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Ultrasonic investigation of molecular associations in the binary mixtures of NMP with substituted benzenes at 308.15, 318.15 K and atmospheric pressure

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ABSTRACT

The densities, viscosities and speeds of sound for the binary mixtures of N-methyl-2-pyrrolidone (NMP) with aniline (AB), bromobenzene (BB), and chlorobenzene (CB), over the entire composition range have been measured at T = (308.15, 318.15) K and atmospheric pressure. From these experimental values, excess free volume, excess internal pressure and deviations in acoustic impedance are computed and fitted to a Redlich–Kister type polynomial. The results are interpreted in terms of molecular interactions between the component molecules. Thermodynamic parameters under study suggest the existence of strong interactions between NMP and AB, or BB, or CB.

Keywords: Density, viscosity, speeds of sound, thermo acoustic properties, Relich-Kister polynomial, molecular interactions.

INTRODUCTION

The present work is a continuation of our research programme on thermodynamic, thermo-acoustic and transport behaviour of binary liquid mixtures of industrially important components [1-3]. In recent years, ultrasonic technique has become a powerful tool [4] in providing information regarding the molecular behavior of liquids and liquid mixtures owing to its ability of characterizing physicochemical behavior of the medium [5]. When two or more liquids are mixed, there occur some changes in physical and thermodynamic properties because of free volume change, change in energy and change in molecular orientations. The deviation from ideality is expressed by many thermodynamic variables particularly by excess properties [6]. Derived thermodynamic and acoustical parameters like internal pressure, free volume and

acoustic impedance etc., are of considerable interest in understanding the inter-molecular interactions in binary liquid mixtures [7].

Lactams are significant class of amides not extensively studied despite their use as solvents and biologic applications. Hence, one of the lactams, N-methyl-2-Pyrrolidone (NMP) is chosen as a common solvent for the present study. NMP known for its solvent power is rapidly becoming the product of choice for paint strippers, agricultural chemicals, and process solvent applications [8]. In this paper we report the internal pressures, free volumes, acoustic impedance and of a binary system N-methyl-2-Pyrrolidone (NMP) + Aniline (AB) or Bromobenzene (BB) or Chlorobenzene (CB) at temperatures 308.15 and 318.15 K

EXPERIMENTAL SECTION

The chemicals, NMP (>99%) obtained from Merck and Chlorobenzene (>99%), Bromobenzene (>99%), Aniline (>99%) procured from S.D. Fine chemicals (India) are further purified by using standard methods [9]. The purity of the chemicals was assessed by comparing their measured densities (ρ), ultrasonic velocities (U) and viscosities (η), which are in good agreement with literature [10-20] values as can be seen in Table 1.

Table 1 Comparison of experimental values of density (ρ), ultrasonic speed (U) and Viscosity (η) of pure liquids with the corresponding literature values at 303.15 K

Liquid	10^{-3} x ρ (Kg m^{-3})		U (m s^{-1})		η (m Pa s)	
	Exptl	Lit.	Exptl	Lit.	Exptl	Lit.
NMP	1.02380	1.02376[10]	1552.8	1552 [11]	1.5546	1.5544[12]
Chlorobenzene	1.09521	1.0957 [13]	1250.0	1252.2 [13] 1249.41 [20]	0.7215	0.7210 [14]
Bromobenzene	1.48149	1.4814 [15]	1138.1	1137.0 [16]	0.9845	0.9844 [14]
Aniline	1.01320	1.0128 [17] 1.0133 [19]	1617.6	1615.2 [17]	3.0368	3.036 [18]

The binary mixtures have been prepared gravimetrically using an electronic balance (Shimadzu AY 120, Japan) with an uncertainty of ± 1x 10^{-7} Kg and are stored in air-tight glass bottles. The viscosity, η, of the pure liquids and liquid mixtures is determined using an Ubbelohde suspended-level viscometer. The viscometer is calibrated with triple distilled water and dry cyclohexane. The estimated uncertainty in the viscosity measurements is found to be ±0.04 %. The densities, ρ, of pure liquids and their mixtures are determined using a 10^{-5} m^3 double-arm pycnometer as described by Nikam et al [21]. The density values from triplicate replication at each temperature are accurate unto 4 parts in 10^5 parts. The ultrasonic velocity of pure components and their mixtures have been measured by single crystal variable path fixed frequency interferometer provided by Mittal Enterprises, New Delhi (Model-F 05). The measured speeds of sound are found to be accurate up to 0.1 m·s^{-1}. Temperature control for the measurement of viscosity, density and ultrasonic velocity is achieved by using a microprocessor assisted circulating water bath, (supplied by Mac, New Delhi) regulated to ±0.01 K, using a proportional temperature controller.

