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Number of moles Estimation for Acetonitrile + 1-Alkanol (C_6, C_8, C_{10}) in Liquid State

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ABSTRACT

Structural properties of liquid mixture related thermodynamic behavior in terms of liquid clusters are considered using third Khasare EOS for pure liquid. Unique solution is possible by evaluating ζ number of moles (the amount of participants in thermodynamic process).Number of moles seems to be a physical variable in present computations. Temperature range for all computations is set up from 293.16 K to a limit such that corresponding volume expansion coefficient for liquid mixture tends zero. The value of ζ is attributed to variations in cluster size over entire mole fraction. Calculations are drawn on sample set of parametric equations in terms of temperature for ultrasonic wave velocity, density, and fairly constant a 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

The density and ultrasonic speed were expressed as a cubical expression in terms of temperature parameter (which is expected to be valid for liquid regions!), for binary liquid mixtures over entire compositions. Normally the deviations from linearity (mole fraction/ volume fraction/weight fraction) for different thermodynamic properties were arbitrarily related to the different types of assumed physical or chemical interactions mainly by crossing the thermodynamic or model domains for a explanations. Basically variations in a set of interdependent parameters or remaining derivable thermodynamic functions with composition of the mixtures are indicative of the structure breaking or forming effect due to variations in geometric packing or different weak/strong chemical interactions. There is no point in analyzing excess parameter in terms of well known theories, because these theories have different set of assumptions and restricted scope for interpretations. As a mathematical exercise only the validity and relative merits of these theories and many empirical relations can be suitably discussed [1] without any predictions in thermodynamic properties. Thermo dynamic study has an enormous importance in understanding the structural and thermo physical behavior of liquids. Due to their insightful importance in physical and chemical sciences, many models have been developed by number of researchers based on fundamental theories of statistical thermodynamics and on empiricism. Theoretical approach for extended scaled particle theory is elaborated (first Khasare EOS) in earlier several papers [2-12]. This Equation of State [EOS] is being used by workers [13-19] in their studies of liquids and liquid mixtures. The theory is developed on perception of hard sphere with perturbation view. Khasare-Deshpande obtained following second EOS [20] as extension of the same approach.

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

The compressibility factor calculated based on above equation is used to study a nano cavity [21-23] in the liquid systems.

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

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

We get third Khasare EOS with above modification as [24-25]

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

For our present work we have used for Acetonitrile + 1-Alkanol (C_6, C_8, C_{10}) in Liquid State.

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. We have used equation of state for a strong repulsive and a weak attractive potential together. For study of real fluids, two parameters, namely radius and binding energy of molecules are necessary. Dimensional less variables such as packing fraction (η) and temperature (τ= k_BT/ε) 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].

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

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

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

An ideal gas is characterized by three state variables: absolute pressure (P), volume (V), and absolute temperature (T). The relationship between them may be deduced from kinetic theory and is called the Ideal gas law:

$P\,V = n\,R\,T = N\,k_B\,T$ [7]

Where n = number of moles (the amount of gas), R= universal gas constant, N = number of molecules, k_B =Boltzmann constant = $(1.38066)10^{-23}$J/K, $k_B = R/N_A$, N_A= Avogadro's number = $(6.0221)\ 10^{23}$ /mol.

To get the unique mathematical solution of above set of equations [5, 6, 7], present variable (ζ =n)[number of moles (the amount of gas)] is brought in to picture. Clustering of molecules is taken into account to correlate model parameters in terms of ζ[number of moles (the amount of gas)] 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

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

[8]

Where v is volume of cavity containing few chemical units, V is volume, ρ = N/V is the density, ε is binding energy of cluster containing chemical units, Presently [$\zeta = \nu$] is used [number of moles (the amount of gas)] to obtain the solution after substituting suitable packing fraction (η) and temperature ($\tau = k_B T/\varepsilon$).

