

Khasare Equation of State for Molecular Cluster Study of Some Organic Liquids

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ABSTRACT

Comparative study of second generation and third generation Khasare's EOS are carried out at critical temperature. Third generation of EOS is used to study the correlation of structural properties and thermodynamic behavior in terms of liquid clusters. Computations are based on ζ , a new parameter introduced to obtain the unique solution. All computations are carried out from 283.15 K to 343.15 K. The value of ζ^l is attributed to cluster forming/breaking. Present calculation is based upon the sample thermodynamic data such as ultrasonic wave, density, volume expansion coefficient and ratio of specific heat (1.3).

Key Words: Equation of State, LJ Potential, Computer Algebra, Molecular Clusters.

PACS: 51.30. +i Thermodynamic properties, equations of state

PACS: 36.40.Ei Phase transitions in clusters

PACS: 05.70.Ce thermodynamics

INTRODUCTION

Study of liquids finds immense importance in the physical and chemical sciences. Large experimental data is published over the years. Also many eminent workers established different significant theories for understanding the behavior of pure liquids, solutions, and liquid mixtures. Structurally related organic liquids and their mixtures find enormous attention in recent years as they have vast applicability in chemical industries. Scaled Particle Theory (SPT) serves as a starting point to develop further insight in the subject. Earlier reasonable theoretical approach for extended scaled particle theory is developed (first generation EOS) in earlier several papers [1-11]. The Equation of State [EOS] [12-18] is developed based upon this idea. Many workers have tested its utility for real liquids in their studies. Using the perception of hard sphere with perturbation view Khasare-Deshpande obtained following second generation EOS [19]

$$z := \frac{-\frac{3}{2}\eta^2 - \frac{5}{4}\eta - 1}{\left(\frac{3}{4}\eta - 1\right)(\eta - 1)^2} + \frac{3432\eta}{35\tau^2\left(\frac{3}{4}\eta - 1\right)}$$

[1]

This was used to carry out the study of nano-cavity [20-22].

The above expression was modified further by putting the constraint of lattice concept by aptly introducing the parameter λ which is defined as

$$\lambda = (1 + f\eta) ; \quad m = 3/4 ; \quad f_{\text{fcc}} = 0.337817454 ; \quad f_{\text{bcc}} = 0.437135330; \quad [2]$$

With this adaptation third generation equation becomes as [23-24]

$$z := \frac{(8\lambda^2 m + (-8m - 9)\lambda + 2m + 6)\eta^2 + (4\lambda^2 m + (-2 - 4m)\lambda + m)\eta - \lambda}{((1 - 2\lambda)^2 m\eta - \lambda)(\eta - 1)^2} \quad [3]$$

$$- \frac{1056((1 - 2\lambda)^2 m - 4\lambda)\eta}{35\tau^2((1 - 2\lambda)^2 m\eta - \lambda)}$$

This paper mainly delineates study of the pure organic liquids listed below with molecular weights shown in brackets.

- | | | |
|----------------------------|-------------------------------|------------------------------|
| 1) 1-4 Dioxane (88) | 2) Methyl alcohol (32) | 3) Benzene (78) |
| 4) Tetra hydro furan (72) | 5) Carbon-tetrachloride (154) | 6) Cyclohexanol (100) |
| 7) Methyl-cyclohexane (98) | 8) Cyclohexane (84) | 9) Tetra hydro pyrrole (71). |

Here computational technique is being developed to obtain some results by considering aggregation of molecular clustering in the liquid state. The properties of hard sphere and concept of revised scaled particle theory is employed to work out thermodynamic parameters. The paper presents mathematical computations in detail.

Two parameters, namely radius and binding energy of molecule are necessary for real fluids. Authors used equation of state for a strong repulsive potential together with a weak attractive potential. Authors used equation of state for a strong repulsive potential together with a weak attractive potential. Dimensional less variable packing fraction (η) and temperature ($\tau = k_B T / \epsilon$) are required for calculating ultrasonic wave velocity, density, and volume expansion coefficient.

