

Thermodynamic properties of binary liquid mixtures of
1-Butanol with aromatic hydrocarbons at 298 to 308.15 K.

Shama B. Lomate



INTRODUCTION :

In the technological, biological and industrial applications binary mixtures are frequently used as these provide a wide choice of solvents with appropriate compositions and properties, such solvents also influence the rate of a reaction differently from those of pure solvents. Therefore, the study of intermolecular interactions in the binary liquid mixtures is of considerable importance. Although this field has been widely exploited, the basic processes are still relatively poorly understood at a detailed molecular level¹. Thermodynamic properties such as densities and ultrasonic velocities of pure liquids and of their binary liquid mixtures over the whole composition range measured at several temperatures are useful for a full understanding of thermodynamic and transport properties as well as practical chemical engineering purposes². The study of excess

Abstract

Densities and ultrasonic velocity of the binary mixtures of Densities and ultrasonic velocity of the binary mixtures of 1-butanol with toluene, ethylbenzene, p-xylene, and o-xylene were measured at 298.15, 303.15, and 308.15 K over the entire composition range. The experimental data were used to calculate excess molar volumes (V^E), deviations in isentropic compressibility ($\Delta\kappa_s$). These results were fitted to Redlich-Kister polynomial equation and the results have been discussed in terms of molecular interaction and structural effects. The excess properties were found to be either positive or negative depending up on the molecular interactions and the nature of liquid mixtures.

Keyword: Binary liquid mixtures, aromatic hydrocarbons, 1-Butanol.

Short Profile

Shama B. Lomate is working as an Assistant Professor at Department of Chemistry in Kalikadevi Arts, Commerce and Science College, Shirur (Ka.) Dist-Beed., India.

functions of binary liquid mixtures is useful in understanding the nature and strength of molecular interactions between the component molecules³. Alcohols are the most well known solvents used to study the hydrophobic effects. In view of their simple molecular structure, increasing hydrophobic character with increasing chain length and high solubility in polar solvents, most of their physical properties have been studied extensively [4]. In the present paper, we report density (ρ) and ultrasonic velocity (u) for the binary mixtures of 1-butanol with aromatic hydrocarbon at different temperatures. The calculated excess quantities from such data have been interpreted in terms of molecular interactions and structural effects.

Assistant Professor ,Department of Chemistry, Kalikadevi Arts, Commerce and Science College, Shirur (Ka.) Dist-Beed., India.

EXPERIMENTAL

All the organic liquids used in the present study were of analytical reagent grade and were obtained from S.D.Fine. These were further purified according to the procedure described in literature^{5,6}. The binary liquid mixtures were prepared by mixing known masses of pure liquids in airtight-stoppered bottles in order to minimize the evaporation losses. All measurements of mass were performed on a Mettler one pan balance (E-METTLER, ZURICH), which can read up to fifth place of decimal, with an accuracy of ± 0.05 mg.

The densities of the pure liquids and their binary mixtures were measured using the single arm capillary pycnometer having bulk volume of approximately 5 cm^3 and a capillary bore with an internal diameter of 0.75 mm. The accuracy in the density measurements was found to be of $\pm 5 \times 10^{-5} \text{ g.cm}^{-3}$.

The ultrasonic velocities were measured at 1MHz with a single crystal variable path interferometer (F-81 Mittal Enterprises, New Delhi) and the accuracy of ultrasonic measurement was $\pm 0.1\%$. For all the measurements, the temperature was controlled by circulating the water through an ultra thermostat JULABO F-25 (made in Germany) which has an accuracy of ± 0.02 °C.

RESULTS AND DISCUSSION

The comparison of physical properties of various pure liquids along with their literature values at 298.15 K are recorded in Table 1. The density, ultrasonic velocity, and their excess properties as excess molar volumes, isentropic compressibility for binary mixtures are presented in Table 2 to 4. The excess molar volumes of binary mixtures were calculated by using equation,

$$V^E = ((x_1M_1+x_2M_2)/\rho) - (x_1V_1 + x_2V_2) \quad (1)$$

Where, x_1 , x_2 , M_1 , M_2 , V_1 and V_2 are mole fractions, molecular weights and molar volumes of first and second components respectively.

