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Khasare equation of state for thermodynamic study of some organic liquids using face centered cubic packing density

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ABSTRACT

Using two parametric (η,τ) *Equation of State, unique cavity in fluid is estimated. The correlation of structural properties and thermodynamic behavior in terms of liquid clusters has been studied. Computations are based on □□□□a new parameter introduced to obtain the unique solution. The upper limit* η_{max} *is predefined close to 0.74. All computations are carried at 303.15 K. The value of* ζ□□□ *is attributed to cluster formation. 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*
***PACS**: 68.03.Cd Surface tension and related phenomena*
***PACS**: 61.20.Gy Theory and models of liquid structure*

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 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 EOS [19]

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

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

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

$$\lambda = (1 + 0.337817454\eta) \qquad [2]$$

With this adaptation equation becomes as [23-24]

$$z := \frac{(8\lambda^2 m + (-8m - 9)\lambda + 2m + 6)\eta^2 + (4\lambda^2 m + (-2 - 4m)\lambda + m)\eta - \lambda}{((1 - 2\lambda)^2 m\eta - \lambda)(\eta - 1)^2} - \frac{1056\ ((1 - 2\lambda)^2 m - 4\lambda)\eta}{35\ \tau^2\ ((1 - 2\lambda)^2 m\eta - \lambda)} \qquad [3]$$

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

1) 1-4 Dioxane (88) 2) Acrylo-nitrile (53) 3) Methyl-methacrylate (100)
4) Benzene (78) 5) Tetra hydro furan (72) 6) Carbon-tetrachloride (154)
7) Acrolein (56) 8) Methyl-cyclohexane (98) 9) Cyclohexane (84)
10) 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 ($\tau = k_B T/\varepsilon$) 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]□□

$$\frac{\beta P}{\varsigma\rho} = Z(\eta, \beta\varepsilon) = \xi(\eta, \tau) \qquad [4]$$

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

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

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

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

[7]

Where v is volume of cavity containing few chemical units, V is volume, P is a pressure, ρ□= 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

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

Where, z is given by eq. [3]

Now m=3/4 and λ□□eq. [2])for face centre lattice are given by following equation

So that eq. (8) become

$$\begin{aligned} z :=\ & ((8\,(1+0.337817454\ \eta)^2\,m+(-8\,m-9)\,(1+0.337817454\ \eta)+2\,m+6)\,\eta^2 \\ & +(4\,(1+0.337817454\ \eta)^2\,m+(-2-4\,m)\,(1+0.337817454\ \eta)+m)\,\eta-1 \\ & -0.337817454\ \eta)\,/\,(((-1-0.675634908\ \eta)^2\,m\,\eta-1-0.337817454\ \eta) \\ & (\eta-1)^2)-\frac{1056\,((-1-0.675634908\ \eta)^2\,m-4-1.351269816\ \eta)\,\eta}{35\,\tau^2\,((-1-0.675634908\ \eta)^2\,m\,\eta-1-0.337817454\ \eta)} \end{aligned}$$

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

$$\frac{Mu^2}{\varsigma\gamma RT}=\frac{\partial(Z\eta)}{\partial\eta}=y \qquad [9]$$

Where

$$\begin{aligned} y :=\ & \Big(((5.405079264\ \ (1+0.337817454\ \ \eta)\,m-2.702539632\ \ m-3.040357086\ )\,\eta^2 \\ & +2\,(8\,(1+0.337817454\ \ \eta)^2\,m+(-8\,m-9)\,(1+0.337817454\ \ \eta)+2\,m+6)\,\eta \\ & +(2.702539632\ \ (1+0.337817454\ \ \eta)\,m-0.675634908\ \ -1.351269816\ \ m)\,\eta \\ & +4\,(1+0.337817454\ \ \eta)^2\,m+(-2-4\,m)\,(1+0.337817454\ \ \eta)+m \\ & -0.337817454\ )\,/\,(((-1-0.675634908\ \ \eta)^2\,m\,\eta-1-0.337817454\ \ \eta)\,(\eta-1)^2) \\ & -((8\,(1+0.337817454\ \ \eta)^2\,m+(-8\,m-9)\,(1+0.337817454\ \ \eta)+2\,m+6)\,\eta^2 \\ & +(4\,(1+0.337817454\ \ \eta)^2\,m+(-2-4\,m)\,(1+0.337817454\ \ \eta)+m)\,\eta-1 \end{aligned}$$