Hence we have following set of equations containing thermodynamic reduced variable [η, τ].

$$\frac{\beta P}{\zeta \rho} = Z(\eta, \beta \epsilon) = \xi(\eta, \tau) \quad [4]$$

$$\frac{Mu^2}{\zeta \gamma RT} = \frac{\partial(Z\eta)}{\partial \eta} = \psi(\eta, \tau) \quad [5]$$

$$\frac{Mu^2 \alpha T}{\zeta \gamma RT} = \frac{\partial(ZT)}{\partial T} = \omega(\eta, \tau) \quad [6]$$

To obtain the unique mathematical solution of above set of equations new variable ζ is brought in to picture. Clustering of molecules is taken into account to associate model parameters in terms of ζ for real fluids. These model parameters have link with properties of liquids such as ultrasonic velocity, bulk density and volume expansion coefficient.

Mathematical model for Fluid

A compressibility factor Z for Lennard-Jones fluids is

$$Z(\eta, \tau) = \frac{\beta P}{\zeta \rho} , \quad \beta = \frac{1}{k_B T} , \quad \beta \epsilon = \frac{1}{\tau} , \quad \eta = \frac{v}{V} = \frac{\pi \rho d^3}{6} , \quad 0 < \zeta < 1 \quad [7]$$

Where v is volume of cavity containing few chemical units, V is volume, P is a pressure, $\rho = N/V$ is the density, T is temperature, ε is binding energy of cluster containing chemical units, ζ parameter used to obtain the solution and k_B is Boltzmann constant.

Final expression for equation of state for a fluid is expressed as

$$\frac{\beta P}{\zeta \rho} = Z(\eta, \tau) = z \quad [8]$$

Where, z is given by eq. [3]

Now m and λ (eq. [2]) for face centre lattice are given by following equation

So that eq. (8) become

$$z := \frac{(-2(1+f\eta)\eta - 9(1+f\eta)\eta^2 + 8\eta^2(1+f\eta)^2 m - 4\eta(1+f\eta)m + 4\eta(1+f\eta)^2 m - 8\eta^2(1+f\eta)m + 6\eta^2 + 2m\eta^2 + m\eta - 1 - f\eta) / ((\eta - 1)^2 (4\eta(1+f\eta)^2 m + m\eta - 4\eta(1+f\eta)m - 1 - f\eta)) - \frac{1056(4(1+f\eta)^2 m + m - 4 - 4f\eta - 4(1+f\eta)m)\eta}{35\tau^2(4\eta(1+f\eta)^2 m + m\eta - 4\eta(1+f\eta)m - 1 - f\eta)}}{35\tau^2(4\eta(1+f\eta)^2 m + m\eta - 4\eta(1+f\eta)m - 1 - f\eta)}$$

From above, we get eq. [9] and eq. [10]