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

$$\frac{\beta P}{\varsigma\rho}=Z(\eta,\tau)=z \qquad [9]$$

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

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

From above, we get eq. [10] and eq. [11]

$$\frac{Mu^2}{\varsigma\gamma RT}=\frac{\partial(Z\eta)}{\partial\eta}=y \qquad [10]$$

Where

$$\begin{aligned} y :=& \Big((-4f\eta-2-9f\eta^2-18(1+f\eta)\eta+16\eta(1+f\eta)^2 m+16\eta^2(1+f\eta)mf \\ &-4(1+f\eta)m-4\eta fm+4(1+f\eta)^2 m+8\eta(1+f\eta)mf-16\eta(1+f\eta)m \\ &-8\eta^2 fm+12\eta+4m\eta+m-f)\Big/((\eta-1)^2 \\ &(4\eta(1+f\eta)^2 m+m\eta-4\eta(1+f\eta)m-1-f\eta))-2(-2(1+f\eta)\eta \\ &-9(1+f\eta)\eta^2+8\eta^2(1+f\eta)^2 m-4\eta(1+f\eta)m+4\eta(1+f\eta)^2 m \\ &-8\eta^2(1+f\eta)m+6\eta^2+2m\eta^2+m\eta-1-f\eta)\Big/((\eta-1)^3 \\ &(4\eta(1+f\eta)^2 m+m\eta-4\eta(1+f\eta)m-1-f\eta))-(-2(1+f\eta)\eta \end{aligned}$$

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

And

$$\frac{Mu^2\alpha T}{\varsigma\gamma RT}=\frac{\partial(ZT)}{\partial T}=x \qquad [11]$$

Where

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

From this set equations [9,10,11] we have following set of equation [12] yields solutions[η,τ]which is independent of variable (ζ =□n)[number of moles (the amount of gas)]

$$\frac{Mu^2}{\gamma PV}=y/z \quad ; \quad \frac{Mu^2\alpha T}{\gamma PV}=x/z \qquad [12]$$

Now this solutions set [η,τ] is to be substituted in equation [9] to get unique value of (ζ =□n) [number of moles (the amount of gas)] . It is important to note that in above set of equations [ζ(η,τ),ψ(η,τ),ω(η,τ)] nearest pole for fcc η_{max} = 0.7404804897 and for bcc , η_{max}□□= 0.6801747616, R = (8.314)10^7 J/mole K; N_A = (6.02215)10^{23} mol $^{-1}$; pressure = P = (1.012928)10^6 = 1,012,928 dynes per square centimeter; M = mw1;V = mw/den; Z_c = P V/(R T); Y_c = M u^2/(γ□R T); X_c = Y_c□α T; ζ = [Z_c / Z(η,τ)] = n; degree of association =1/□ζ; and Ordering = (1– ζ□);

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

$$if\ \frac{\beta P}{\varsigma\rho} = Z(\eta, \beta\varepsilon) = \xi(\eta, \tau) = 1, then, \varsigma = 1 \qquad [12]$$

ζ [number of moles (the amount of gas)] and observed behavior of a mathematical function ζ□□□which can be associated to degree of association is represented as

$$\varsigma^{-1}(\alpha) = \varsigma^{-1}(+0) = +\infty \ \& \ \varsigma^{-1}(\alpha) = \varsigma^{-1}(-0) = -\infty \qquad [13]$$

Extrapolated experimental observation closer to one degree Kelvin below boiling point and associated ζ^{-1} computations suggest above equation (12). Deviation of ζ [number of moles (the amount of gas)] 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 (α). Input values for data at various temperature is generated for each step of ts= 10 degrees centigrade. Ratio of specific heat is taken as γ□= 1.3 for computations.

Table 1: Set of Equations for Ultrasonic wave velocity, Density & Association/Polymerization in parametric form in for Acetonitrile-1-Hexanol

[ts=temperature in degree Celsius; mwa:=102.17;mwb:=41.05;
*mw1:= (1-mol)*mwa+mol*mwb; gamma:=1.3;]*

mol:=0.00000; $dens := 0.833499999990081 - 0.000719999999113352\ ts - 0.257656939188852\ 10^{-13}\ ts^2 + 0.243898215221782\ 10^{-15}\ ts^3$ $vel := 142097.142857328 - 624.666666683175\ ts + 9.05714285762275\ ts^2 - 0.0933333333378777\ ts^3$
mol:=0.0992; $dens := 0.831234285714585 - 0.000710000000024448\ ts - 0.285714285067447\ 10^{-6}\ ts^2 - 0.556446208594593\ 10^{-17}\ ts^3$ $vel := 136389.428571994 - 159.333333384196\ ts - 5.42857142708522\ ts^2 + 0.0533333333191922\ ts^3$
mol:=0.2171; $dens := 0.826825714288853 - 0.000526666666949183\ ts - 0.671428570601864\ 10^{-5}\ ts^2 + 0.666666665878962\ 10^{-7}\ ts^3$ $vel := 128793.714285140 + 448.000000051558\ ts - 23.0142857157907\ ts^2 + 0.220000000014305\ ts^3$
mol:=0.3356; $dens := 0.824125714285433 - 0.000546666666642891\ ts - 0.671428571493655\ 10^{-5}\ ts^2 + 0.666666666724663\ 10^{-7}\ ts^3$

