Intermolecular Interaction of Benzene in P-Dioxane and Methylcyclohexane

S.G.Goswami[1], S.G.Charalwar[2]

[1]Department of Physics, S.M.M College of science Nagpur, Maharashtra, India

Abstract: ***Ultrasonic investigation finds extensive applications in probing into the physic-chemical behavior of binary liquid mixtures leading to an understanding of molecular interactions in pure liquid and liquid mixtures. There are many attempts to develop a theory of liquid state based on simple consideration of molecular behaving like hard sphere having attractive force as perturbative force. The equation of state for Lenard jones fluid has been derived. In the formation of an expression for work obtained from partition function through the perturbation approach and found faithful reproduction of ultrasonic velocity and density data, theoretically at the given temperature it has been applied to the binary liquid mixtures of benzene in p-dioxane and methylcyclohexane. There is a close agreement with experimental value and the thermodynamic picture build up in this formation could be considered as good representation of molecular clusters in liquid state.***

Keywords: Ultrasonic velocity, benzene, p-dioxane, methylcyclohexane, adiabatic compressibility, molar volume

1. Introduction

A large majority of liquid is complex and consists of polyatomic nonspherical molecule in which same additional molecular forces exist. Various equations of state [1-3] for hard sphere fluids have come forward. Bhatti [4] has reported ultrasonic investigation on acoustical parameters of liquid on a hard sphere model; Sharma [5] tested the validity of an equation of state for real fluids and several expressions for the various acoustical parameters to relate them with Gruneisen parameters. Gopalrao [6] formulated an equation of state for square well fluid and derive same thermodynamic parameters for it by extending Flory's [7] equation to mixture of unrelated type of molecules. Khasare [8-9] modified an equation of state; it has been observed that Khasare's theory is the extension perturbation theories of the past. The equation of state for Lenard Jones fluid has been derived in the formation an expression for work, obtained from partition function through perturbation approach and found faithful reproduction of ultrasonic velocity and density data, theoretically at the given temperature. The thermodynamic properties of liquids are intimately related to the intermolecular forces [10-11]. This dependence can be used for precise understanding of molecular cluster in the light of Lennard-Jones potential parameters. These parameters show the attractive and repulsive forces resulting in strong and weak association [12]. The present paper reports the results for application of the approach based on Khasare's model equation of state to the binary liquid mixture of benzene in p-dioxane, methylcyclohexane and cyclohexanol.

2. Theoretical and Computational Approach

Khasare's theory is two scaling parameter model i.e.hard core diameter and depth of potential, the choice of the perturbing potential decides the nature of molecular interaction in binary liquid mixture. The earlier partition theories used an approach on obtaining expression of free energy functions. This faced with different problems divergency and convergency and as such could not give better result. Better result could only be obtained when second order perturbation were applied. The deciding factor has been the level at which perturbation is applied. Khasare's [13-15] approach deals with the work done defined in scaled particle theory reference frame and expanding the work function using perturbation technique. The single order perturbation is found to be suitable for obtaining best result. The most important aspect of Khasare's theory is its provision of concentration dependence effect on basic parameter and therefore it is capable of predicting thermodynamic parameter i.e. ultrasonic velocity and density simultaneously for logical input parameters. The relations outlined are found to give transformation of thermodynamic data to interaction potential energy parameter. This transformation could be considered applicable to construct of molecule cluster. Using described model of equation of state corresponding to an assumed potential the experimental data , i.e. ultrasonic velocity, density and thermal expansion coefficient are used with a suitable choice for the hard sphere diameter of a molecule or molecule aggregates in a pure liquid and a binary liquid mixture. Starting with one mole of a real fluid as working substance the equation of state is written as,

$$\frac{\beta P}{\rho}=\frac{1}{(1-n)}+\frac{3En}{(1-n)^2}+\frac{3Fn^2}{(1-n)^3}+\frac{W}{n}[n+\log(1-n)]$$

And thermodynamic relation yield the following set of equations,

$$\frac{Mu^2}{\Upsilon RT}=\frac{\{1+6E\{\frac{n}{1-n}\}+9F\{\frac{n}{1-n}\}^2\}}{(1-n)}-\frac{WN}{(1-n)}$$

$$\alpha t=\frac{\frac{1}{(1-n)}+\frac{3En}{(1-n)^2}+\frac{3Fn^2}{(1-n)^2}}{\frac{Mu^2}{\Upsilon RT}}$$

