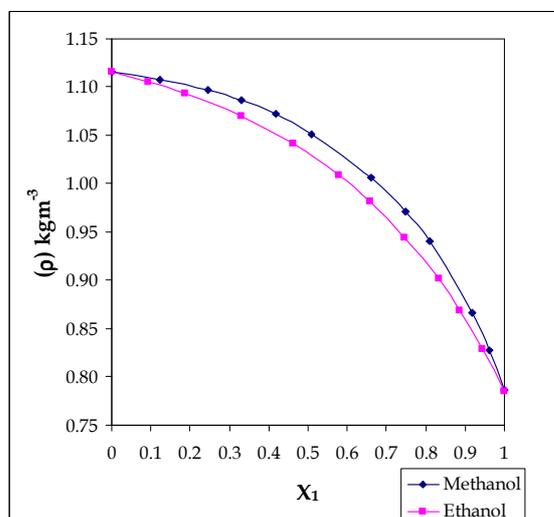


**Fig. 1 (A) Density (ρ) Vs. mole fraction for binary systems of methanol (1) and ethanol (1) with p-anisaldehyde at 298.15 K**
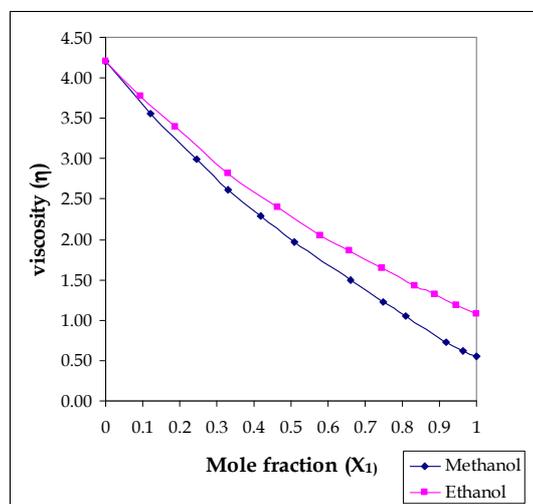


**Fig. 1 (B) Viscosity (η) Vs. mole fraction for binary systems of methanol (1) and ethanol (1) with p-anisaldehyde at 298.15 K**

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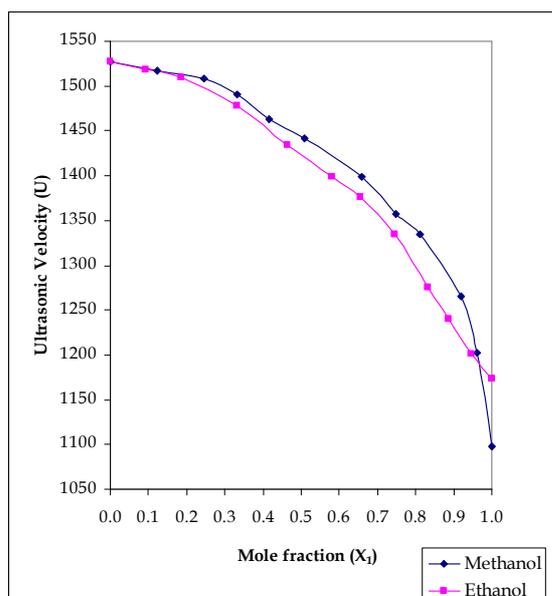


**Fig. 1 (C) Ultrasonic velocity (U) Vs. mole fraction for binary systems of methanol (1) and ethanol (1) with p-anisaldehyde at 298.15 K**
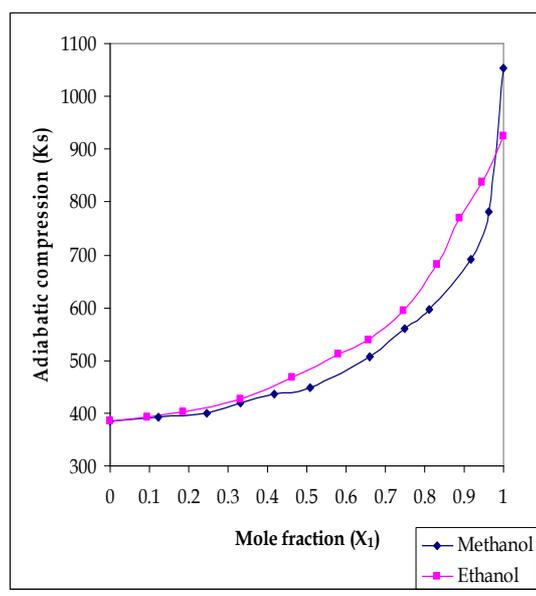