$vel := 130153.714285449 + 272.000000023659\ ts - 18.4142857149705\ ts^2 + 0.180000000006457\ ts^3$

mol:=0.4487;

$dens := 0.824517142861482 - 0.000850000000389881\ ts + 0.857142868529750\ 10^{-6}\ ts^2 - 0.108294211568891\ 10^{-15}\ ts^3$

$vel := 131117.999999640 + 116.666666698905\ ts - 13.6000000009371\ ts^2 + 0.133333333342206\ ts^3$

mol:=0.5747;

$dens := 0.819699999998395 - 0.000819999999855213\ ts - 0.424448455248878\ 10^{-14}\ ts^2 + 0.405050412991973\ 10^{-16}\ ts^3$

$vel := 127736.857143178 + 378.333333304770\ ts - 21.3571428563152\ ts^2 + 0.206666666658852\ ts^3$

mol:=0.6945;

$dens := 0.817708571419152 - 0.00106333333248717\ ts + 0.642857140386613\ 10^{-5}\ ts^2 - 0.666666664317879\ 10^{-7}\ ts^3$

$vel := 117509.428571587 + 1244.66666665245\ ts - 45.9285714281561\ ts^2 + 0.433333333329382\ ts^3$

mol:=0.7864;

$dens := 0.811382857145834 - 0.000850000000265745\ ts - 0.857142849429629\ 10^{-6}\ ts^2 - 0.729389511803701\ 10^{-16}\ ts^3$

$vel := 121516.285714468 + 833.999999983767\ ts - 32.7857142852443\ ts^2 + 0.299999999995566\ ts^3$

mol:=0.8622;

$dens := 0.810942857137571 - 0.00113333333285967\ ts + 0.614285712905930\ 10^{-5}\ ts^2 - 0.666666665357640\ 10^{-7}\ ts^3$

$vel := 126792.571427318 + 373.666666778704\ ts - 19.3714285746846\ ts^2 + 0.173333333364156\ ts^3$

mol:=0.9254;

$dens := 0.811634285734280 - 0.00145666666845844\ ts + 0.0000137142857664832\ ts^2 - 0.133333333828588\ 10^{-6}\ ts^3$

$vel := 132905.142856700 - 174.333333293657\ ts - 2.04285714401216\ ts^2 - 0.00666666665571562\ ts^3$

mol:=1.0000;

$$dens := 0.808234285724032 - 0.00151666666754055\ ts + 0.0000137142857397586\ ts^2 - 0.133333333575155\ 10^{-6}\ ts^3$$

$$vel := 135720.285714239 - 193.333333329167\ ts - 5.48571428583408\ ts^2 + 0.0533333333344559\ ts^3$$

Table 2: Molecular Cluster (ζ□□□ at various temperatures in Acetonitrile-1-Hexanol

[Numerical Presentations, Xp = temperature in degree Celsius, Yp = ζ^{-1} =□Association□Polymerization].

mol:=0.00000; Xp:=Vector([20,30,40,50,60,70,80]):
Yp:=Vector([9749.245487, 8514.764734, 7303.251235, 6116.276644, 4957.387502, 3834.810190, 2770.403432]):

$$Pol := 12227.3667479314 - 123.792326762911\ ts - 0.0348745192811002\ ts^2 + 0.00130489505552519\ ts^3$$

mol:=0.0992; Xp:=Vector([20,30,40,50,60,70,80]):
Yp:=Vector([10165.71800, 8573.718472, 7019.136396, 5505.115779, 4038.166606, 2636.590330, 1369.708468]):

$$Pol := 13296.2865385731 - 153.816674670760\ ts - 0.212896878806836\ ts^2 + 0.00339134444442695\ ts^3$$

mol:=0.2171; Xp:=Vector([20,30,40,50,60,70,80]):
Yp:=Vector([11158.89190, 7954.020961, 6867.270181, 7891.961671, 11865.36228, 21557.07097, 47679.49589]):