Where

$\boldsymbol{\Upsilon}=1+\frac{R}{CP}(\alpha t)^2\frac{Mu^2}{RT}$, $\alpha=\frac{1}{V}\{\frac{dv}{dT}\}$

$E=\frac{3y_1y_2}{y_3}$, $F=\frac{3y^3_2}{y^2_3}$, $G=\sum_{j=1}^{3}Xj(4\beta\varepsilon j)\frac{4\pi Rj^3}{3}$

$W=\frac{G}{gy_3}$, $yn=\sum_{j=1}^{2}XjRj^n$, $g=\frac{4\pi}{3}$, $\boldsymbol{\sigma}=Rj$,

$n=g\boldsymbol{\rho}y_3$, $\boldsymbol{\rho}=\frac{N}{V}$, $Xj=\frac{Nj}{N}$= mole fraction ,

For calculating the molecular cluster size, one has to assume that λ-monomers from homomolecular cluster. These may be assumed, in a first order of approximation to have analogues. Molecular weight which is λ-times the molar volume for a cluster, and thus λ-times the specific heat at constant pressure at monomer. However the density does not depend upon the scaling factor λ as,

Density$=\frac{\lambda \text{ molecular weight of monomer}}{\lambda \text{ molecular volume of monomer}}$

The observed thermodynamic parameters such as $\frac{Mu^2}{\Upsilon RT}$ *and* $\frac{Mu^2\alpha T}{\Upsilon RT}$ of two components in the binary mixture has been given as input data to calculate the value of potential parameter $\boldsymbol{\sigma}_1$, $\boldsymbol{\varepsilon}_1$ and $\boldsymbol{\sigma}_2$, $\boldsymbol{\varepsilon}_2$ for the two component liquids . The only variable factor is the assumed molecular weight in the liquid state. In case the value of $\boldsymbol{\varepsilon}$ turns out to be negative, then one has to use an integral value of molecular weight such that $\boldsymbol{\varepsilon}$ becomes positive . In a liquid mixture the parameters for one component liquid molecule are perturbed in the presence of other component. Hence the corrections are applied in the form of the following set of equations employing minimum number of interaction parameters .

$V_1^c=V_1[1+\alpha_1X(1-X)]$, $[Cp^c]_1 = [Cp]_1[1+d_2x(1-x)]$

$\boldsymbol{\sigma}_1^c=\boldsymbol{\sigma}_1[1+b_1x(1-x)]$, $\boldsymbol{\varepsilon}_1^c=\boldsymbol{\varepsilon}_1[1+c_1x(1-x)]$

$V_2^c=V_2[1+\alpha_2X(1-X)]$, $[Cp^c]_2= [Cp]\,[1+d_2x(1-x)]$

$\boldsymbol{\sigma}_2^c=\boldsymbol{\sigma}_2[1+b_2x(1-x)]$, $\boldsymbol{\varepsilon}_2^c=\boldsymbol{\varepsilon}_2[1+c_2x(1-x)]$

And, $V=X_1V_1^c+X_2V_2^c$

$V= (1-X)V_1+X_2V_2+(1-X)x[A+Bx]$

$x_1=1-x$; $X_2=x$; $q_2=\frac{A}{V_1}$; $a_1=\frac{(A+B)}{V_2}$

Where the subscript 1,2 denote the component molecules in the binary liquid mixtures and a, b, c and d are the minimum numbers of interaction parameters in the mixture corresponding to molar volume V, a hard core diameter $\boldsymbol{\sigma}$, a depth of minimum potential $\boldsymbol{\varepsilon}$, and specific heat Cp respectively while x is the mole fraction .These corrected values of interaction parameters have been used to generate thermodynamic parameters in pure liquids & binary liquid mixture .In case the calculated value do not match with those of experimental ones, then one had to change the value of molecular weight by selecting the value of scaling factor λ in equation (A) the integral value of λ denote the state of molecule , namely monomeric, dimeric , trimetric etc. A computer program developed to generate theoretical thermodynamic parameters for very small concentration ranges to 0.1 to 0.2, 0.2 to 0.3, 0.3 to 0.4,…0.9 to 1.0 of the two pure liquid components in a given binary liquid mixture of the two liquids.

