

Khasare Equation of State for Molecular Cluster Study for Tetrahydrofuran - Cyclohexane Mixture for 288.15 K to 333.15 K

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ABSTRACT

Structural properties of liquid mixture related thermodynamic behavior in terms of liquid clusters are considered using third Khasare EOS. Unique solution is obtained by introducing order parameter ζ ($0 < \zeta < 1$; $\zeta \mapsto 0$ maximum ordering) on the mathematical ground, in numerical computations. The choice of order parameter can strongly influence the composition of clusters. Temperature range for all computations is set between, 288.16 K to 333.16 K. The value of ζ^{-1} is attributed to variations in cluster size over entire mole fraction. Calculations are drawn on sample data for ultrasonic wave velocity, 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

Studies of physicochemical properties of liquids and liquid mixtures centers around, understanding of molecular structures, and is of great importance to physicist and chemists. The structures and dynamics of pure and mixed liquids at molecular levels have received much attention and still remain a major subject of growing interest in chemical physics. Physicochemical analysis method can be used for getting sound information for a specific interaction between the components and the structure of the binary liquid mixtures. The thermodynamic studies of binary solutions have attracted much attention of scientists and experimental data on a number of systems are available from review and publications. Number of researchers presented models based on fundamental theories of statistical thermodynamics and are used by many scholars. Theoretical approach for extended scaled particle theory is elaborated (first Khasare EOS) in earlier several papers [1-11]. This Equation of State [EOS] is being used by workers [12-18] in their studies of liquids and liquid mixtures. The theory is developed on perception of hard sphere with perturbation view. Following EOS was obtained by Khasare-Deshpande (second Khasare EOS) [19] as extension of the same approach.

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

The compressibility factor calculated based on above equation is used to study nano-cavity [20-22] in the liquid systems.

Molecular Clusters, ranging in size from a few to several, constitute an appealing field of research in physics, chemistry and materials science. Finite size and their weak defined structures molecular clusters offer possibility to get better view of intermolecular interactions. Systematic variation [23-24] of cluster size allows bridge the gap between gas phase molecules and condensed matter. Hence, essential question in the most cluster studies is how many particles are required to find the physical chemical properties of bulk matter.

Structural properties of liquid mixture related thermodynamic behavior in terms of liquid clusters are considered using third Khasare EOS[25-26] which is modification of the equ.[1] by introducing order parameter ζ^{-1} on mathematical argument in numerical computations. The choice of order parameter can strongly manipulate the composition of clusters.

In the present framework which aims to study the thermodynamic properties of organic binary liquid mixture of Tetrahydrofuran (C_4H_8O) and Cyclohexane (C_6H_{12}) of different molar concentrations at different temperatures in range the of 288.16 K to 333.16 K. Data for real fluids for ultrasonic wave velocity, density, volume expansion coefficient and ratio of specific heat (1.3) taken as an input for the computations.

Mathematical computations are obtained by taking into account molecular clustering in the liquid state. Hard sphere system is used as a reference point to workout thermodynamic parameters. For study of real fluids, two parameters, namely radius and binding energy of molecules are necessary. 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.

Lattice density packing fraction concept is used as a limiting value for solution of EOS as a further modification. Here we have introduced λ , defined as

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

We get third Khasare EOS with above modification as [23-24]

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

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

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

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

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

Unique mathematical solution is obtained by using new variable ζ . Clustering of molecules is taken into account to correlate model parameters in terms of order parameters ζ^{-1} for real fluids. These model parameters have association 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

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

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

So that eq. (8) become

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

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

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

Where

$$y := \left((-4f\eta - 2 - 9f\eta^2 - 18(1+f\eta)\eta + 16\eta(1+f\eta)^2 m + 16\eta^2(1+f\eta)mf - 4(1+f\eta)m - 4\eta fm + 4(1+f\eta)^2 m + 8\eta(1+f\eta)mf - 16\eta(1+f\eta)m - 8\eta^2 fm + 12\eta + 4m\eta + m - f) / ((\eta - 1)^2) \right)$$