The ultrasonic velocity is obtained by using the knowledge of wavelength and frequency,

$$u = \lambda \times f \quad (2)$$

The measured values of ultrasonic velocities are used to calculate isentropic compressibility using equation,

$$\kappa_s = 1 / u^2 \rho \quad (3)$$

The deviation of isentropic compressibility of binary mixtures were calculated by using equation,

$$\Delta\kappa_s = \kappa_s - x_1\kappa_{s1} - x_2\kappa_{s2} \quad (4)$$

Where κ_s is the isentropic compressibility of the mixture, κ_{s1} , κ_{s2} , x_1 and x_2 are the isentropic compressibility of pure components 1 and 2, mole fractions of components 1 and 2 respectively.

The calculated excess molar volumes (V^E) and deviation in isentropic compressibility ($\Delta\kappa_s$) are reported in Table. 2, were correlated by Redlich-Kister polynomial⁷, by using the relation,

$$\Delta Y = x_1x_2 \sum a_i (x_1 - x_2)^i \quad (5)$$

The coefficients in eq.5 were estimated by the least squares fit method and the standard deviations were calculated by using the relation,

$$\sigma = [\sum (\Delta Y_{Exp.} - \Delta Y_{Cal.})^2 / (D - N)]^{0.5} \quad (6)$$

Where D and N are the number of data points and parameters, respectively.

Regression results for excess molar volumes and deviation in isentropic compressibility, of binary mixtures of 1-butanol with aromatic hydrocarbon such as toluene, ethylbenzene, p-xylene, and o-xylene at 298.15 K, 303.15 K, 308.15 K temperatures reported in Table 5.

The graphical variation of excess molar volume (V^E) for the binary mixtures of 1-butanol with the four aromatic hydrocarbons with increasing mole fractions of 1-butanol at 298.15 K is shown in Fig. 1. The values of excess molar volumes are found to be positive for all the systems. It is established that, sign and magnitude of (V^E) gives a good estimate of the unlike interactions in the binary mixtures. Generally, (V^E) can be considered as arising from three types of interactions between component molecules:

i) Physical interaction mainly consisting of dispersion forces or weak dipole-dipole interaction and making a positive contribution^{2,3}.

ii) Chemical or specific interactions which includes charge transfer, formation of hydrogen bonds and other complex forming interactions resulting in negative contribution.

iii) The structural contributions arising from geometrical fitting of one component into other due to difference in molar volumes resulting in negative (V^E). The systems where dispersion, induction and dipolar forces are operating, the values of excess molar volume are found to be positive, whereas the existence of specific interactions between the mixing components of the various binary systems tends to make excess molar volume negative⁸. The positive V^E values at equimolar concentration follow the order p- xylene > o- xylene > ethylbenzene > toluene. The maxima in V^E values at 298.15 K vary from 0.6071 to 0.3566 cm³ mol⁻¹.

Fig. 2 shows the graphical variation of isentropic compressibility ($\Delta\kappa_s$) for the binary mixtures of 1-butanol with four aromatic hydrocarbons with increasing mole fractions of 1-butanol at 298.15 K. The values of isentropic compressibility are found to be positive for all the systems. The negative values of $\Delta\kappa_s$ for the systems represent strong specific interactions whereas the positive values represent the weak interactions or dominance of dispersion forces^{9,10}. The similar trend observed in V^E and $\Delta\kappa_s$. The positive $\Delta\kappa_s$ values at equimolar concentrations follows

the order p-xylene > o-xylene > ethylbenzene > toluene.

Hence in conclusion, one can say that some dispersion type of interaction is observed in the case of all these binary mixtures which make the effect of dispersion forces more dominating. It has been reported that normally dispersive interaction between unlike molecules is weaker than those between like molecules¹¹.

Table 1. Comparison of experimental densities and ultrasonic velocities of pure liquids with literature values at 298.15 K

| Pure liquids | ρ (g.cm ⁻³) | | u (ms ⁻¹) | |
|---------------|------------------------------|-----------------------|-----------------------|----------------------|
| | Expt | Lit | Expt | Lit |
| 1-Butanol | 0.80572 | 0.80770 ¹² | 1244.3 | - |
| Toluene | 0.86219 | 0.86211 ¹³ | 1302.5 | 1161.0 ⁵ |
| Ethyl benzene | 0.86247 | 0.86253 ⁵ | 1318.4 | 1144.0 ⁵ |
| o-xylene | 0.87169 | 0.87558 ¹⁴ | 1354.3 | 1172.0 ¹⁴ |
| p-xylene | 0.85676 | 0.85670 ¹⁴ | 1309.7 | 1190.0 ¹⁴ |