$$
\begin{aligned}
&-0.337817454\ \eta)\,(-1.351269816\ (-1-0.675634908\ \eta)\,m\,\eta\\
&+(-1-0.675634908\ \eta)^2\,m-0.337817454\ )\,/\,(\\
&((-1-0.675634908\ \eta)^2\,m\,\eta-1-0.337817454\ \eta)^2\,(\eta-1)^2)-2\,(\\
&(8\,(1+0.337817454\ \eta)^2\,m+(-8\,m-9)\,(1+0.337817454\ \eta)+2\,m+6)\,\eta^2\\
&+(4\,(1+0.337817454\ \eta)^2\,m+(-2-4\,m)\,(1+0.337817454\ \eta)+m)\,\eta-1\\
&-0.337817454\ \eta)\,/\,(((-1-0.675634908\ \eta)^2\,m\,\eta-1-0.337817454\ \eta)\\
&(\eta-1)^3)-\frac{1056\,(-1.351269816\ (-1-0.675634908\ \eta)\,m-1.351269816\ )\,\eta}{35\,\tau^2\,((-1-0.675634908\ \eta)^2\,m\,\eta-1-0.337817454\ \eta)}\\
&-\frac{1056\,((-1-0.675634908\ \eta)^2\,m-4-1.351269816\ \eta)}{35\,\tau^2\,((-1-0.675634908\ \eta)^2\,m\,\eta-1-0.337817454\ \eta)}+1056\\
&((-1-0.675634908\ \eta)^2\,m-4-1.351269816\ \eta)\,\eta\,(\\
&-1.351269816\ (-1-0.675634908\ \eta)\,m\,\eta+(-1-0.675634908\ \eta)^2\,m\\
&-0.337817454\ )\,/\,(35\,\tau^2\,((-1-0.675634908\ \eta)^2\,m\,\eta-1-0.337817454\ \eta)^2)\Big)\,\eta\\
&+((8\,(1+0.337817454\ \eta)^2\,m+(-8\,m-9)\,(1+0.337817454\ \eta)+2\,m+6)\,\eta^2\\
&+(4\,(1+0.337817454\ \eta)^2\,m+(-2-4\,m)\,(1+0.337817454\ \eta)+m)\,\eta-1\\
&-0.337817454\ \eta)\,/\,(((-1-0.675634908\ \eta)^2\,m\,\eta-1-0.337817454\ \eta)\\
&(\eta-1)^2)-\frac{1056\,((-1-0.675634908\ \eta)^2\,m-4-1.351269816\ \eta)\,\eta}{35\,\tau^2\,((-1-0.675634908\ \eta)^2\,m\,\eta-1-0.337817454\ \eta)}
\end{aligned}
$$

And

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

Where

$$
\begin{aligned}
x:=&\frac{1056\,((-1-0.675634908\ \eta)^2\,m-4-1.351269816\ \eta)\,\eta}{35\,\tau^2\,((-1-0.675634908\ \eta)^2\,m\,\eta-1-0.337817454\ \eta)}+(\\
&(8\,(1+0.337817454\ \eta)^2\,m+(-8\,m-9)\,(1+0.337817454\ \eta)+2\,m+6)\,\eta^2\\
&+(4\,(1+0.337817454\ \eta)^2\,m+(-2-4\,m)\,(1+0.337817454\ \eta)+m)\,\eta-1\\
&-0.337817454\ \eta)\,/\,(((-1-0.675634908\ \eta)^2\,m\,\eta-1-0.337817454\ \eta)\\
&(\eta-1)^2)
\end{aligned}
$$

It is important to note that in above set of equations [ζ(η,τ),ψ(η,τ),ω(η,τ□] nearest pole η_{max}□□is 0.7404804897.