$$\begin{aligned}
& (4 \eta (1+f \eta)^2 m+m \eta-4 \eta (1+f \eta) m-1-f \eta))-2(-2(1+f \eta) \eta \\
& -9(1+f \eta) \eta^2+8 \eta^2(1+f \eta)^2 m-4 \eta(1+f \eta) m+4 \eta(1+f \eta)^2 m \\
& -8 \eta^2(1+f \eta) m+6 \eta^2+2 m \eta^2+m \eta-1-f \eta) /((\eta-1)^3 \\
& (4 \eta(1+f \eta)^2 m+m \eta-4 \eta(1+f \eta) m-1-f \eta))-(-2(1+f \eta) \eta \\
& -9(1+f \eta) \eta^2+8 \eta^2(1+f \eta)^2 m-4 \eta(1+f \eta) m+4 \eta(1+f \eta)^2 m \\
& -8 \eta^2(1+f \eta) m+6 \eta^2+2 m \eta^2+m \eta-1-f \eta) \\
& (4(1+f \eta)^2 m+8 \eta(1+f \eta) m f+m-4(1+f \eta) m-4 \eta f m-f) /((\eta-1)^2 \\
& (4 \eta(1+f \eta)^2 m+m \eta-4 \eta(1+f \eta) m-1-f \eta)^2) \\
& -\frac{1056(8(1+f \eta) m f-4 f-4 f m) \eta}{35 \tau^2(4 \eta(1+f \eta)^2 m+m \eta-4 \eta(1+f \eta) m-1-f \eta)} \\
& -\frac{1056(4(1+f \eta)^2 m+m-4-4 f \eta-4(1+f \eta) m)}{35 \tau^2(4 \eta(1+f \eta)^2 m+m \eta-4 \eta(1+f \eta) m-1-f \eta)}+1056 \\
& (4(1+f \eta)^2 m+m-4-4 f \eta-4(1+f \eta) m) \eta \\
& (4(1+f \eta)^2 m+8 \eta(1+f \eta) m f+m-4(1+f \eta) m-4 \eta f m-f) / (35 \tau^2 \\
& (4 \eta(1+f \eta)^2 m+m \eta-4 \eta(1+f \eta) m-1-f \eta)^2) \left. \vphantom{\frac{1056(8(1+f \eta) m f-4 f-4 f m) \eta}{35 \tau^2(4 \eta(1+f \eta)^2 m+m \eta-4 \eta(1+f \eta) m-1-f \eta)}} \right\} \eta+(-2(1+f \eta) \eta \\
& -9(1+f \eta) \eta^2+8 \eta^2(1+f \eta)^2 m-4 \eta(1+f \eta) m+4 \eta(1+f \eta)^2 m \\
& -8 \eta^2(1+f \eta) m+6 \eta^2+2 m \eta^2+m \eta-1-f \eta) /((\eta-1)^2 \\
& (4 \eta(1+f \eta)^2 m+m \eta-4 \eta(1+f \eta) m-1-f \eta)) \\
& -\frac{1056(4(1+f \eta)^2 m+m-4-4 f \eta-4(1+f \eta) m) \eta}{35 \tau^2(4 \eta(1+f \eta)^2 m+m \eta-4 \eta(1+f \eta) m-1-f \eta)}
\end{aligned}$$

And

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

Where

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

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

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

Deviation of ζ from 1 can be endorsed to liquid phase, hence we define Ordering= [1- ζ].

RESULTS

The experimental data, results for molecular cluster at various temperatures are presented in the tabular form.

Following table gives the input values for Velocity, Density and Volume expansion coefficient (alpha). Input values for data at various temperature is generated for each step of $t_e = 15$ degrees centigrade. Ratio of specific heat is taken as 1.3 for computations.