3. Experimental Details

The experimental data evolved in the laboratory was used for the present theoretical investigation. The liquid of benzene, cyclohexane , methylcyclohexane and methyl alcohol were analar grade & redistilled before use. The binary mixture of different mole fraction of two components in system benzene -p-dioxane, , benzene – methylcyclohexane, benzene-cyclohexanol were prepared immediately before use. The velocity of ultrasonic waves (u) at a frequency of 2MHz and density ($\boldsymbol{\rho}$) in these binary liquids mixtures were measured by employing ultrasonic interferometer and the hydrostatic sinker method in the temperature range 10-40^{0}C and ultra thermostate U-10 min of the samples constant to 0.1^{0}C. The accuracy of one part in 10^4 in the velocity and one part in 10^4 in the density measurement are achieved. The variation of u and $\boldsymbol{\rho}$ in this mixtures were found to be linear with the temperature and hence method of least squares was applied and the values of u and $\boldsymbol{\rho}$ at different temperatures were calculated from the equation

$u=u_0+[du/dT]_{T=0}$. $\rho = \boldsymbol{\rho}_0+[d\rho/dT]_{T=0}$

The Cp value used for the calculation was taken from the literature [16-19].

4. Results of Theoretical Investigation

The result of ultrasonic velocity(U) density($\boldsymbol{\rho}$) depth of minimum potential for the mixture ($\beta\boldsymbol{\varepsilon}_{AB}$) the depth of minimum potential of liquid component A presence of liquid component B ($\beta\boldsymbol{\varepsilon}_{AA}$) , the depth of minimum potential of liquid component B in presence of liquid component A ($\beta\boldsymbol{\varepsilon}_{BB}$) the hard sphere diameter of liquid component A in presence of liquid component B ($\boldsymbol{\sigma}_{AA}$) the hard sphere diameter of component B in presence of liquid A($\boldsymbol{\sigma}_{BB}$) and the packing fraction (n) at temperature 303.15^{0}K employing the Khasare's theory on the basis of model equation of state for fluid mixture have been presented in table 1,2,and 3 for the respective binary liquid mixture system the value of experimental velocities and densities of these binary liquid mixture system have also been presented in table 1,2,and 3 for comparison with theoretically evaluate values at same temperature while the value of u & $\boldsymbol{\rho}$ are obtained at mole fraction ratio of 0.1,0.2,0.3……1.0 the value parameter $\beta\boldsymbol{\varepsilon}_{AB}$, $\beta\boldsymbol{\varepsilon}_{AA}$, $\boldsymbol{\sigma}_{AA}$, $\boldsymbol{\sigma}_{BB}$ have been obtained at mole fraction 0.05 ,0.15,0.25………..0.95 respectively the input parameter required for evaluating above thermodynamic data has been given in table 4.The variation of $\beta\boldsymbol{\varepsilon}_{AB}$,$\beta\boldsymbol{\varepsilon}_{AA}$, $\boldsymbol{\sigma}_{AA}$, $\boldsymbol{\sigma}_{BB}$ verses molar concentration of two liquid component (Cm) in binary liquid mixture has been graphically presented in figure 1 to 9.

4.1 Benzene + p-dioxane

The variation of $\beta\boldsymbol{\varepsilon}_{AB}$ and η verses Cm of p-dioxane in benzene show constant increase of these parameters and both the variations are almost identical . This observed increasing $\beta\boldsymbol{\varepsilon}_{AB}$ and η with Cm of p-dioxane shows presence of molecular interaction in this mixtures. Benzene is considered to be very weakly associative liquid (almost normal) and p-dioxane is known to give strong interactions with associtative liquids. A weak associative molecular interaction is therefore expected between p-dioxane and benzene. On the other hand, this is seen from the $\beta\boldsymbol{\varepsilon}_{AB}$, η , $\beta\boldsymbol{\varepsilon}_{AA}$, $\beta\boldsymbol{\varepsilon}_{BB}$, $\boldsymbol{\sigma}_{AA}$, $\boldsymbol{\sigma}_{BB}$ (fig 1 - 3)

4.2 Benzene+ methylcyclohexane

The larger $\beta\boldsymbol{\varepsilon}_{AB}$, η , $\beta\boldsymbol{\varepsilon}_{AA}$, $\beta\boldsymbol{\varepsilon}_{BB}$, $\boldsymbol{\sigma}_{AA}$ and $\boldsymbol{\sigma}_{BB}$ variations in a mixture containing p-dioxane than methylcyclohexane in benzene (fig 4-9) indicate a stronger molecular interaction in p-dioxane mixture than that in methylcyclohexane mixture. The hetromolecular interaction is not due to specific process , such as H-bonding or lone pair interaction , but is a ring – ring interaction . The larger size methyl group in methylcyclohexane would prohibited a closer approach between two rings in benzene- methylcyclohexane , resulting a weak molecular interaction .