Table 2. Values of densities ρ for binary liquid mixtures of 1-butanol with aromatic hydrocarbons from T= (298.15 to 308.15) K.1-butanol+toluene

| | ρ /g.cm ⁻³ | | | X1 |
|--------|----------------------------|-------------|-------------|----|
| | T/K= 298.15 | T/K= 303.15 | T/K= 308.15 | |
| 0.0000 | 0.86219 | 0.85752 | 0.85283 | |
| 0.0816 | 0.85725 | 0.85243 | 0.84771 | |
| 0.1605 | 0.85257 | 0.84769 | 0.84291 | |
| 0.2371 | 0.84801 | 0.84313 | 0.83838 | |

| | | | |
|--------------------------|---------|---------|---------|
| 0.3113 | 0.84371 | 0.83885 | 0.83404 |
| 0.3833 | 0.83962 | 0.83472 | 0.82994 |
| 0.4532 | 0.83567 | 0.83076 | 0.82604 |
| 0.5210 | 0.83189 | 0.82701 | 0.82231 |
| 0.5869 | 0.82828 | 0.82344 | 0.81875 |
| 0.6509 | 0.82479 | 0.81999 | 0.81539 |
| 0.7132 | 0.82136 | 0.81672 | 0.81219 |
| 0.7737 | 0.81808 | 0.81351 | 0.80914 |
| 0.8326 | 0.81486 | 0.81046 | 0.80616 |
| 0.8899 | 0.81181 | 0.80752 | 0.80338 |
| 0.9457 | 0.80879 | 0.80476 | 0.80068 |
| 1.0000 | 0.80572 | 0.80193 | 0.79811 |
| 1-butanol + ethylbenzene | | | |
| $P/g.cm^{-3}$ | | | |
| | | | X1 |
| | T/K= | T/K= | T/K= |
| | 298.15 | 303.15 | 308.15 |
| 0.0000 | 0.86247 | 0.85801 | 0.85348 |
| 0.0928 | 0.85727 | 0.85275 | 0.84823 |
| 0.1806 | 0.85245 | 0.84771 | 0.84324 |
| 0.2637 | 0.84786 | 0.84305 | 0.83845 |

| | | | |
|--------|---------|---------|---------|
| 0.3425 | 0.84345 | 0.83857 | 0.83391 |
| 0.4173 | 0.83931 | 0.83434 | 0.82966 |
| 0.4885 | 0.83536 | 0.83032 | 0.82565 |
| 0.5562 | 0.83168 | 0.82654 | 0.82183 |
| 0.6208 | 0.82787 | 0.82291 | 0.81822 |
| 0.6824 | 0.82437 | 0.81943 | 0.81477 |
| 0.7412 | 0.82098 | 0.81616 | 0.81161 |
| 0.7975 | 0.81771 | 0.81309 | 0.80857 |
| 0.8514 | 0.81456 | 0.81009 | 0.80566 |
| 0.9030 | 0.81145 | 0.80722 | 0.80295 |
| 0.9525 | 0.80853 | 0.80451 | 0.80041 |
| 1.0000 | 0.80572 | 0.80193 | 0.79811 |

1-butanol + p-xylene

$P/g.cm^{-3}$

| | X1 | T/K= 298.15 | T/K= 303.15 | T/K= 308.15 |
|--------|---------|----------------|----------------|----------------|
| 0.0000 | 0.85676 | 0.85236 | 0.84792 | |
| 0.0928 | 0.85143 | 0.84701 | 0.84261 | |
| 0.1806 | 0.84665 | 0.84211 | 0.83773 | |
| 0.2637 | 0.84232 | 0.83762 | 0.83321 | |

| | | | |
|----------------------|---------|---------|---------|
| 0.3425 | 0.83826 | 0.83358 | 0.82902 |
| 0.4173 | 0.83449 | 0.82976 | 0.82511 |
| 0.4885 | 0.83093 | 0.82618 | 0.82141 |
| 0.5562 | 0.82763 | 0.82288 | 0.81802 |
| 0.6208 | 0.82449 | 0.81981 | 0.81487 |
| 0.6824 | 0.82156 | 0.81684 | 0.81191 |
| 0.7412 | 0.81867 | 0.81405 | 0.80919 |
| 0.7975 | 0.81585 | 0.81138 | 0.80659 |
| 0.8514 | 0.81317 | 0.80892 | 0.80421 |
| 0.9030 | 0.81063 | 0.80641 | 0.80199 |
| 0.9525 | 0.80812 | 0.80407 | 0.79986 |
| 1.0000 | 0.80572 | 0.80193 | 0.79811 |
| 1-butanol + o-xylene | | | |
| $P/g.cm^{-3}$ | | | |
| | | | X1 |
| | T/K= | T/K= | T/K= |
| | 298.15 | 303.15 | 308.15 |
| 0.0000 | 0.87578 | 0.87169 | 0.86854 |
| 0.0928 | 0.86914 | 0.86502 | 0.86165 |
| 0.1806 | 0.86309 | 0.85882 | 0.85535 |
| 0.2637 | 0.85747 | 0.85309 | 0.84947 |
| 0.3425 | 0.85217 | 0.84771 | 0.84393 |