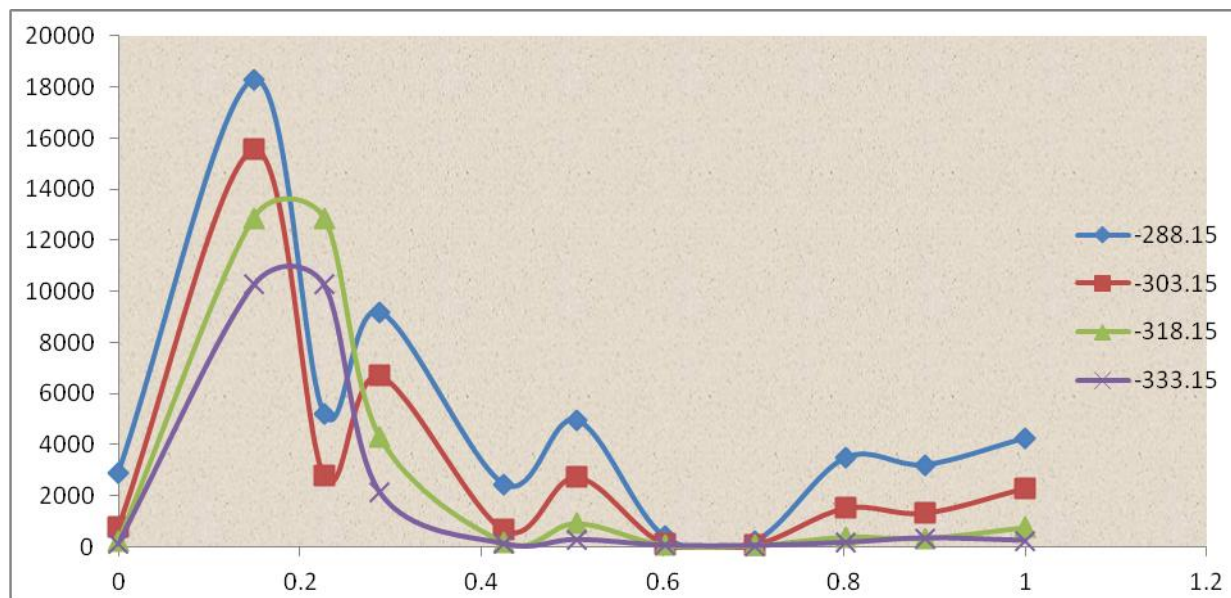
Table 1: Experimental data for Ultrasonic wave velocity & Density for organic liquid mixture

"mol:=0.0000;temp:=273.16+te; mwa:=72;mbw:=84; dens:=(906.8611-1.0315*te)/1000;alpha:=-diff(ln(dens),te); alpha1:=alpha;alphan:=temp*alpha1";	mw1:=(1-mol)*mwa+mol*mbw;gama:=1.3; te:=60;den:=dens;vel:=(1389.7431-4.4833*te)*100;
"mol:=0.14972;temp:=273.16+te; mwa:=72;mbw:=84; dens:=(875.0034-0.7119*te)/1000;alpha:=-diff(ln(dens),te); alpha1:=alpha;alphan:=temp*alpha1";	mw1:=(1-mol)*mwa+mol*mbw;gama:=1.3; te:=60;den:=dens;vel:=(1377.4931-4.6293*te)*100;
"mol:=0.22690;temp:=273.16+te; mwa:=72;mbw:=84; dens:=(867.3715-0.9239*te)/1000;alpha:=-diff(ln(dens),te); alpha1:=alpha;alphan:=temp*alpha1";	mw1:=(1-mol)*mwa+mol*mbw;gama:=1.3; te:=60;den:=dens;vel:=(1364.2993-4.3840*te)*100;
"mol:=0.28838;temp:=273.16+te; mwa:=72;mbw:=84; dens:=(854.4741-0.8249*te)/1000;alpha:=-diff(ln(dens),te); alpha1:=alpha;alphan:=temp*alpha1";	mw1:=(1-mol)*mwa+mol*mbw;gama:=1.3; te:=60;den:=dens;vel:=(1350.3831-4.1453*te)*100;
"mol:=0.42548;temp:=273.16+te; mwa:=72;mbw:=84; dens:=(843.8275-0.9621*te)/1000;alpha:=-diff(ln(dens),te); alpha1:=alpha;alphan:=temp*alpha1";	mw1:=(1-mol)*mwa+mol*mbw;gama:=1.3; te:=60;den:=dens;vel:=(1361.7331-4.6253*te)*100;
"mol:=0.50555;temp:=273.16+te; mwa:=72;mbw:=84; dens:=(830.2495-0.8799*te)/1000;alpha:=-diff(ln(dens),te); alpha1:=alpha;alphan:=temp*alpha1";	mw1:=(1-mol)*mwa+mol*mbw;gama:=1.3; te:=60;den:=dens;vel:=(1358.5398-4.5820*te)*100;
"mol:=0.60219;temp:=273.16+te; mwa:=72;mbw:=84; dens:=(825.0288-1.0188*te)/1000;alpha:=-diff(ln(dens),te); alpha1:=alpha;alphan:=temp*alpha1";	mw1:=(1-mol)*mwa+mol*mbw;gama:=1.3; te:=60;den:=dens;vel:=(1356.7631-4.5893*te)*100;
"mol:=0.70118;temp:=273.16+te; mwa:=72;mbw:=84; dens:=(818.5818-1.0394*te)/1000;alpha:=-diff(ln(dens),te); alpha1:=alpha;alphan:=temp*alpha1";	mw1:=(1-mol)*mwa+mol*mbw;gama:=1.3; te:=60;den:=dens;vel:=(1357.8464-4.6347*te)*100;
"mol:=0.80150;temp:=273.16+te; mwa:=72;mbw:=84; dens:=(802.8362-0.8795*te)/1000;alpha:=-diff(ln(dens),te); alpha1:=alpha;alphan:=temp*alpha1";	mw1:=(1-mol)*mwa+mol*mbw;gama:=1.3; te:=60;den:=dens;vel:=(1361.9931-4.7133*te)*100;
"mol:=0.88959;temp:=273.16+te; mwa:=72;mbw:=84; dens:=(793.9868-0.8748*te)/1000;alpha:=-diff(ln(dens),te); alpha1:=alpha;alphan:=temp*alpha1";	mw1:=(1-mol)*mwa+mol*mbw;gama:=1.3; te:=60;den:=dens;vel:=(1370.3531-4.8333*te)*100;
mol:=1.00000;temp:=273.16+te; mwa:=72;mbw:=84; dens:=(786.6264-0.8367*te)/1000;alpha:=-diff(ln(dens),te); alpha1:=alpha;alphan:=temp*alpha1";	mw1:=(1-mol)*mwa+mol*mbw;gama:=1.3; te:=60;den:=dens;vel:=(1364.5498-4.6480*te)*100;