$$Pol := -2082.59616366621 + 1433.63970084492\ ts - 50.0898774984876\ ts^2 + 0.497762830055782\ ts^3$$

mol:=0.3356; Xp:=Vector([20,30,40,50,60,70,80]):
Yp:=Vector([10770.14302, 7418.446853, 6237.104074, 7207.110806, 11150.57222, 20756.60394, 46042.11886]):

$$Pol := -665.565412154739 + 1288.19172963257\ ts - 46.7431468989454\ ts^2 + 0.472787516861217\ ts^3$$

mol:=0.4487; Xp:=Vector([20,30,40,50,60,70,80]):
Yp:=Vector([7086.531663, 6341.347117, 5644.292010, 4996.408866, 4397.740526, 3847.028134, 3341.587784]):

$$Pol := 8730.60849343107 - 87.3154995180396\ ts + 0.258503997980108\ ts^2 - 0.000113150333358898\ ts^3$$

mol:=0.5747;Xp:=Vector([20,30,40,50,60,70,80]):
Yp:=Vector([7369.378440, 5605.335525, 3907.796283, 2327.285304, 1052.170528, 413.9610123, 194.6499580]):

$$Pol := 10416.2066686162 - 121.664556458239\ ts - 2.01171573315162\ ts^2 + 0.0242297718249793\ ts^3$$

mol:=0.6945; Xp:=Vector([20,30,40,50,60,70,80]):
Yp:=Vector([4284.200505, 3863.813287, 1638.285945, 216.4414307, 57.70098559, 19.62743228, 6.857156424]):

$$Pol := 6394.41608928406 - 46.7381986524295\ ts - 2.93552375021793\ ts^2 + 0.0318729851542702\ ts^3$$

mol:=0.7864; Xp:=Vector([20,30,40,50,60,70,80]):
Yp:=Vector([4537.243016, 1768.105913, 424.7868238, 177.1506358, 99.83975918, 60.66962432, 36.39718151]):

$$Pol := 15411.4629318982 - 772.913061991934\ ts + 12.7359411353802\ ts^2 - 0.0685684022553813\ ts^3$$

mol:=0.8622; Xp:=Vector([20,30,40,50,60,70,80]):
Yp:=Vector([868.2194184, 536.1692075, 201.2356357, 81.59699224, 36.34671189, 16.84246069, 7.875013419]):

$$Pol := 2201.22826278854 - 86.5629256620474\ ts + 1.13164795833517\ ts^2 - 0.00489246484337305\ ts^3$$

mol:=0.9254; Xp:=Vector([20,30,40,50,60,70,80]):
Yp:=Vector([148.0483177, 218.4392266, 133.2324767, 55.20162494, 22.63604956, 10.08129116, 5.022901028]):

$Pol := -165.136707747798 + 28.8993495503774\ ts - 0.723877272819610\ ts^2 + 0.00488691516411474\ ts^3$

mol:=1.0000;Xp:=Vector([20,30,40,50,60,70,80]):
Yp:=Vector([89.65199656, 117.3202698, 84.20777714, 41.92349369, 18.82006362, 8.521451251, 4.054385291]):

$Pol := -75.0733892488222 + 14.9038453470466\ ts - 0.370102120927058\ ts^2 + 0.00246080335555731\ ts^3$

Table 3: Set of Equations for Ultrasonic wave velocity, Density & Association/Polymerization in parametric form in Acetonitrile-1-Octanol (ts=temperature in degree Celsius;)

*mwa:= 130.23;;mwb:=41.05;mw1:=(1-mol)*mwa+mol*mwb;gamma:=1.3;*

mol:=0.00000;

$dens := 0.833065714279724 - 0.000223333332795183\ ts - 0.0000137142857299991\ ts^2 + 0.133333333482735\ 10^{-6}\ ts^3$

$vel := 144910.000001214 - 347.000000108849\ ts - 3.09999999682788\ ts^2 + 0.0599999999698917\ ts^3$

mol:=0.1285;

$dens := 0.827674285709081 + 0.0000400000004664401\ ts - 0.0000212857142993043\ ts^2 + 0.200000000128959\ 10^{-6}\ ts^3$

$vel := 139989.428569865 - 37.6666665267284\ ts - 12.2285714326420\ ts^2 + 0.146666666705234\ ts^3$

mol:=0.2176;