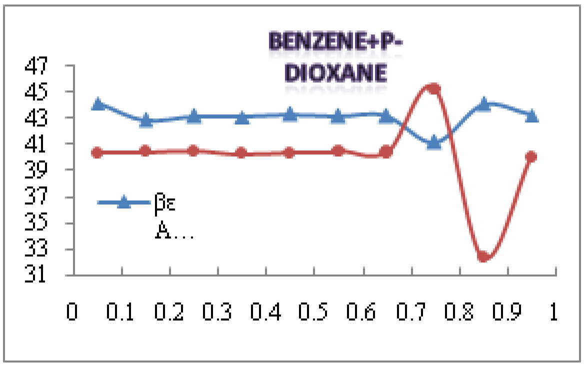

Figure 1: variation of $\beta\varepsilon_{AA}$ & $\beta\varepsilon_{BB}$ versus C_m

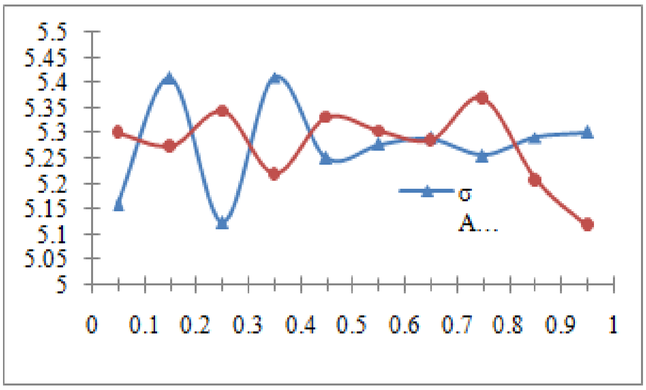

Figure 2: variation of σ_{AA} & σ_{BB} versus Cm in Benzene+p-dioxane

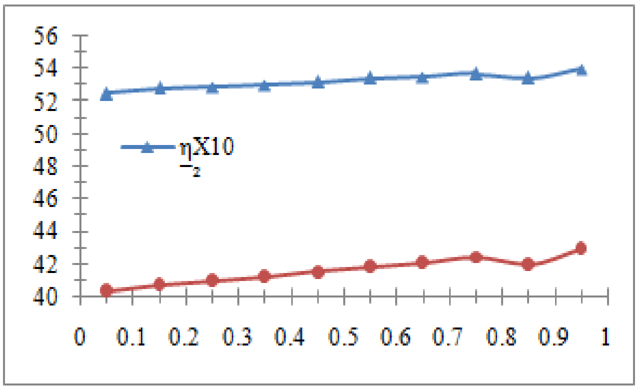

Figure 3: variation of $\beta\varepsilon_{AB}$ & η versus Cm in Benzene+p-dioxane

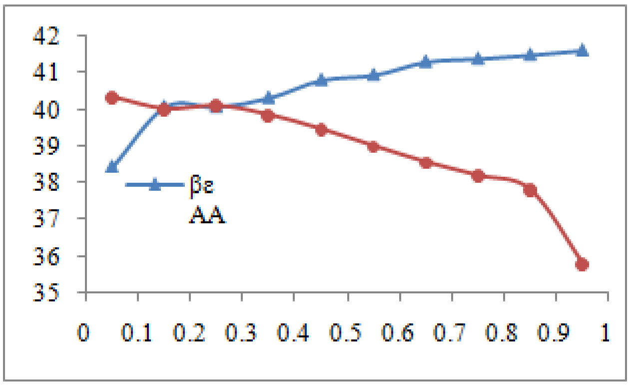

Figure 4: variation of $\beta\varepsilon_{AA}$ & $\beta\varepsilon_{BB}$ versus Cm in Benzene+methylcyclohexane