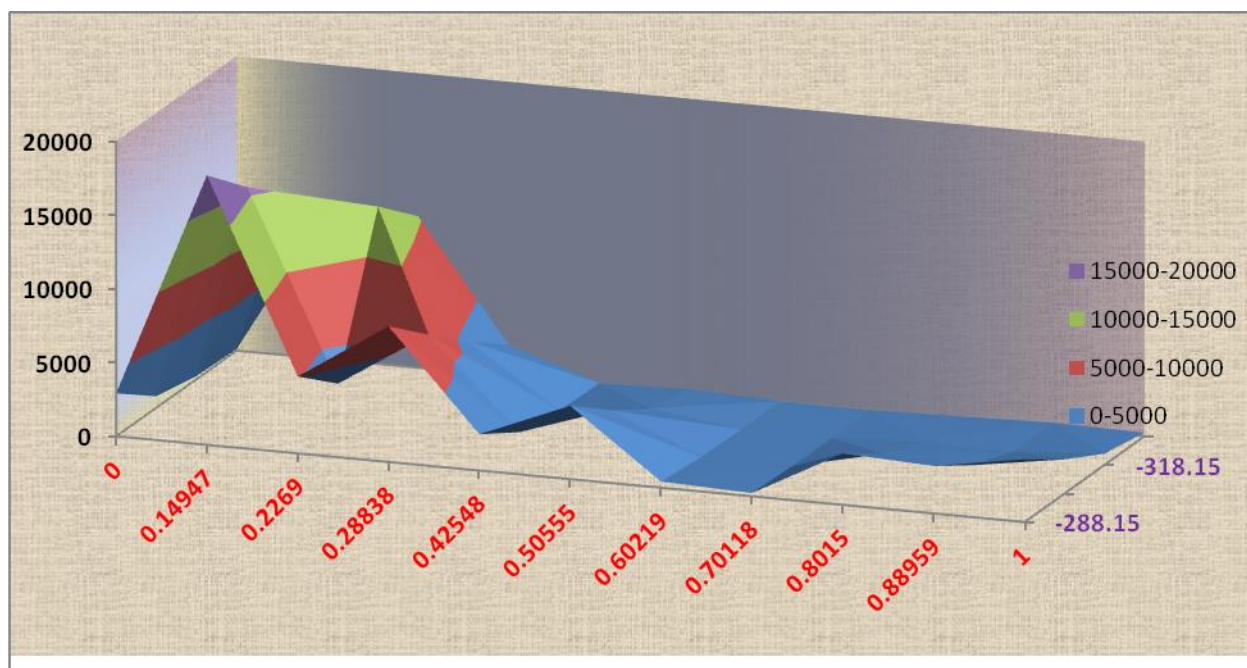
Table 2: Molecular Cluster (ζ^{-1}) at various temperatures in Tetrahydrofuran-Cyclohexane