RESULTS AND DISCUSSION

Assuming that ultrasonic absorption is negligible, using experimental results of density, viscosity and ultrasonic velocity, the thermodynamic and thermoacoustic parameters such as free volume (V_f), internal pressure (π_i), acoustic impedance (Z) and their excess parameters have been calculated using the following standard expressions and are presented in Table 2.

Table 2 Density (ρ), viscosity (η), ultrasonic velocity (U), excess free volume (V_f^E), excess internal pressure (π_i^E), excess acoustic impedance (Z^E) for the binary mixtures of NMP at 308.15 and 318.15 K.

x	ρ	η	U	$10^8.V_f^E$	$10^{-8}.\pi_i^E$	$10^3.Z^E$	ρ	η	U	$10^8.V_f^E$	$10^{-8}.\pi_i^E$	$10^3.Z^E$
	Kg m^{-3}	m Pa s	ms^{-1}	m^3mol^{-1}	Pa	Kg m^{-2} s^{-1}	Kg m^{-3}	m Pa s	ms^{-1}	m^3mol^{-1}	Pa	Kg m^{-2} s^{-1}
NMP + AB												
	308.15 K						318.15 K					
0.0000	1008.90	2.6395	1595.8	0.0000	0.0000	0.0000	1000.40	2.0475	1556.0	0.0000	0.0000	0.0000
0.0954	1013.41	2.5785	1593.4	-0.5367	0.0942	9.8435	1005.81	1.9993	1553.9	-0.4984	0.0651	12.3549
0.1918	1017.01	2.5153	1590.4	-1.0637	0.1841	17.6594	1009.40	1.9602	1552.1	-1.0342	0.1375	22.2276
0.2892	1020.03	2.4451	1588.1	-1.5563	0.2622	25.2998	1012.03	1.9041	1549.5	-1.4678	0.1821	29.8524
0.3876	1022.20	2.3603	1584.9	-1.9876	0.3201	30.7120	1014.20	1.8441	1546.3	-1.8588	0.2210	36.2073
0.4870	1023.95	2.2376	1580.8	-2.2425	0.3267	34.5790	1015.45	1.7691	1541.0	-2.1293	0.2369	39.0611
0.5875	1025.01	2.0761	1572.8	-2.2598	0.2815	33.4015	1016.21	1.6592	1532.1	-2.0849	0.1998	37.5567
0.6890	1024.88	1.9151	1563.5	-2.1335	0.2301	29.0688	1016.15	1.5504	1519.0	-1.9454	0.1661	30.5889
0.7915	1024.10	1.7582	1552.0	-1.8519	0.1808	21.5324	1015.40	1.4371	1506.2	-1.5695	0.1179	22.9563
0.8952	1022.72	1.5911	1540.0	-1.2145	0.1073	12.6362	1013.52	1.3188	1492.5	-0.8732	0.0537	12.8122
1.0000	1019.90	1.4110	1526.4	0.0000	0.0000	0.0000	1010.30	1.2106	1478.0	0.0000	0.0000	0.0000
NMP + BB												
	308.15 K						318.15 K					
0.0000	1474.90	0.9545	1123.0	0.0000	0.0000	0.0000	1460.50	0.7925	1096.2	0.0000	0.0000	0.0000
0.1084	1431.92	1.0283	1157.9	-1.6672	0.0288	12.5014	1418.72	0.8492	1130.4	-1.7589	0.0086	14.4119
0.2149	1388.13	1.0937	1194.2	-2.5583	0.0447	22.7790	1375.62	0.9063	1165.0	-2.9988	0.0211	24.7516
0.3193	1343.60	1.1531	1231.0	-2.9951	0.0546	29.4437	1331.66	0.9583	1200.3	-3.5938	0.0272	31.8055
0.4219	1298.72	1.2055	1269.5	-3.0500	0.0564	34.4055	1287.07	1.0073	1237.0	-3.7757	0.0310	36.5707
0.5226	1253.35	1.2531	1309.0	-2.8826	0.0553	36.3396	1242.06	1.0513	1275.0	-3.5874	0.0297	38.9508
0.6215	1207.40	1.2954	1350.0	-2.5277	0.0499	35.5389	1196.62	1.0892	1314.1	-3.0976	0.0221	38.4552
0.7186	1161.12	1.3306	1391.7	-2.0124	0.0394	31.1493	1150.91	1.1252	1354.0	-2.4917	0.0175	34.7814
0.8141	1114.51	1.3631	1436.0	-1.4143	0.0285	25.1545	1104.70	1.1555	1395.5	-1.6946	0.0073	28.3469
0.9078	1067.45	1.3918	1481.3	-0.7591	0.0179	15.2658	1057.99	1.1837	1437.4	-0.8464	0.0005	17.6004
1.0000	1019.90	1.4110	1526.4	0.0000	0.0000	0.0000	1010.30	1.2106	1478.0	0.0000	0.0000	0.0000
NMP + CB												
	308.15 K						318.15 K					
0.0000	1087.24	0.6795	1231.0	0.0000	0.0000	0.0000	1072.67	0.6434	1195.2	0.0000	0.0000	0.0000
0.1055	1082.40	0.7744	1259.7	-3.2874	0.0729	2.0659	1068.90	0.7258	1223.0	-2.9518	0.0415	2.9363
0.2097	1077.26	0.8709	1287.5	-5.2818	0.1391	2.7801	1064.32	0.8105	1250.0	-4.9097	0.0830	4.0640
0.3127	1071.80	0.9624	1316.0	-6.1556	0.1845	3.8126	1059.50	0.8944	1277.1	-5.9151	0.1160	5.0094
0.4144	1066.00	1.0490	1344.6	-6.3156	0.2128	4.4530	1054.35	0.9733	1305.2	-6.3318	0.1463	6.5783
0.5149	1059.65	1.1295	1374.0	-5.9570	0.2224	5.1190	1048.50	1.0469	1334.0	-6.0909	0.1587	7.9146
0.6142	1052.60	1.1957	1404.1	-5.0803	0.1996	5.4262	1042.00	1.1115	1362.9	-5.2790	0.1465	8.3839
0.7124	1045.31	1.2571	1434.0	-4.0107	0.1665	5.0113	1035.03	1.1666	1392.1	-4.1346	0.1180	8.3810
0.8094	1037.60	1.3131	1464.5	-2.7791	0.1216	4.4193	1027.60	1.2197	1421.2	-2.7710	0.0769	7.4573
0.9052	1029.07	1.3660	1495.0	-1.4614	0.0691	2.3778	1019.61	1.2724	1449.4	-1.4013	0.0392	4.6099
1.0000	1019.90	1.4110	1526.4	0.0000	0.0000	0.0000	1010.30	1.3195	1478.0	0.0000	0.0000	0.0000