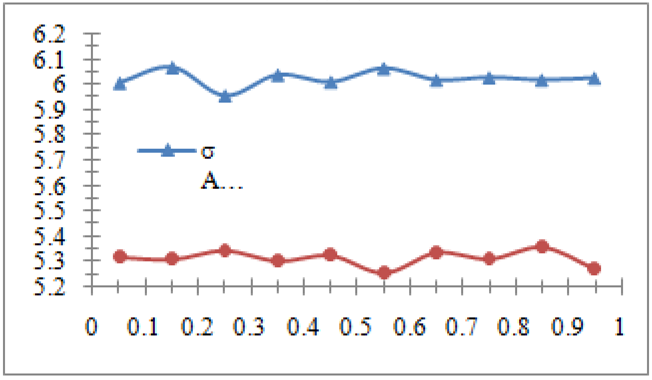

Figure 5: variation of σ_{AA} & σ_{BB} versus Cm in Benzene+methylcyclohexane

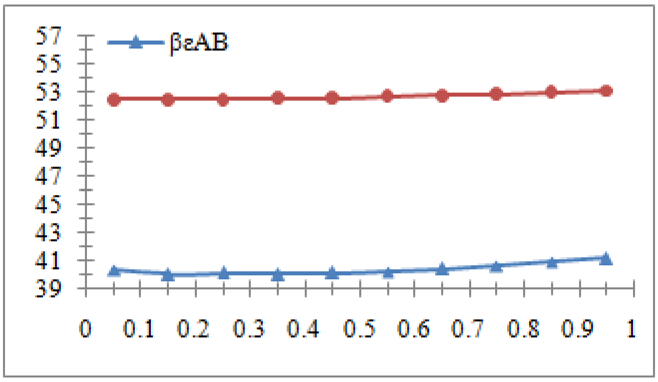

Figure 6: variation of $\beta\varepsilon_{AB}$ & η versus Cm in Benzene+methylcyclohexan

Table 1 shows the values of experimentally measured ultrasonic velocity [u_{expt}], density [ρ_{expt}] and theoretically calculated parameters U_{SBK} , ρ_{SBK} and corresponding reduced depth of potential for mixture [$\beta\varepsilon_{AB}$] and individual liquid component in presence of the other [$\beta\varepsilon_{AA}$, $\beta\varepsilon_{BB}$], hard sphere diameter for the individual liquid component molecules in presence of the other [σ_{AA}, σ_{BB}] at temperature 303.15^{0}K. {u x cm.sec^{-1};ρ x gm.cc^{-1};σ x 10^{-8}cm}

Table 1: Benzene+p-dioxane

Cm	uexpt	uSBK	ρexpt	ρSBK	βεAB	βεAA	βεBB	σAA	σBB	η
0.00	1272.8	1272.80	0.8728	0.8728						
0.05	-				40.348	44.186	40.348	5.160	5.302	0.525
0.10	1281.4	1281.39	0.8949	0.8949						
0.15					40.710	42.899	40.443	5.410	5.274	0.528
0.20	1285.1	1285.13	0.9015	0.9015						

0.25					40.945	43.171	40.468	5.124	5.344	0.529
0.30	1288.9	1288.80	0.9270	0.9270						
0.35					41.216	43.105	40.309	5.412	5.220	0.530
0.40	1294.1	1294.08	0.9310	0.9310						
0.45					41.520	43.304	40.380	5.250	5.332	0.532
0.50	1299.1	1299.14	0.9494	0.9494						
0.55					41.809	43.183	40.459	5.278	5.304	0.534
0.60	1303.3	1303.26	0.9643	0.9643						
0.65					42.072	43.199	40.408	5.290	5.286	0.535
0.70	1308.7	1308.67	0.9811	0.9811						
0.75					42.399	41.173	45.277	5.256	5.370	0.537
0.80	1282.6	1282.57	0.9949	0.9949						
0.85					41.979	44.076	32.338	5.292	5.208	0.534
0.90	1319.0	1318.97	1.0105	in 1.0105						
0.95	Benzene+p-dioxane				42.962	43.249	40.047	5.302	5.118	0.540
1.00	1324.0	1323.61	1.0145	1.0145						