$dens := 0.826074285708953 + 0.0000200000004788897\ ts - 0.0000212857142996938\ ts^2 + 0.200000000132887\ 10^{-6}\ ts^3$

$vel := 135691.714286058 + 227.666666635488\ ts - 19.5142857133679\ ts^2 + 0.213333333324541\ ts^3$

mol:=0.3158;

$dens := 0.826800000008287 - 0.000253333334075250\ ts - 0.0000139999999784083\ ts^2 + 0.133333333128661\ 10^{-6}\ ts^3$

$vel := 135307.999998730 + 138.666666780320\ ts - 16.2000000033051\ ts^2 + 0.173333333364639\ ts^3$

mol:=0.4260;

$dens := 0.824000000004855 - 0.000273333333767811\ ts - 0.0000139999999873595\ ts^2 + 0.133333333213546\ 10^{-6}\ ts^3$

$vel := 141322.571428538 - 499.666666663964\ ts + 1.92857142850037\ ts^2 + 0.00666666666727245\ ts^3$

mol:=0.5327;

$dens := 0.822808571419169 - 0.000496666665825683\ ts - 0.757142859588310\ 10^{-5}\ ts^2 + 0.666666668982940\ 10^{-7}\ ts^3$

$vel := 152436.000000483 - 1616.66666670981\ ts + 35.1000000012536\ ts^2 - 0.313333333345201\ ts^3$

mol:=0.6770; $dens := 0.825082857138004 - 0.00123666666623418\ ts + 0.0000131428571303271\ ts^2 - 0.133333333215064\ 10^{-6}\ ts^3$ $vel := 143963.714286169 - 981.000000040976\ ts + 17.6857142869158\ ts^2 - 0.160000000011469\ ts^3$
mol:= 0.7273; $dens := 0.822317142859216 - 0.00122666666685143\ ts + 0.0000128571428624969\ ts^2 - 0.133333333383884\ 10^{-6}\ ts^3$ $vel := 137800.000000201 - 445.666666684928\ ts + 2.00000000053913\ ts^2 - 0.0133333333385125\ ts^3$
mol:= 0.8431; $dens := 0.821317142856176 - 0.00175333333324513\ ts + 0.0000268571428545299\ ts^2 - 0.266666666641496\ 10^{-6}\ ts^3$ $vel := 126517.428570404 + 565.666666758333\ ts - 28.1285714312388\ ts^2 + 0.273333333358613\ ts^3$
mol:= 0.9193; $dens := 0.814051428564498 - 0.00146666666604666\ ts + 0.0000145714285533986\ ts^2 - 0.133333333162555\ 10^{-6}\ ts^3$ $vel := 120201.999998347 + 1207.00000014814\ ts - 48.6000000043162\ ts^2 + 0.480000000040957\ ts^3$
mol:=1.0000; $dens := 0.808234285724032 - 0.00151666666754055\ ts + 0.0000137142857397586\ ts^2 - 0.133333333575155\ 10^{-6}\ ts^3$ $vel := 135720.285714239 - 193.333333329167\ ts - 5.48571428583408\ ts^2 + 0.0533333333344559\ ts^3$

Table 4: Molecular Cluster (ζ□□□ at various temperatures in Acetonitrile-1-Octanol

[Numerical Presentations, Xp = temperature in degree Celsius, Yp = ζ^{-1} =Association□Polymerization].

mol:=0.00000; Xp:=Vector([20,30,40,50,60,70,75.925]): Yp:=Vector([12753.48548, 8256.807801, 7520.789464, 10592.81524, 21825.44529, 78945.72494, 77617585.10]): $Pol := -0.161201593131337\ 10^9 + 0.138849020481999\ 10^8\ ts - 358563.962247177\ ts^2 + 2829.61903100412\ ts^3$
mol:=0.1285;Xp:=Vector([20,30,40,50,60,69.9999]): Yp:=Vector([16339.32758, 8441.478564, 7135.865753, 11816.84831, 33750.83248, 85008648.35]): $Pol := -0.177937498477789\ 10^9 + 0.162909965455430\ 10^8\ ts - 455067.627271681\ ts^2 + 3933.05634111735\ ts^3$
mol:= 0.2176; Xp:=Vector([20,30,40,50,60,70,70.477]): Yp:=Vector([15998.51723, 8024.738117, 6653.203550, 11274.44259, 32550.59549, 1043657.076, 65442711.01]):