Erying et al [22] obtained the relationship between the internal pressure P_i, the external pressure P and the free volume V_f of a liquid as follows:

$$V_f = [KRT/(P_i+P)\ (\rho+V_f^{1/3}/K)^2]^3$$

The above relationship shows that free volume of a molecule at a particular temperature and pressure depends only on the internal pressure of the liquid in which it is immersed. The free

volumes of the binary mixtures have been computed using its relationship with the ultrasonic velocity and viscosity as follows:

$$V_f = \left[\frac{M_{eff}U}{K\eta}\right]^{3/2} \qquad \text{…….. (1)}$$

where 'K' (= 4.28 x 10^9 in S. I system) is a temperature independent proportionality constant and the other symbols have their usual meaning.

Suryanarayana and Kuppuswami [23] used an indirect alternative method for computing the internal pressure of a liquid from its viscosity, density and ultrasonic velocity as shown below

$$\pi_i = \text{bRT}\left[\frac{K\eta}{U}\right]^{1/2}\left[\frac{\rho^{2/3}}{M^{7/6}}\right] \qquad \text{…….. (2)}$$

where '*b*' is a packing factor, 'R' is Universal gas constant, '*T*' is the absolute temperature and other symbols have their usual meaning.

The acoustic impedance is the parameter related to elastic properties of the medium and calculated by using the expression

$$\text{Z} = \rho U \qquad \text{…….. (3)}$$

The excess properties such as V_f^E, Z^E and π_i^E have been calculated using the equation

$$Y^E = Y_{mix} - (x_1Y_1 + x_2Y_2) \qquad \text{…….. (4)}$$

where Y^E is V_f^E or Z^E or π_i^E and x_1 and x_2 are mole fractions of liquid 1 and 2 respectively.