$$\frac{Mu^2}{\zeta RT} = \frac{\partial(Z\eta)}{\partial\eta} = y \quad [9]$$

Where

$$y := \left(\begin{array}{l} (-4f\eta - 2 - 9f\eta^2 - 18(1+f\eta)\eta + 16\eta(1+f\eta)^2 m + 16\eta^2(1+f\eta)m f \\ - 4(1+f\eta)m - 4\eta fm + 4(1+f\eta)^2 m + 8\eta(1+f\eta)m f - 16\eta(1+f\eta)m \\ - 8\eta^2 fm + 12\eta + 4m\eta + m - f) / ((\eta - 1)^2 (4\eta(1+f\eta)^2 m + m\eta - 4\eta(1+f\eta)m - 1 - f\eta)) - 2(-2(1+f\eta)\eta \\ - 9(1+f\eta)\eta^2 + 8\eta^2(1+f\eta)^2 m - 4\eta(1+f\eta)m + 4\eta(1+f\eta)^2 m \\ - 8\eta^2(1+f\eta)m + 6\eta^2 + 2m\eta^2 + m\eta - 1 - f\eta) / ((\eta - 1)^3 (4\eta(1+f\eta)^2 m + m\eta - 4\eta(1+f\eta)m - 1 - f\eta)) - (-2(1+f\eta)\eta \\ - 9(1+f\eta)\eta^2 + 8\eta^2(1+f\eta)^2 m - 4\eta(1+f\eta)m + 4\eta(1+f\eta)^2 m \\ - 8\eta^2(1+f\eta)m + 6\eta^2 + 2m\eta^2 + m\eta - 1 - f\eta) \\ (4(1+f\eta)^2 m + 8\eta(1+f\eta)m f + m - 4(1+f\eta)m - 4\eta fm - f) / ((\eta - 1)^2 (4\eta(1+f\eta)^2 m + m\eta - 4\eta(1+f\eta)m - 1 - f\eta)^2) \\ - \frac{1056(8(1+f\eta)m f - 4f - 4fm)\eta}{35\tau^2(4\eta(1+f\eta)^2 m + m\eta - 4\eta(1+f\eta)m - 1 - f\eta)} \\ - \frac{1056(4(1+f\eta)^2 m + m - 4 - 4f\eta - 4(1+f\eta)m)}{35\tau^2(4\eta(1+f\eta)^2 m + m\eta - 4\eta(1+f\eta)m - 1 - f\eta)} + 1056 \end{array} \right)$$

$$\begin{aligned}
& (4(1+f\eta)^2 m + m - 4 - 4f\eta - 4(1+f\eta)m)\eta \\
& (4(1+f\eta)^2 m + 8\eta(1+f\eta)mf + m - 4(1+f\eta)m - 4\eta fm - f) / (35\tau^2) \\
& (4\eta(1+f\eta)^2 m + m\eta - 4\eta(1+f\eta)m - 1 - f\eta^2) \Big) \eta + (-2(1+f\eta)\eta \\
& - 9(1+f\eta)\eta^2 + 8\eta^2(1+f\eta)^2 m - 4\eta(1+f\eta)m + 4\eta(1+f\eta)^2 m \\
& - 8\eta^2(1+f\eta)m + 6\eta^2 + 2m\eta^2 + m\eta - 1 - f\eta) / ((\eta - 1)^2) \\
& (4\eta(1+f\eta)^2 m + m\eta - 4\eta(1+f\eta)m - 1 - f\eta)) \\
& - \frac{1056(4(1+f\eta)^2 m + m - 4 - 4f\eta - 4(1+f\eta)m)\eta}{35\tau^2(4\eta(1+f\eta)^2 m + m\eta - 4\eta(1+f\eta)m - 1 - f\eta)}
\end{aligned}$$

And

$$\frac{Mu^2\alpha T}{\varsigma\gamma RT} = \frac{\partial(ZT)}{\partial T} = x \quad [10]$$

Where

$$\begin{aligned}
x := & \frac{1056(4(1+f\eta)^2 m + m - 4 - 4f\eta - 4(1+f\eta)m)\eta}{35\tau^2(4\eta(1+f\eta)^2 m + m\eta - 4\eta(1+f\eta)m - 1 - f\eta)} + (-2(1+f\eta)\eta \\
& - 9(1+f\eta)\eta^2 + 8\eta^2(1+f\eta)^2 m - 4\eta(1+f\eta)m + 4\eta(1+f\eta)^2 m \\
& - 8\eta^2(1+f\eta)m + 6\eta^2 + 2m\eta^2 + m\eta - 1 - f\eta) / ((\eta - 1)^2) \\
& (4\eta(1+f\eta)^2 m + m\eta - 4\eta(1+f\eta)m - 1 - f\eta))
\end{aligned}$$

It is important to note that in above set of equations [$\zeta(\eta, \tau), \psi(\eta, \tau), \omega(\eta, \tau)$] nearest pole for fcc $\eta_{max} = 0.7404804897$ and for bcc $\eta_{max} = 0.6801747616$, $R = (8.314)10^7$ J/mole K; $N_A = (6.02215)10^{23}$ mol⁻¹; pressure = (101.2928) kPa.