$Pol := -0.853852544642222\ 10^{8} + 0.770838532653631\ 10^{7}\ ts - 211554.998123617\ ts^{2} + 1792.61456548761\ ts^{3}$
mol:= 0.3158; Xp:=Vector([20,30,40,50,60,70,78.108]): Yp:=Vector([13195.02435, 7815.497036, 6608.306976, 9382.244104, 19808.62274, 63082.73154, 98049154.60]): $Pol := -0.182742688259885\ 10^{9} + 0.156448010559621\ 10^{8}\ ts - 400880.588800562\ ts^{2} + 3135.50020000741\ ts^{3}$
mol:= 0.4260; Xp:=Vector([20,30,40,50,60,70,78.684]): Yp:=Vector([13131.74945, 7485.856679, 6167.836249, 8965.453230, 19523.07688, 61565.42522, 87428626.29]): $Pol := -0.157058831789078\ 10^{9} + 0.134288698496439\ 10^{8}\ ts - 343542.973289896\ ts^{2} + 2682.13709589853\ ts^{3}$
mol:= 0.5327; Xp:=Vector([20,30,40,50,60,70,80]): Yp:=Vector([11488.26516, 7217.946002, 5222.561989, 5192.422464, 7502.689665, 13678.00032, 28649.96465]): $Pol := 13753.3725712104 + 141.444132608999\ ts - 18.2151676342912\ ts^{2} + 0.233931041555590\ ts^{3}$
mol:= 0.6770; Xp:=Vector([20,30,40,50,60,70,80]): Yp:=Vector([4657.835621, 6057.306180, 3563.632641, 205.2996250, 33.84021822, 11.35765987, 5.246895369]): $Pol := -2024.02618282137 + 684.980749818083\ ts - 19.1200633453215\ ts^{2} + 0.136754228257843\ ts^{3}$
mol:= 0.7273; Xp:=Vector([20,30,40,50,60,70,80]): Yp:=Vector([4751.959047, 5904.861422, 3016.563622, 159.4942517, 30.48458569, 9.985862944, 4.123286108]): $Pol := 332.045976127913 + 510.377709209065\ ts - 15.5545082346434\ ts^{2} + 0.114808856513231\ ts^{3}$
mol:= 0.8431; Xp:=Vector([20,30,40,50,60,70,80]): Yp:=Vector([407.2973689, 3688.359662, 1032.608231, 55.62690386, 10.93323698, 2.972908873, 0.9657000307]): $Pol := -8620.76959363720 + 793.650407119842\ ts - 18.0758773112601\ ts^{2} + 0.119464724396709\ ts^{3}$
mol:= 0.9193; Xp:=Vector([20,30,40,50,60,70,80]): Yp:=Vector([193.1137896, 445.9625195, 275.9148638, 88.75075508, 28.24814218, 8.996792621, 2.825273397]): $Pol := -856.467327108290 + 90.7577142680494\ ts - 2.09402789924413\ ts^{2} + 0.0137317758971232\ ts^{3}$
mol:=1.0000;Xp:=Vector([20,30,40,50,60,70,80]): Yp:=Vector([89.65199656, 117.3202698, 84.20777714, 41.92349369, 18.82006362, 8.521451251, 4.054385291]): $Pol := -75.0733892488222 + 14.9038453470466\ ts - 0.370102120927058\ ts^{2} + 0.00246080335555731\ ts^{3}$

Table 5: Set of Equations for Ultrasonic wave velocity, Density & Association/Polymerization in parametric form for Acetonitrile-1-Decanol (ts=temperature in degree Celsius;)

*mwa:= 158.28;mwb:=41.05;mw1:=(1-mol)*mwa+mol*mwb;gamma:=1.3;*

mol:=0.00000; $dens := 0.842834285706051 - 0.000649999999260976\ ts - 0.285714307271857\ 10^{-6}\ ts^{2} + 0.204778111149302\ 10^{-15}\ ts^{3}$ $vel := 140134.285713410 - 86.3333332547209\ ts - 0.885714288007410\ ts^{2} - 0.0266666666448835\ ts^{3}$
mol:= 0.1197; $dens := 0.837608571436258 - 0.000396666667356149\ ts - 0.757142855132263\ 10^{-5}\ ts^{2} + 0.666666664757207\ 10^{-7}\ ts^{3}$