These excess functions are fitted to Redlich – Kister [24] type polynomial equation.

$$Y_{cal}^E = x_1x_2\sum a_{j-1}(x_2 - x_1)^{j-1} \qquad \text{……. (5)}$$

The values of coefficient a_{j-1} are evaluated by the method of least squares with all points weighed equally and the standard deviations are calculated using

$$\sigma_{YE} = \left[\frac{\Sigma(Y_{obs}^E - Y_{cal}^E)^2}{(m-n)}\right]^{1/2} \qquad \text{……. (6)}$$

where 'm' is the number of experimental data points and 'n' is the number of coefficients considered (n = 5 in the present calculation).

It is evident from Tables 2, that all the three binary systems exhibit non-linear increase/decrease in *U*, V_f, *Z* and π_i values with composition of NMP. This indicates the presence of intermolecular interactions between the component molecules of the mixture [18,25]. In order to substantiate the presence of interactions (either adhesive or cohesive forces) between the molecules, it is essential to study excess parameters like excess free volume (V_f^E), excess internal pressure

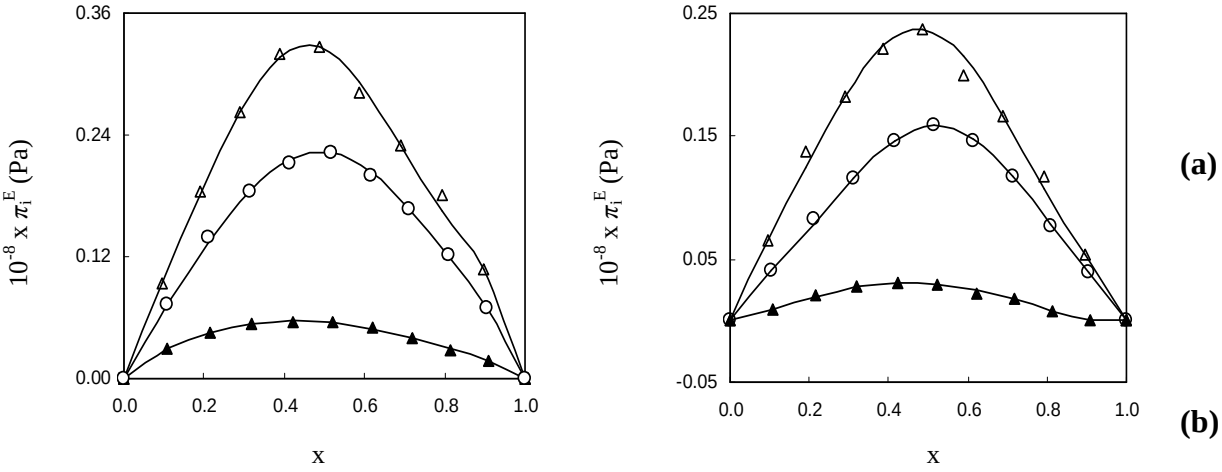
(π_i^E), excess acoustic impedance (Z^E) etc., as these parameters are found to be more sensitive towards intermolecular interactions in the liquid mixtures [25].

In the pure state molecules of NMP, CB, BB are associated through dipole – dipole interactions [16] and aniline exist in associated form through hydrogen bonding between like molecules. When substituted benzenes are added to NMP it results in considerable decrease in intermolecular spaces between molecules leading to decrease in free volume and hence increase in internal pressure. So negative values of V_f^E and positive π_i^E values are observed in the present case. Our finding is in good agreement with the views proposed by Jacobson [26].

The V_f^E values are found to decrease (Table 2) with increase in the concentration of NMP, attaining a minimum value between 0.4-0.5 mole fraction of NMP. This indicates that the associated structure of the polar component (NMP) due to dipolar association has been broken by solvent molecules. The negative V_f^E values indicate the contributions made by the strong dipole-dipole interactions between the unlike molecules of the components [27].

Excess values of π_i^E (Figures 1) in the binary mixtures of NMP with CB or BB or AB show a maximum value between 0.4- 0.5 mole fraction of NMP, then decrease with further increase in its concentration. This indicates the weakening of intermolecular interaction between component molecules. Thus based on the magnitude of positive values in π_i^E, the order of the interaction, in the substituted benzenes under investigation at 308.15 and 318.15 K with NMP is as follows: AB > CB > BB.