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 η= v/V, and τ > 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 results are presented in the tabular and graphical form.

Table 1 Experimental and model parameters

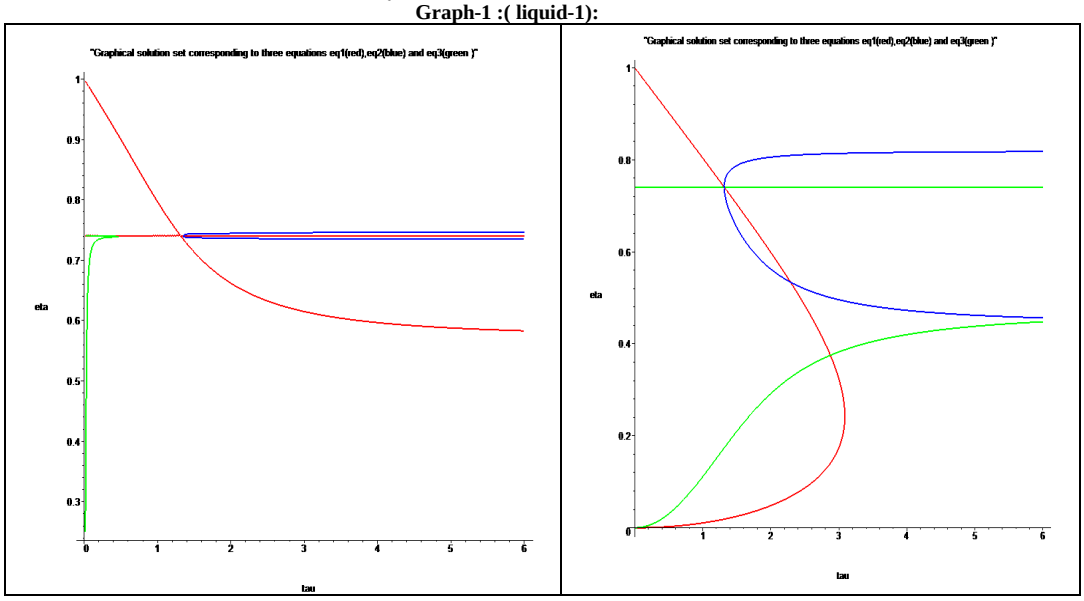
Sr No,	Liquid	Velocity cm/s	Density (gm/cm^3)	Volume Expansion Coefficient(10^{-4})	1/ζ	Radius (AU)
1	1-4 Dioxane	132400	1.0270	9.32	10057.75	5.220083
2	Acrylonitrile	143000	0.8060	32.47	1.459525	4.290907
3	MethylMethacrylate	114000	0.9225	25.14	2.745095	5.227368
4	Benzene	129800	0.8784	9.32	9706.26246	5.282383
5	Tetrahydrofuran	127800	0.8811	11.71	877.42608	5.131792
6	Carbontetrachloride	92000	1.5834	10.90	2853.85130	5.445772
7	Acrolein	137400	0.8489	24.30	3.80462650	4.447519
8	Methylcyclohexane	121000	0.7601	10.68	2703.32116	5.979991
9	Cyclohexane	124800	0.7657	10.93	2459.57644	5.666194
10	Tetrahydropyrrole	136900	0.8524	9.70	8429.29836	5.170848