For fluid, present equation of state is tested by considering $\eta = v/V$, and $\tau > 0$. The term v/V is taken as the probability for creating a cavity in fluid, assuming presence of group of molecules in cavity.

Boundary condition for gas phase can be put as

$$if \frac{\beta P}{\varsigma\rho} = Z(\eta, \beta\varepsilon) = \xi(\eta, \tau) = 1, then, \varsigma = 1$$

For deviation of ζ from 1 can be attributed to liquid phase hence we define Ordering = [1- ζ].

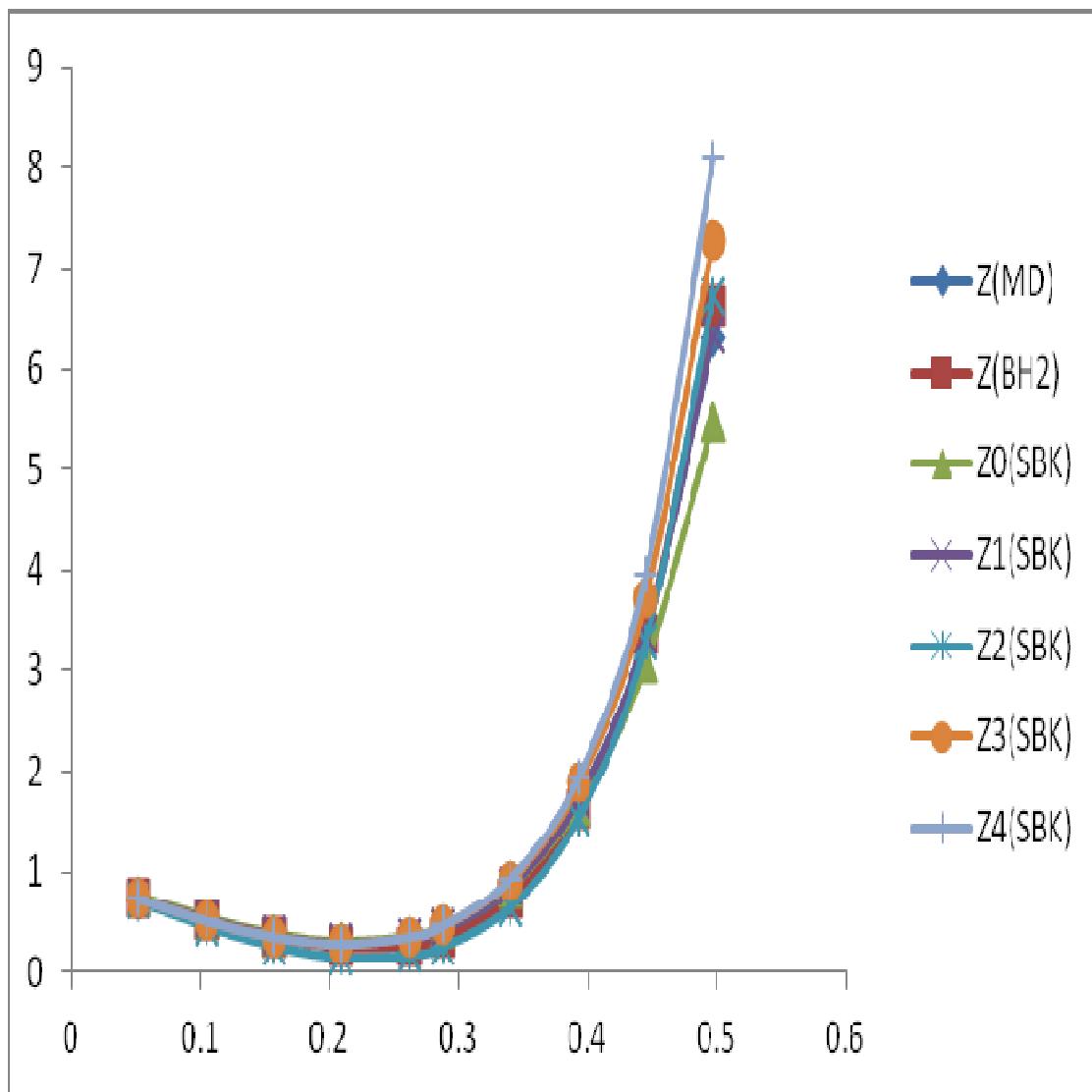
RESULTS

The EOS, data, results and molecular cluster are presented in the tabular form.