S.No.	Mol.Frac.	ζ^{-1} (288.15)	ζ^{-1} (303.15)	ζ^{-1} (318.15)	ζ^{-1} (333.15)
1	0	2903.584602	767.2047032	207.1014446	110.4755936
2	0.14947	18285.90362	15546.53391	12876.25755	10279.92532
3	0.22690	5214.844085	2787.822693	12876.25755	10279.92532
4	0.28838	9198.744856	6697.068881	4304.187346	2122.527226
5	0.42548	2456.568989	662.3817755	194.9651176	106.9326744
6	0.50555	4968.835481	2739.310765	923.2323289	278.9437642
7	0.60219	412.2166532	129.4459188	73.60863354	51.83666559
8	0.70118	212.6543762	90.29972130	56.72975718	41.80604359
9	0.80150	3482.039535	1525.850165	390.3068658	162.1615293
10	0.88959	3216.748384	1335.546488	337.7918257	148.2179314
11	1.00000	4258.909430	2306.973957	758.5623530	241.0072790

Values of Molecular Cluster (ζ^{-1}) at various Temperatures for Tetrahydrofuran - Cyclohexane Mixture for 288.15 K to 333.15 K X-axis Molecular cluster: X-axis molar concentration



Values of Molecular Cluster (ζ^{-1}) at various Temperatures for Tetrahydrofuran - Cyclohexane Mixture for 288.15 K to 333.15 K X-axis molar concentration: Y-axis Molecular cluster : Z-axis temperature in Kelvin



DISCUSSION

From graph it is seen that the cluster formation is concentration dependent and local maxima are observed in the increasing order of concentration. Thus we may assume that at least three specific structures are favored when concentrations of Tetrahydrofuran is more predominant. It is convenient to associate local minima at [0.22690, 0.42548, 0.70118] favoring cluster breaking activity of these formed structures. Increasing concentration of Cyclohexane shows the increasing disorder. Hence structure dissemination process can be thought due to rise in concentration of Cyclohexane. With rise in temperature towards boiling point activity weakens. All these views

sustain due to introduction of order parameter. One can visualize association, dissociation, ordering or concealing process by considering excess adiabatic compressibility and excess bulk volume.

It was seen in our earlier studies [13], increase in adiabatic compressibility in a mixture of two liquids Tetrahydrofuran and Cyclohexane denotes a weakening of the intermolecular interactions. The hetero molecular interaction is a cause of rearrangement in the geometry of the clusters. The new geometry of the clusters will depend upon the specific geometry of the molecules, if the geometry is such that the volume of clusters increases, it will lead to an increase in volume of the mixture i.e. excess molar volume would be positive as observed in this case. The dissociation would predominantly occur in one of the component liquids in which homo molecular interaction is extremely weak as compared to the hetero molecular interactions. One may be in a position to identify the dissociating component from the excess adiabatic compressibility and excess volume variation with composition of liquids, the maximum occurring for the higher concentration of the component. The dissociative processes are predominant in their respective concentration ranges.

In this study, we have limited only to qualitative results and cannot determine the detailed mechanisms governing mixture states at molecular levels.

CONCLUSION

The choice of order parameter can strongly influence the composition of clusters. Occurrence of parameter ζ gives unique solution of η and τ . Association of ζ^{-1} to clustering can give a reasonable picture of thermodynamic parameters under studies.

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