Table2:benzene+methylcyclohexane

Cm	uexpt	uSBK	**ρ**expt	**ρ**SBK	β**ε**AB	β**ε**AA	β**ε**BB	**σ**AA	**σ**BB	**η**
0.00	1272.8	1272.80	0.8728	0.8728						
0.05					40.355	38.458	40.355	6.008	5.318	0.525
0.10	1246.1	1246.10	0.8467	0.8467						
0.15					40.046	40.089	40.037	6.070	5.308	0.525
0.20	1234.9	1234.92	0.8310	0.8310						
0.25					40.111	40.085	40.121	5.958	5.344	0.525
0.30	1222.8	1222.80	0.8232	0.8232						
0.35					40.048	40.337	39.871	6.040	5.302	0.526
0.40	1211.3	1211.32	0.9092	0.9092						
0.45					40.128	40.821	39.473	6.012	5.324	0.526
0.50	1202.3	1202.28	0.7979	0.7979						
0.55					40.212	40.958	39.011	6.066	5.254	0.527
0.60	1197.3	1197.27	0.7872	0.7872						
0.65					40.418	41.318	38.570	6.020	5.336	0.528
0.70	1193.6	1193.59	0.7796	0.7796						
0.75					40.638	41.401	38.205	6.030	5.310	0.529
0.80	1189.6	1189.58	0.7699	0.7699						
0.85					40.950	41.507	37.806	6.020	5.358	0.530
0.90	1187.3	1187.31	0.7643	0.7643						
0.95					41.202	41.631	35.790	6.028	5.270	0.531
1.00	1189.0	1188.99	0.7560	0.7560						

Table 4: some physical parameters (input data) for pure liquids at 303.15K

Liquids	Molecular Weight	Density **ρ** Kg-m³	U.S. Velocity m/s	β**ε**	**σ**A^0
Benzene	78.04	0.8728	1272.8	40.51	5.495
p-dioxane	88.11	1.0145	1324.0	42.85	5.291
Methylcyclohexane	98.00	0.7560	1189.0	41.41	5.575

5. Conclusions

In the system benzene+p.dioxane, benzene is considered to be very weakly associative liquid and p dioxane known to give strong interaction with associative liquid. A weak assocoiative molecular interaction is therefore expected between p-dioxane and benzene. In system benzene+methylcyclohexane the intermolecular interaction is not due to a specific process such as H-bonding or lone pair interaction but is a ring-ring interaction resulting a weak molecular interaction. The khasare's theory is capable of predicting thermodynamic parameter i.e ultrasonic velocity and density simultaneously for logical input parameter at different concentration in various binary liquid mixtures having weak as well as strong intermolecular interactions to high degree of accuracy at given temperature.

References

[1] ReissH, Frisch H & Lebowitz J L, J Chem phys31 (1959)369
[2] Barker J A, Henderson d & Watt R O, Phys Rev Lett a, 31(1970)48.
[3] Guha A & Mandal A K, Indian J pure & Appl Phys, 26(1988)340
[4] Bhatti S S & Singh D P, Acustica, 50(1980)29.
[5] Sharma B K, Pramana, 14(1980)447
[6] Gopal Rao R V & Jardar R N, Indian J Pure &Appl Phys, 14(1976)905
[7] Khasare S B , Indian J Pure & Appl phys 25(1987)489;29(1991)19;29(1991)547.
[8] Khasare S B , Indian J Pure & Appl Phys,25(1987)182.
[9] Khasare S B, Indian J Pure & Appl Phys, 26(1988)487.

[10] Chimankar O P & Pawar N R, International Journal of Research in Engineering & Technology (IJRET), Volume-03, Issue-06, 2014

[11] Bhandakkar V D, Chimankar O P & Pawar N R, J. Chem Pharm Res,2 (2010), 873

[12] Chimankar O. P., Bhandakkar V. D., Pawar N. R. and Padole N. N., IOP Conf. Series: Material Science and Engineering ,2012, doi: 10.1088/1757-899X/42/1/ 012030

[13] Khasare S B, Indian J Pure & Appl Phys, 29(1991)19.

[14] Khasare S B, Indian J Pure & Appl Phys, 29(1991)547.

[15] Khasare S B, Indian J Pure & Appl Phys, 31(1993)224.

[16] Timmermans J, Physico-chemical constant of pure organic compounds, Elesevier Amsterdam, 1 & 2 (1950, 1965)

[17] Dreisbach P P , Physical properties of chemical compounds , 1,2&3 (ed. American chemical society) Washington D C (1955)

[18] Ed. Dean J A, Lange’s hand of chemistry, McGraw hill Book Company (1979)

[19] Rao C N R, A hand book of chemistry and physics, Affilited E W press Pvt Ltd, New Delhi (1976)