| | | | |
|--------|---------|---------|---------|
| 0.4173 | 0.84717 | 0.84267 | 0.83871 |
| 0.4885 | 0.84244 | 0.83785 | 0.83382 |
| 0.5562 | 0.83788 | 0.83334 | 0.82914 |
| 0.6208 | 0.83351 | 0.82895 | 0.82471 |
| 0.6824 | 0.82924 | 0.82477 | 0.82047 |
| 0.7412 | 0.82512 | 0.82069 | 0.81642 |
| 0.7975 | 0.82112 | 0.81676 | 0.81248 |
| 0.8514 | 0.81714 | 0.81291 | 0.80872 |
| 0.9030 | 0.81325 | 0.80909 | 0.80501 |
| 0.9525 | 0.80944 | 0.80545 | 0.80148 |
| 1.0000 | 0.80572 | 0.80193 | 0.79811 |

Table3. Values of ultrasonic velocities u for binary liquid mixture of 1-butanol with aromatic hydrocarbos from $T= (298.15\text{to } 308.15) \text{ K}$. 1-butanol+toluene

| X1 | u/ms^{-1} | | |
|--------|--------------------|--------|--------|
| | T/K= | T/K= | T/K= |
| | 298.15 | 303.15 | 308.15 |
| 0.0000 | 1302.5 | 1280.9 | 1260.1 |
| 0.0816 | 1278.3 | 1255.3 | 1235.3 |
| 0.1605 | 1258.2 | 1235.6 | 1214.5 |
| 0.2371 | 1243.5 | 1219.6 | 1198.0 |
| 0.3113 | 1232.0 | 1207.4 | 1185.4 |

| | | | |
|--------------------------|--------|--------|--------|
| 0.3833 | 1223.5 | 1198.5 | 1175.7 |
| 0.4532 | 1218.1 | 1191.7 | 1168.7 |
| 0.5210 | 1214.3 | 1187.3 | 1164.5 |
| 0.5869 | 1212.7 | 1185.9 | 1162.4 |
| 0.6509 | 1213.1 | 1185.9 | 1162.4 |
| 0.7132 | 1214.5 | 1187.8 | 1164.6 |
| 0.7737 | 1217.7 | 1191.7 | 1168.9 |
| 0.8312 | 1223.2 | 1196.8 | 1175.8 |
| 0.8899 | 1228.4 | 1203.8 | 1185.1 |
| 0.9457 | 1235.8 | 1211.7 | 1195.8 |
| 1.0000 | 1244.3 | 1222.3 | 1208.5 |
| 1-butanol + ethylbenzene | | | |
| u/ms^{-1} | | | |
| | | | X1 |
| | T/K= | T/K= | T/K= |
| | 298.15 | 303.15 | 308.15 |
| 0.0000 | 1318.4 | 1296.7 | 1277.6 |
| 0.0928 | 1278.6 | 1257.6 | 1233.9 |
| 0.1806 | 1250.6 | 1227.1 | 1201.6 |
| 0.2637 | 1229.1 | 1204.0 | 1179.0 |
| 0.3425 | 1213.1 | 1187.5 | 1161.9 |
| 0.4173 | 1202.2 | 1176.0 | 1150.1 |

| | | | |
|--------|--------|--------|--------|
| 0.4885 | 1194.8 | 1167.6 | 1143.0 |
| 0.5562 | 1191.1 | 1162.7 | 1138.5 |
| 0.6208 | 1190.5 | 1162.3 | 1138.6 |
| 0.6824 | 1192.0 | 1163.3 | 1140.7 |
| 0.7412 | 1196.2 | 1168.0 | 1146.0 |
| 0.7975 | 1202.6 | 1172.8 | 1152.8 |
| 0.8514 | 1210.4 | 1182.4 | 1163.3 |
| 0.9030 | 1219.7 | 1193.4 | 1175.1 |
| 0.9525 | 1213.1 | 1204.3 | 1190.0 |
| 1.0000 | 1244.3 | 1222.3 | 1208.5 |