**Fig. 1 (D) Adiabatic compression ($K_s$) Vs. mole fraction for binary systems of methanol (1) and ethanol (1) with p-anisaldehyde at 298.15 K**
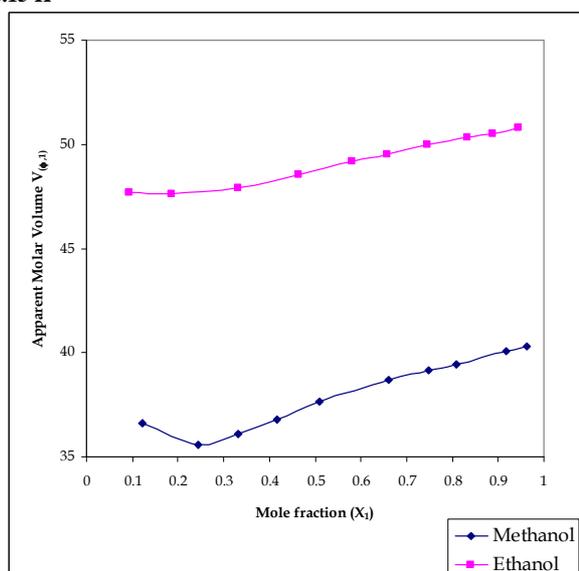


**Fig. 1 (E) Apparent molar volume $V_{(\phi,1)}$ Vs. mole fraction for binary systems of methanol (1) and ethanol (1) with p-anisaldehyde at 298.15 K**

## CONCLUSION

This paper reports experimental data for density viscosity and ultrasonic velocity for binary mixture of methanol + p-anisaldehyde and ethanol + p-anisaldehyde. Over entire range of mole fraction at 298.15 K from these experimental data the related parameters were calculated. The observed decrease of ultrasonic velocity indicates the solute-solvent interaction. The existence of molecular interaction in solute-solvent is favoured in System I and II, confirmed from the U, $\rho$, $\eta$, $K_s$, $L_f$, z, $R_A$, $\pi_{int}$ and $V_{(\phi,1)}$ data. The existence of molecular interaction in the mixture is in the order methanol > ethanol.

## REFERENCES

[1] Mehra K.S., *Indian J. Pure and Appl Phy*, **2000**, 38, 760.
[2] Fort R.J. and W.R. Moore, *Trans faraday society*, **1965**, 61, 2102.
[3] Kinocid, *J.Am. Chem Soc*, SI, **1929**, 2950.
[4] Granberg L. and Nissan, *Nature*, **1946**, 164, 799.
[5] Patil S.R., U.G. Deshpande and A.R. Hiray, *Rasayan J. Chem*, **2010**, 66-73.

[6] Nikam P.S. and Hirey, *Indian J. Pure and Appl Phys*, **1991**, 29, 155.

[7] Johari G.K. and Misra R.C., *Indian J. Pure and Appl Phys*, **1987**, 29, 155.

[8] RC Scaduta, *Free Radical Med*, **1995**, 18 (2), 271.

[9] Hischfelder J.O., Kurtiss C.F. and Bird R.B., *Molecular theory of gases and liquids*, (John Willy, New York - 01), **1954**, 256.

[10] P.Vigoures, *Ultrasonic*, Chapman and Hall, London, **1952**.

[11] Miyanga Stamura K. and Murakarmi, S.J. *Chem Thermodynamics*, **1992**, 48, 1767.

[12] Bhath S.S., Vivek J.S. and Singh D.P., *Acoustica*, **1982**, 50, 291.

[13] Shanti N., Subrathinam P.L. and Emayavavyramban M, **2010**, 7, 648.

[14] Sumathi T. and Uma Maheshwari, *Indian J. Pure and Appl Phys*, **2009**, 47, 782.

[15] Rajendren V., *Indian J. Pure and Appl Phys*, **1996**, 34, 52.

[16] J. Ishwara Bhata and N.S. Shree Varaprasada, *Indian J of Pure and Appl Phys*, Vol 40, **April 2003**, 275.

[17] Kapdi U.R., D.G. Hundiwale, N.B. Patil, M. Lande, *Fluid phase equilibrium*, **2001**, 201, 335-341.

[18] Bedare G.R., et. al., *Euro J. Appl Eng Sci Res*, **2012**, 1 (1) : 1.

[19] Ishwara Bhat J and Shivakumar H.R., *Indian J.Chem A*, **1998**, 37, 252.

[20] Nikumbh, A.B., Kulkarni, G,K., *Der Chemica Sinica,* **2012**, 3(5), 1260.

[21] Chimankar, Omprakash P.,Dudhe, Chandragupt M.,Tabhane,Priyanka, *Der Chemica Sinica.* **2012**, 3(4), 944.

[22] Aravind R. Mahajan and Sunil R. Mirgane, *Advances in Applied Science Research*, **2012**, 3 (5):3243.

[23] Chimankar ,O.P., Shriwas ,R.S., Tabhane ,V.A., *Advances in Applied Science Research*. **2010**,1(3),78.

[24] Thakur ,S.K., Chouhan ,S., *Advances in Applied Science Research*. **2011**, 2(2) ,208.

[25] Patil ,S.S., Mirgane, S.R., B.R. Arbad; *Advances in Applied Science Research*. **2012**, 3(4), 2378.