Table 1: Comparative study of equation of State at critical temperature

S. No.	η	Z(MD)	Z(BH2)	$Z_0(\tau_c)$	$Z_1(\tau_c)$	$Z_2[\tau_c]$	$Z_3[\tau_{fcc}]$	$Z_4[\tau_{bcc}]$
1	0.052	0.72	0.74	0.7542	0.75	0.7135	0.7436	0.7403
2	0.105	0.52	0.52	0.5368	0.54	0.4601	0.5231	0.5190
3	0.157	0.35	0.36	0.3765	0.38	0.2667	0.3650	0.3615
4	0.209	0.27	0.26	0.2996	0.30	0.1561	0.2938	0.2921
5	0.262	0.30	0.27	0.3546	0.35	0.1776	0.3614	0.3626
6	0.288	0.41	0.35	0.4519	0.45	0.2615	0.4708	0.4750
7	0.340	0.80	0.74	0.8467	0.87	0.6521	0.9199	0.9387
8	0.393	1.73	1.64	1.6502	1.73	1.5393	1.8814	1.9511
9	0.445	3.37	3.36	3.0614	3.35	3.2829	3.7202	3.9587
10	0.497	6.32	6.32	5.4691	6.33	6.7099	7.2791	8.0935

Graph-1: Comparative study of equation of state at critical temperature



Here we used $\lambda = \lambda_{\text{fcc}}$ or $\lambda = \lambda_{\text{bcc}}$ so that $\eta = 0.74$ or $\eta = 0.68$ for solid-state as a boundary condition can be imposed which similar to $\eta = 0$, for $Z = 1.0$ for gas-state, where following is the suitable empirical function.

$$\lambda_{\text{fcc}} = (1 + 0.337817454 \eta); \lambda_{\text{bcc}} = (1 + 0.437135330 \eta); \quad [11]$$

$Z_0(\tau_c)$ [SBK-MSD], τ (critical) = 3.312373150; η (critical) = 0.1572541882; rms-deviation₁ = 0.2890522064,
 $Z_1(\tau_c)$ [SBK], τ (critical) = 3.258762327; η (critical) = 0.1579722415; rms-deviation₁ = 0.0.036835, $Z_1(\tau_c)$ [BH2],
rms-deviation₁ = 0.0.041593, $Z_2(\tau_2)$ [SBK], τ_2 = 3.164; rms-deviation₂ = 3.258762327;
 $Z_3(\tau_c)$ [SBK], τ (fcc) = 3.258762327; η = 0.1546269541; rms-deviation₃ = 0.3299431994
 $Z_4(\tau_c)$ [SBK], τ (bcc) = 3.242842579; η = 0.1538974793; rms-deviation₄ = 0.5974345121.

Table 2: Thermodynamic data such as Velocity, density and volume expansion coefficient (alpha) data in terms of temperature (te=degree centigrade), ratio of specific heat=1.3:

"Liquid(1):=1-4 Dioxane";	"temp:=273.16+te;mw1:=88;gama:=1.3; dens:=(1039.9751-0.9151*te)/1000;alpha:=-(diff(ln(dens),te)); te:=10;den:=dens;vel:=(1450.9465-4.2447*te)*100;alpha1:=alpha; alphat:=temp*alpha1";
"Liquid(2):=Methyalcohol";	"temp:=273.16+te;mw1:=32;gama:=1.3; dens:=(800.9831-0.8353*te)/1000;alpha:=-(diff(ln(dens),te)); te:=10;den:=dens;vel:=(1183.6869-3.2527*te)*100;alpha1:=alpha; alphat:=temp*alpha1";
"Liquid(3):=Benzene";	"temp:=273.16+te;mw1:=78.00;gama:=1.3; dens:=(891.9408-0.8938*te)/1000;alpha:=-(diff(ln(dens),te)); te:=10;den:=dens;vel:=(1401.3231-4.2713*te)*100;alpha1:=alpha; alphat:=temp*alpha1";
"Liquid(4):=Tetrahydrofuran";	"temp:=273.16+te;mw1:=72.00;gama:=1.3; dens:=(906.8611-1.0315*te)/1000;alpha:=-(diff(ln(dens),te)); te:=70;den:=dens;vel:=(1389.7431-4.4833*te)*100;alpha1:=alpha; alphat:=temp*alpha1";
"Liquid(5):=Carbontetrachloride";	"temp:=273.16+te;mw1:=154;gama:=1.3; dens:=(1626.3210-1.7205*te)/1000;alpha:=-(diff(ln(dens),te)); te:=70;den:=dens;vel:=(998.2997-3.1200*te)*100;alpha1:=alpha; alphat:=temp*alpha1";
"Liquid(6):=Cyclohexanol";	"temp:=-273.16+te;mw1:=100;gama:=1.3; dens:=(953.6185-0.6605*te)/1000;alpha:=-(diff(ln(dens),te)); te:=10;den:=dens;vel:=(1645.2765-6.4587*te)*100;alpha1:=alpha; alphat:=temp*alpha1";
"Liquid(7):=Methylcyclohexane";	"temp:=273.16+te;mw1:=98;gama:=1.3; dens:=(780.3847-0.8120*te)/1000;alpha:=-(diff(ln(dens),te)); te:=10;den:=dens;vel:=(1314.8365-4.1947*te)*100;alpha1:=alpha; alphat:=temp*alpha1";
"Liquid(8):=Cyclohexane";	"temp:=273.16+te;mw1:=84;gama:=1.3; dens:=(786.6264-0.8367*te)/1000;alpha:=-(diff(ln(dens),te)); te:=10;den:=dens;vel:=(1364.5498-4.6480*te)*100;alpha1:=alpha; alphat:=temp*alpha1";
"Liquid(9):=Tetrahydropyrrole";	"temp:=-273.16+te;mw1:=71;gama:=1.3; dens:=(873.040-0.8273*te)/1000;alpha:=-(diff(ln(dens),te)); te:=70;den:=dens;vel:=(1474.1564-4.2247*te)*100;alpha1:=alpha; alphat:=temp*alpha1";