1-butanol + o-xylene

u/ms^{-1}

| X1 | T/K= 298.15 | T/K= 303.15 | T/K= 308.15 |
|--------|----------------|----------------|----------------|
| 0.0000 | 1354.3 | 1328.4 | 1268.5 |
| 0.0928 | 1291.3 | 1250.5 | 1223.1 |
| 0.1806 | 1244.5 | 1203.1 | 1189.0 |
| 0.2637 | 1231.1 | 1169.0 | 1164.3 |
| 0.3425 | 1192.9 | 1148.5 | 1148.0 |
| 0.4173 | 1178.9 | 1135.6 | 1136.9 |

| 0.4885 | 1170.7 | 1129.6 | 1131.6 |
|----------------------|----------------|----------------|----------------|
| 0.5562 | 1167.0 | 1128.2 | 1129.8 |
| 0.6208 | 1167.1 | 1131.2 | 1132.0 |
| 0.6824 | 1170.1 | 1136.2 | 1136.9 |
| 0.7412 | 1177.1 | 1144.6 | 1144.0 |
| 0.7975 | 1186.3 | 1154.0 | 1155.0 |
| 0.8514 | 1198.1 | 1167.6 | 1165.3 |
| 0.9030 | 1214.0 | 1185.2 | 1179.6 |
| 0.9525 | 1228.7 | 1201.5 | 1190.0 |
| 1.0000 | 1244.3 | 1222.3 | 1208.5 |
| 1-butanol + p-xylene | | | |
| u/ms^{-1} | | | |
| X1 | T/K= 298.15 | T/K= 303.15 | T/K= 308.15 |
| 0.0000 | 1309.7 | 1288.5 | 1268.5 |
| 0.0928 | 1260.0 | 1239.3 | 1223.1 |
| 0.1806 | 1226.3 | 1205.0 | 1189.0 |
| 0.2637 | 1203.9 | 1181.3 | 1164.3 |
| 0.3425 | 1191.0 | 1167.9 | 1148.0 |
| 0.4173 | 1184.6 | 1159.4 | 1136.9 |
| 0.4885 | 1182.1 | 1154.7 | 1131.6 |

| | | | |
|--------|--------|--------|--------|
| 0.5562 | 1182.6 | 1154.8 | 1129.8 |
| 0.6208 | 1186.0 | 1157.6 | 1132.0 |
| 0.6824 | 1191.5 | 1161.9 | 1136.9 |
| 0.7412 | 1198.5 | 1169.0 | 1144.0 |
| 0.7975 | 1205.8 | 1177.6 | 1155.0 |
| 0.8514 | 1216.0 | 1187.4 | 1165.3 |
| 0.9030 | 1224.3 | 1197.8 | 1179.6 |
| 0.9525 | 1234.5 | 1209.5 | 1190.0 |
| 1.0000 | 1244.3 | 1222.3 | 1208.5 |

Table 4. Coefficients of Redlich-Kisters equation and the corresponding standard deviations (σ) for the binary mixtures at 298.15 K

| System | a_1 | a_2 | a_3 | σ |
|---|-----------|------------|-----------|-----------|
| V^E ($\text{m}^3 \text{mol}^{-1}$) | | | | |
| 1-Butanol + Toluene | 1.4365 | -0.1971 | -0.1157 | 0.0032 |
| 1-Butanol + Ethylbenzene | 1.7961 | -0.0642 | 0.1086 | 0.0030 |
| 1-Butanol + p-xylene | 1193.3056 | -7994.7792 | 8509.7285 | 1265.8830 |
| 1-Butanol + o-xylene | 1.9690 | -0.6381 | 0.0932 | 0.0020 |
| $\Delta\kappa_s$ (T Pa^{-1}) | | | | |
| 1-Butanol + Toluene | 281.0483 | -1.6830 | -0.1134 | 0.3351 |

| | | | | |
|--------------------------|----------|-----------|----------|--------|
| 1-Butanol + Ethylbenzene | 422.9669 | 36.3160 | -2.5029 | 0.4264 |
| 1-Butanol + p-xylene | 489.3122 | -137.8839 | -474616 | 4.4901 |
| 1-Butanol + o-xylene | 628.3631 | -8.1705 | -29.0321 | 1.2767 |