Table 2 Table for packing density η and ordering

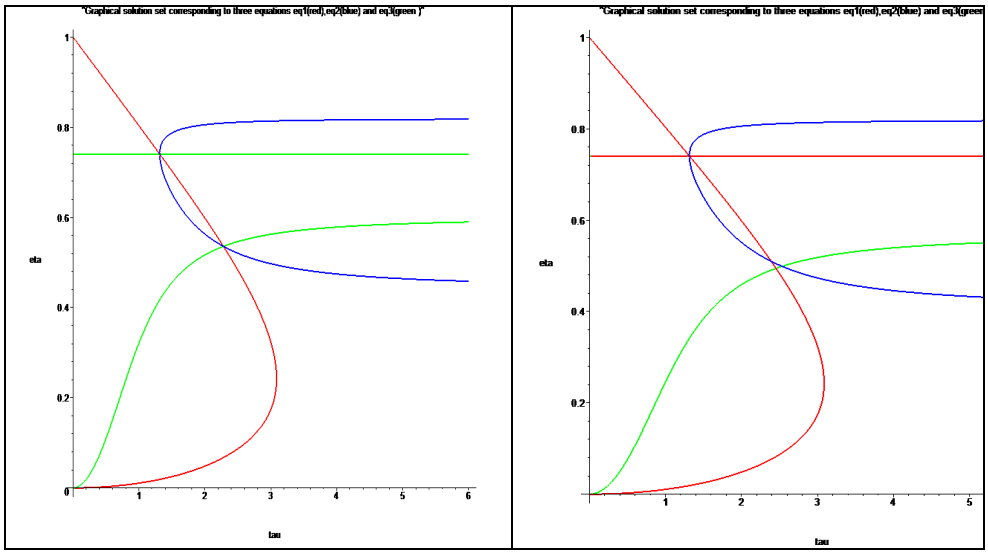
Sr. No.	Liquid	η	τ	(1-ζ)
1	1-4 Dioxane	0.7402616436	1.317052472	0.9999005742
2	Acrylonitrile	0.5357619659	2.281403603	0.3148458198
3	Methylmethacrylate	0.5357619659	2.281403603	0.3148458198
4	Benzene	0.7402061045	1.317402266	0.9998969737
5	Tetrahydrofuran	0.7375052570	1.330743989	0.9988603028
6	Carbon tetrachloride	0.7396057303	1.320362632	0.9996495963
7	Acrolein	0.5946852533	2.017975203	0.7371621106
8	Methylcyclohexane	0.7396250882	1.320356317	0.9996300846
9	Cyclohexane	0.7394673876	1.321097417	0.9995934259
10	Tetrahydropyrrole	0.7401771542	1.317500573	0.9998813662

"Graphical solution set corresponding to three equations ξ(η,τ) (red line), ψ(η,τ) (blue line) and ω(η,τ) (green line), for liquid-1, Yaxis = η X-axis = τ temp =303.15;"

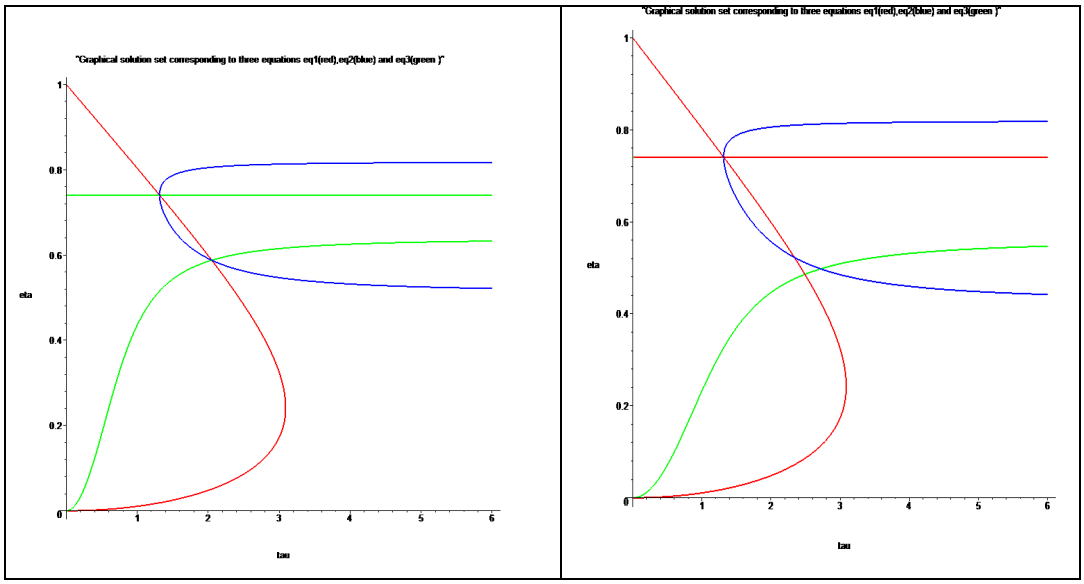
Graph-1 :(liquid-1):