Graph-2: Molecular Cluster (ζ^{-1}) at various temperatures

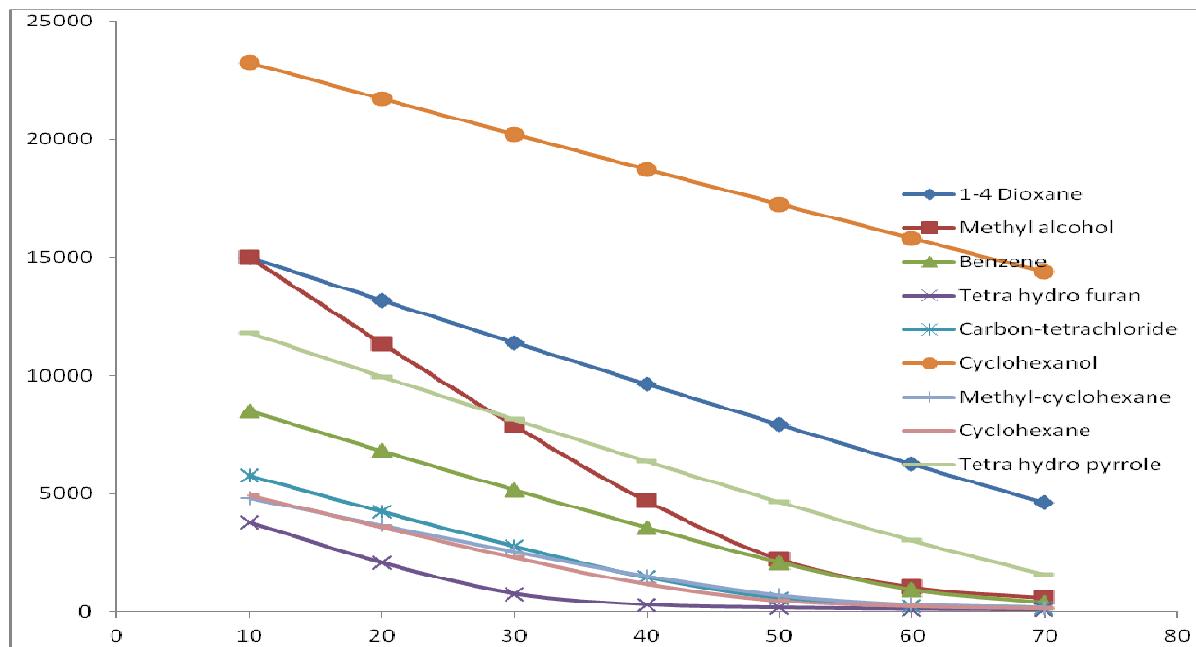


Table 3: Molecular Cluster (ζ^{-1}) at various temperatures

S. No.	Temp	ζ^{-1} (1)	ζ^{-1} (2)	ζ^{-1} (3)	ζ^{-1} (4)
1	10	14994.92125	14991.40215	8511.093768	3778.478406
2	20	13179.85076	11361.03671	6814.077945	2073.623731
3	30	11397.18539	7884.969336	5162.862540	767.2047032
4	40	9648.222005	4697.233040	3572.815969	287.4672091
5	50	7935.442610	2241.990557	2095.451566	160.5869371
6	60	6263.171842	1050.958923	934.4160265	110.4755936
7	70	4641.868253	616.0957465	400.8569412	84.58877970

Table 4: Molecular Cluster (ζ^{-1}) at various temperatures

S. No.	Temp	ζ^{-1} (5)	ζ^{-1} (6)	ζ^{-1} (7)	ζ^{-1} (8)	ζ^{-1} (9)
1	10	5769.107053	23249.39901	4827.727689	4940.599525	11817.82899
2	20	4237.428281	21720.58188	3667.696146	3590.014627	9962.382333
3	30	2772.723672	20211.22899	2553.230564	2306.973957	8146.456918
4	40	1453.468783	18721.72838	1522.041792	1180.463736	6374.650827
5	50	572.6918186	17251.88243	710.9679094	482.9235576	4657.671575
6	60	264.0850921	15802.51821	319.1034686	241.0072790	3026.140666
7	70	162.7288078	14373.69369	184.1863833	155.1250789	1591.371641

DISCUSSION

Calculations show that Cyclohexanol [23249, 14374, 61.8%], 1-4 Dioxane [14995, 4642, 30.9%], methyalcohol [14991, 616, 4.1%] and Tetra hydro pyrrol [11818, 1591, 13.5%] are highly associative while Benzene [8511, 401, 4.7%] shows moderate clustering. Carbon tetrachloride [5769, 163, 2.8%], Cyclohexane [4941, 155, 3.1%], Methylcyclohexane [4828, 184, 3.8%], Tetra hydro furan [3778, 84, 2.2%] seems to remain less associative.

In the given set of liquids, Cyclohexanol [61.8%], 1-4 Dioxane [30.9%], Tetra hydro pyrrol [13.5%], Benzene [4.7%], methyalcohol [4.1%], Methylcyclohexane [3.8%], Cyclohexane [3.1%], Carbon tetrachloride [2.8%], Tetra hydro furan [2.2%] forms groups based on definition of cluster decay rate as [ζ^{-1} (minimum)*100/ ζ^{-1} (maximum)] descending order over temperature range 283.15 K to 343.15 K.

We have limited to qualitative results hence there is a scope for comparison with experiments and other models in the literature.

CONCLUSION

Each calculation shows unique solution of η and τ due to occurrence of parameter ζ . Here ζ^{-1} is associated to cluster size, so that built up picture seems to be virtually reliable.

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