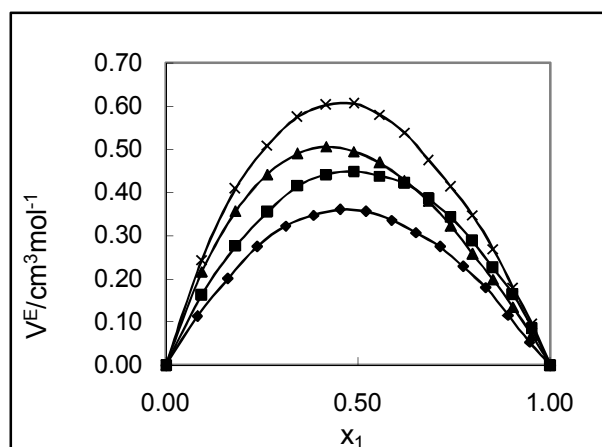


Fig 1 Variation of excess molar volume V^E against mole fraction x_1 of 1-butanol at 298.15 K: (×) p-xylene (▲) o-xylene, (■) ethyl benzene, (◆) toluene.

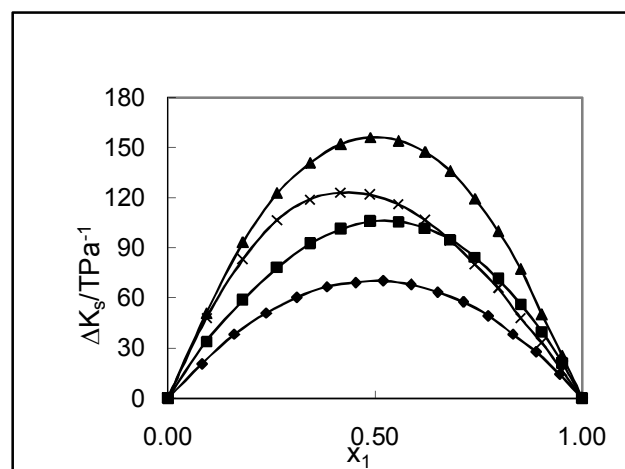


Fig 2 Graphical variation of deviation in isentropic compressibility ΔK_s against mole fraction x_1 of 1-butanol at 298.15 K: (×) p-xylene (▲) o-xylene, (■) ethyl benzene, (◆) toluene.

REFERENCES

1. A. Ali, Abida, and S. Hyder, *Physics and Chemistry of Liquids.*, 2004, **42**, 411.
2. N. N. Wankhede, M. K. Lande, B. R. Arbad,, *J. Chem. Eng. Data.*, 2005, **50**,969
3. D. S. Wankhede, N. N. Wankhede, M. K. Lande, B. R. Arbad, *J. Solution,Chem.*,2005,**34**, 233.
4. T. M. Aminabhavi, M. I. Aralaguppi, S. B. Harogoppad and R. H. Balundgi, *J. Chem. Eng. Data.* **38**: 31 (1993).
5. J. A. Riddick, W. B. Bunger, and T. K. Sakano, "Organic Solvents : Techniques of Chemistry", Vol.2, 4th ed., Willey Interscience, New York, 1986.
6. A. I. Vogel, B. S. Furniss, A. J. Hannaford, P.W.G. Smith, A. R. Tatchel, "Text book Practical Organic Chemistry", John Willey and Sons, New York, 1989.Vol.2, 4th ed, Willey Interscience, New York, 1963.
7. O. Redlich, A.T. Kister, *Indian. Eng. Chem.*, 1948, **40**, 345.
8. N. V. Sastry, M. C. Patel, *J. Chem. Eng. Data.*, 2003, **48**, 1019.
9. C. Gandhi. P. Venkatesu and M. V. Prabhakar Rao, *J.Chem. Eng. Data*, 2000, **45**, 590.
10. J. M. Resa, C. Conzalez, R. G.Concha and M. Iglesias,. *Physics and Chemistry of Liquids.*, 2004, **42**, 521.
11. J. M. Resa, C. Conzalez, R. G.Concha and M. Iglesias,. *Physics and Chemistry of Liquids.*, 2004, **42**, 521.
12. V. K. Rattan, S. Singh, and B. P. S. Sethi, *J. Chem. Eng. Data*, 49, 1074, **2004**.
13. J. Wismakai, R. Infante,R. D. Peralta and L. F. Ramos, *J. Phys. Chem. Liq.*, 39, 625, **2001**.
14. L. Serrano, J. A. Silva, and F. Farelo, *J. Chem. Eng. Data*, 35, 288, **1990**.