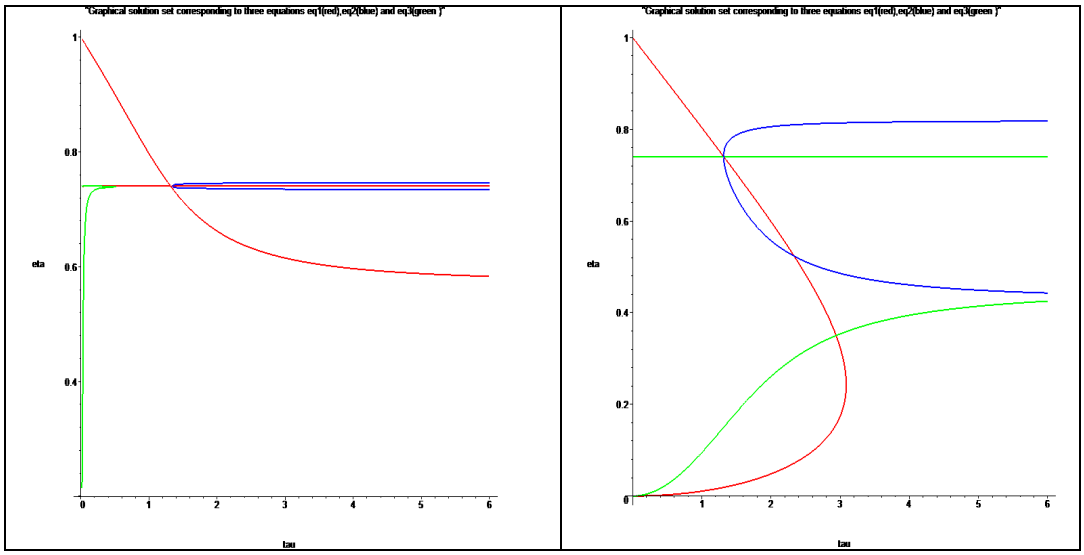
Graph-2 :(liquid-2):



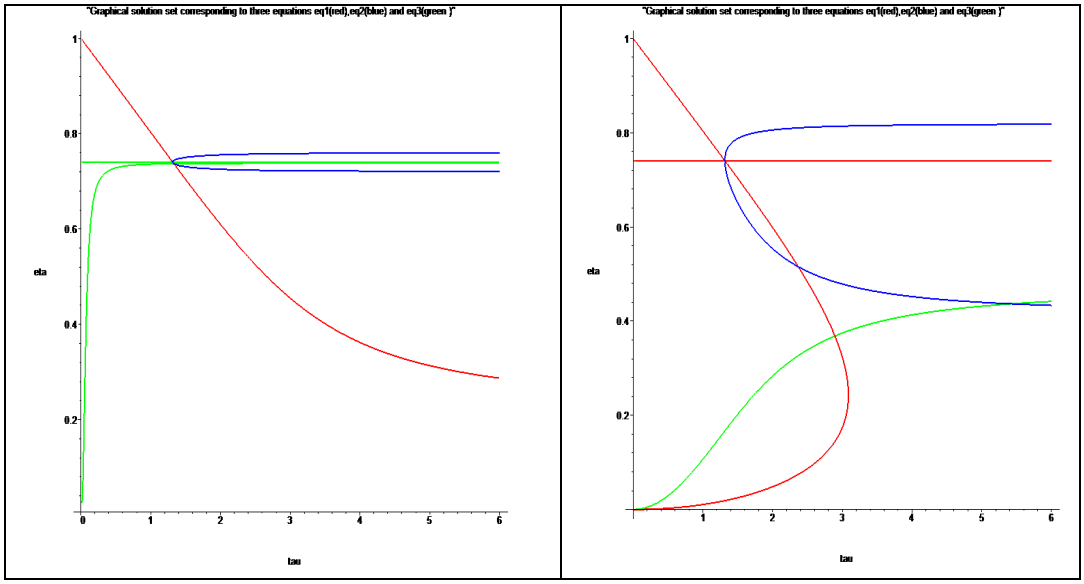
Graph-3 :(liquid-3):