Figure 1 Variation of π_i^E with composition of N-methyl-2-pyrrolidone (x) for the binary liquid mixtures NMP +Aniline (Δ), NMP +Chlorobenzene (o) and NMP + Bromobenzene (▲) at 308.15 K (a) and 318.15 K (b)



** In the above figure symbols indicate experimental values and solid curves indicate Redlich-Kister values*

The presence of stronger interactions, are further substantiated by the positive values of Z^E for these binary liquid mixtures. Specific acoustic impedance is a quantity which depends on the molecular packing of the systems. In the present investigation Z^E values (Table 2) show positive deviations, confirming that strong magnitude of interactive forces, existing between the unlike molecules of the component liquids in all the three binary systems, over the entire composition range

of NMP. Positive trends in Z^E have also been reported for binary mixtures of oxolane + aniline and substituted anilines [17]

The values of the adjustable coefficients A_{j-1} of Redlich-Kister polynomial along with the standard deviations for excess free volume (V_f^E), excess internal pressure (π_i^E), and excess acoustic impedance (Z^E) at temperatures 308.15 and 318.15 K are presented in Table 3.

Table 3 Coefficients A_{j-1} of the Redlich-Kister equation, Eq.(6) and the analogous standard deviations of excess parameters for the binary mixtures of NMP at 308.15, 318.15 K

	T/K	A_0	A_1	A_2	A_3	A_4	σ
(x) NMP+ (1-x) chlorobenzene							
10^8 x V_f^E (m^3 mol^{-1})	308.15	-24.191	-11.501	-0.684	0.410	-3.474	0.0386
10^{-8} x π^E (Pa)	308.15	0.893	0.064	-0.422	-0.130	0.401	0.0031
10^3 x Z^E (Kg m^{-2} s^{-1})	308.15	20.201	-9.710	3.954	9.841	5.309	0.1983
10^8 x V_f^E (m^3 mol^{-1})	318.15	-24.656	-8.935	4.390	-0.707	-5.056	0.0389
10^{-8} x π^E (Pa)	318.15	0.633	-0.083	-0.541	0.112	0.396	0.0023
10^3 x Z^E (Kg m^{-2} s^{-1})	318.15	30.962	-24.320	0.030	17.111	28.176	0.1884
(x) NMP+ (1-x) bromobenzene							
10^8 x V_f^E (m^3 mol^{-1})	308.15	-11.770	-4.851	-1.623	-0.560	-1.094	0.0124
10^{-8} x π^E (Pa)	308.15	0.225	0.078	-0.017	-0.034	0.101	0.0009
10^3 x Z^E (Kg m^{-2} s^{-1})	308.15	144.77	-20.31	-14.91	-17.85	48.28	0.4133
10^8 x V_f^E (m^3 mol^{-1})	318.15	-14.620	-5.346	-0.234	0.536	1.328	0.0254
10^{-8} x π^E (Pa)	318.15	0.121	0.039	-0.072	0.014	-0.065	0.0015
10^3 x Z^E (Kg m^{-2} s^{-1})	318.15	154.82	-28.18	12.39	-12.69	39.38	0.1836
(x)NMP+ (1-x)aniline							
10^8 x V_f^E (m^3 mol^{-1})	308.15	-9.043	2.516	1.959	2.756	-4.557	0.0246
10^{-8} x π^E (Pa)	308.15	1.298	0.387	-0.955	-0.669	1.072	0.0078
10^3 x Z^E (Kg m^{-2} s^{-1})	308.15	138.82	-13.85	-68.92	0.75	72.71	0.3374
10^8 x V_f^E (m^3 mol^{-1})	318.15	-8.586	2.361	3.032	-0.241	-2.228	0.0445
10^{-8} x π^E (Pa)	318.15	0.944	0.184	-0.825	-0.107	0.603	0.0094
10^3 x Z^E (Kg m^{-2} s^{-1})	318.15	156.24	6.55	-94.51	-5.09	107.73	0.5379

Increase in temperature causes variation in the excess thermodynamic properties as the local structure of the liquids are destroyed, thus affecting their intermolecular free length and kinetic energy so the values of excess free volume (V_f^E), excess internal pressure (π_i^E), and excess acoustic impedance (Z^E) varies with temperature (Table 2). Similar temperature dependence results are reported earlier by several researchers [17,28].

CONCLUSION

From the thermo-acoustic, thermodynamic studies of the binary liquid mixtures of N-methyl-2-Pyrrolidone + Chlorobenzene, + Bromobenzene, + Aniline at 308.15 and 318.15 K and at atmospheric pressure, it is clear that all the three binary systems exhibited non-linear increase /decrease in *U*, V_f, and π_i values with the composition of NMP which indicate the presence of intermolecular interactions between the component molecules of the mixtures. The values of V_f^E for all the three binary mixtures are negative and the values of Z^E, π_i^E were positive over the entire range of composition of NMP and the temperatures under study. The observed thermoacoustic results suggest a strong interaction between NMP and the substituted benzenes under study.