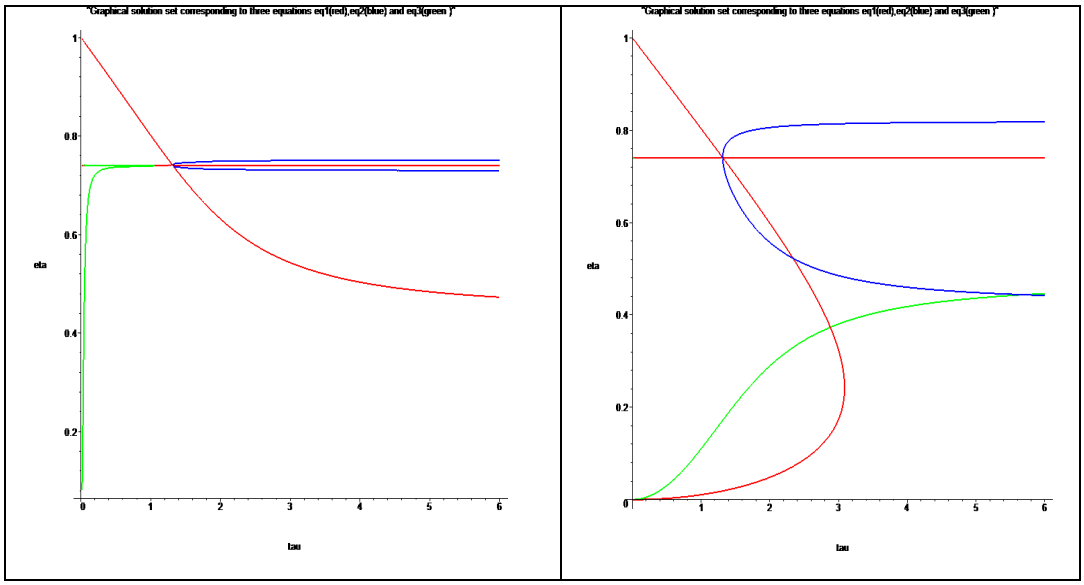
Graph-4 :(liquid-4):



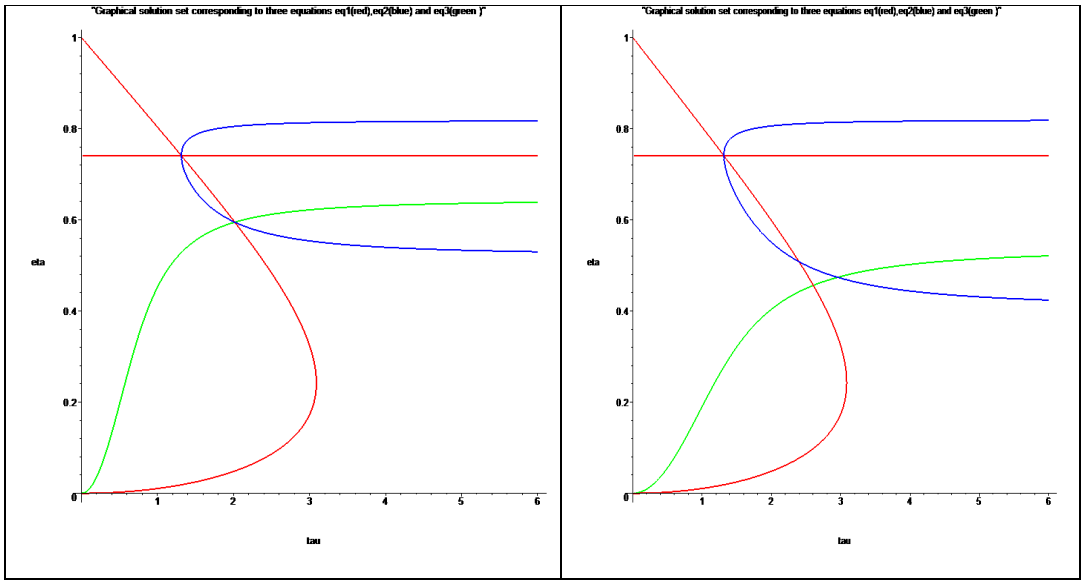
Graph-5 :(liquid-5):



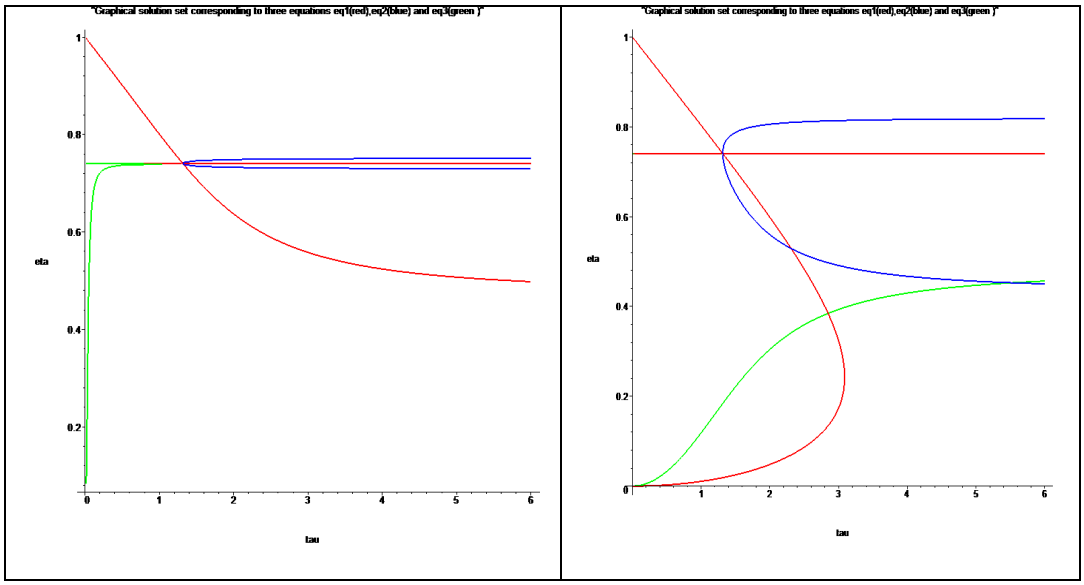
Graph-6 :(liquid-6):



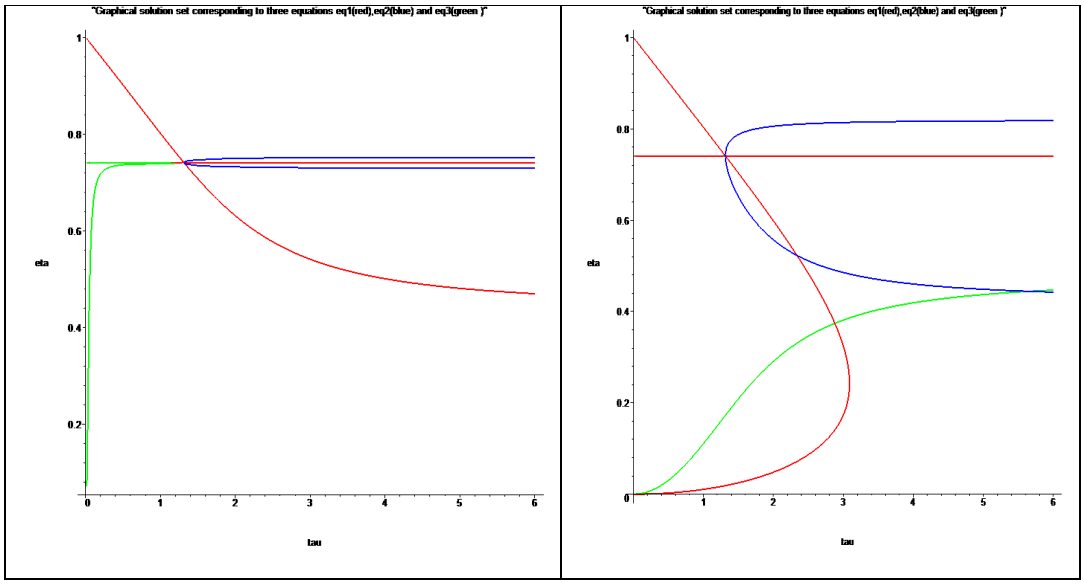
Graph-7 :(liquid-7):