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REFERENCES

[1] G.V. Ramarao; A.V. Sarma; C. Rambabu. *Indian J. Pure Appl. Phys.*, **2004,** 42, 820-826.
[2] G.V. Ramarao; A.V. Sarma; D. Ramachandran; C. Rambabu. *Indian J. Pure Appl. Phys*., **2005,** 43, 602-608.
[3] G.V. Ramarao; A.V. Sarma; P.B. Sandhyasri; C. Rambabu. *Indian J. Pure Appl. Phys*., **2007,** 45, 135-142.
[4] K. Sreekanth; D.S. Kumar; M. Kondaiah; D. Krishnarao. *J. Chem. Pharm. Res.,* **2011**, 3(4), 29-41.
[5] R. Venis; R. Rajkumar. *J. Chem. Pharm. Res.,* **2011**, 3(2), 878-885.
[6] K. Narendra; Ch. Srinivasu; Sk. Fakruddin; P. Narayanamurthy. *J. Chem. Thermodyn.*, **2011,** 43, 1604-1611.
[7] A. Tadkalkar; P. Pawar; G.K. Bichile. *J. Chem. Pharm. Res.,* **2011**, 3(3), 165-168.
[8] P.G. Kumari; P. Venkatesu; K.R. Mohan; M.V.P. Rao; D.H.L. Prasad. *Fluid Phase Equilib.*, **2007,** 252, 137-142.
[9] J.A. Riddick, W.B. Bunger, T.K Sakano, Organic Solvents, 4th ed., Wiley-Interscience, New York, **1986**
[10] Y. Changsheng; G. He; H. Yifu; P. Ma. *J. Chem. Eng. Data*., **2008,** 53, 1639-1642.
[11] P.G. Kumari; P. Venkatesu; M.V.P. Rao; M.J. Lee; H.M. Lin. *J. Chem. Thermodyn*., **2009,** 41, 184-188.
[12] Y. Changsheng; W. Xu; P. Ma. *J. Chem. Eng. Data*., **2004,** 49, 1794-1801.
[13] A. Ali; A.K. Nain; V.K. Sharma; S. Ahmad. *Phys. Chem. Liq*., **2004,** 42, 375-383.
[14] N.N. Jyoti; I.A. Mrityunjaya; T.M. Aminabhavi; *J. Chem. Eng. Data*., **2003,** 48, 628-631.
[15] M.V. Rathnam; R. Rajeev Kumar Singh; M.S. Kumar. *J. Chem. Eng. Data*., **2008,** 53, 265-270.
[16] G. Manisha; S. Divya; S. Parveen; S. Shashi; J.P. Shukla. *Phys. Chem. Liq*., **2009,** 47, 113-122.
[17] S.L. Oswal; V. Pandiyan; B. Krishnakumar; P. Vasantharani. *Thermochim. Acta*., **2010,** 507–508, 27-34.
[18] R. Thiyagarajan; P. Lakshmanan. *C. R. Chim*., **2007,** 10, 1157-1161.
[19] P. Ramamurthy; Joan Ollver; David Campbell. *J. Chem. Eng. Data*., **1985,** 30, 355-360.
[20] A.S. Al-Jimaz; J.A. Al-Kandary; Abdul-Haq; M. Abdul-Latif. *J. Chem. Eng. Data*., **2007,** 52, 206-214.
[21] P.S. Nikam; T.R. Mahale; M. Hasan. *J. Chem. Eng. Data*., **1998,** 43, 436-440.
[22] J.O. Hirschfelder; D.P. Stevenson; H. Erying. *J. Chem. Phys*., **1937,** 5, 896-901.
[23] J. Kuppusami; C.V. Suryanarayana. *Indian. J. Acoust. Soc*., **1977,** 5, 102-106
[24] O. Redlich; A.T Kister. *Ind. Eng. Chem*., **1948,** 40, 345-348.
[25] T.S. Rao; N. Veeraiah; C. Rambabu. *Indian J. Pure Appl. Phys*., **2002**, 40, 850-856.
[26] B. Jacobson. *J. Chem. Phys*., **1952**, 20, 927-929.
[27] S. Thirumaran; S. Sudha. *J. Chem. Pharm. Res.,* **2010**, 2(1), 327-337
[28] J. Chen; R. Shen; W. Liu; Y. Guoqi. *J. Chem. Thermodyn*., **2007,** 39, 934-941.