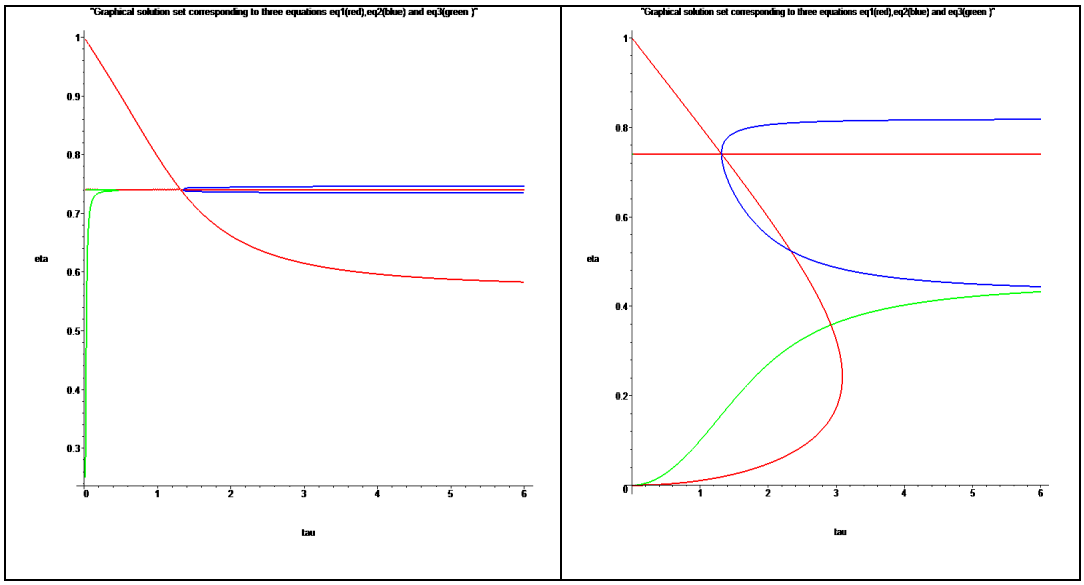
Graph-8 :(liquid-8):



Graph-9 :(liquid-9):



Graph-10 :(liquid-10):



DISCUSSION

Calculations show that 1-4 Dioxane, Benzene, and tetrahydopyrrole are highly associative while Carbon tetrachloride, Methylcyclohexane, cyclohexane tetrahydofuran shows moderate clustering. Acrolein, Methylmethacrelate Acrylonitrile seems to remain less associative. In the given set of liquids, Methylcyclohexane and cyclohexane; Carbontetratrachloride, benzene, methylmethacrelate and 1-4 Dioxane; THF and THP; Acrolein and Acrolonitrile forms four groups based on cavity formation descending order.

1-4 Dioxane, Benzene, Tetrahydopyrrole Carbon tetrachloride, Methyl-cyclohexane, Cyclohexane Tetrahydofuran show packing fraction close to FCC structure whereas. Acrolein, Methylmethacrelate Acrylonitrile show significant deviation from FCC like structure.

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

CONCLUSION

Each graph on left hand side shows unique solution of η and τ due to occurrence of parameter ζ. While graphs on right hand side show non unique solution for $\zeta=1$

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