$vel := 135569.142855759 + 165.666666790890\ ts - 7.84285714648076\ ts^2 + 0.0333333333677547\ ts^3$

mol:= 0.2426;

$dens := 0.838134285721437 - 0.000670000000638179\ ts - 0.285714267198316\ 10^{-6}\ ts^2 - 0.175019613397851\ 10^{-15}\ ts^3$

$vel := 140309.714285862 - 351.000000013599\ ts + 5.28571428612113\ ts^2 - 0.0800000000039540\ ts^3$

mol:= 0.3280;

$dens := 0.838408571433296 - 0.000903333333757858\ ts + 0.642857144097079\ 10^{-5}\ ts^2 - 0.666666667845970\ 10^{-7}\ ts^3$

$vel := 148075.714287671 - 1246.00000017547\ ts + 33.9857142908284\ ts^2 - 0.380000000048544\ ts^3$

mol:= 0.4509;

$dens := 0.832899999990081 - 0.000719999999113352\ ts - 0.257656939188852\ 10^{-13}\ ts^2 + 0.243898215221782\ 10^{-15}\ ts^3$

$vel := 144585.428571926 - 1009.66666671146\ ts + 24.8714285727390\ ts^2 - 0.273333333345816\ ts^3$

mol:= 0.5444;

$dens := 0.829899999986661 - 0.000739999998807060\ ts - 0.346836007557892\ 10^{-13}\ ts^2 + 0.328468274825027\ 10^{-15}\ ts^3$

$vel := 131673.142856081 + 115.666666761498\ ts - 10.0428571456107\ ts^2 + 0.0733333333593778\ ts^3$

mol:= 0.6467;

$dens := 0.829125714285891 - 0.00103333333335089\ ts + 0.728571428627477\ 10^{-5}\ ts^2 - 0.666666666724215\ 10^{-7}\ ts^3$

$vel := 117225.142856036 + 1316.66666676603\ ts - 44.6428571457580\ ts^2 + 0.393333333360910\ ts^3$

mol:= 0.7408;

$dens := 0.822099999998395 - 0.000819999999855213\ ts - 0.424448455248878\ 10^{-14}\ ts^2 + 0.405050412991973\ 10^{-16}\ ts^3$

$vel := 118147.142855746 + 1139.66666679192\ ts - 38.7428571465073\ ts^2 + 0.333333333367977\ ts^3$

mol:= 0.8424;

$dens := 0.818374285713326 - 0.00109333333324712\ ts + 0.671428571176987\ 10^{-5}\ ts^2 - 0.666666666427647\ 10^{-7}\ ts^3$

$vel := 110966.571428039 + 1724.00000004757\ ts - 54.9714285728101\ ts^2 + 0.480000000013069\ ts^3$

mol:= 0.9191;

$$dens := 0.815648571437070 - 0.00138666666742954\ ts + 0.0000134285714508299\ ts^2 - 0.133333333544826\ 10^{-6}\ ts^3$$

$$vel := 126798.285714252 + 362.000000003353\ ts - 16.4857142858218\ ts^2 + 0.120000000001105\ ts^3$$

mol:=1.0000;

$$dens := 0.808234285724032 - 0.00151666666754055\ ts + 0.0000137142857397586\ ts^2 - 0.133333333575155\ 10^{-6}\ ts^3$$

$$vel := 135720.285714239 - 193.333333329167\ ts - 5.48571428583408\ ts^2 + 0.0533333333344559\ ts^3$$

Table 6: Molecular Cluster (ζ□□□ at various temperatures in Acetonitrile-1-Decano

[Numerical Presentations, Xp = temperature in degree Celsius, Yp = ζ^{-1} =□Association□Polymerization].

mol:=0.00000; Xp:=Vector([20,30,40,50,60,70,80]):
Yp:=Vector([8712.284987, 7676.377449, 6661.745622, 5668.781431, 4698.550637, 3753.180208, 2837.822805]):

$$Pol := 10833.0864555020 - 107.561038469596\ ts + 0.0686872522651704\ ts^2 + 0.000331390111089708\ ts^3$$

mol:= 0.1197; Xp:=Vector([20,30,40,50,60,70,80]):
Yp:=Vector([11299.04086, 8169.374231, 6844.888437, 7085.653061, 9277.414317, 14953.35218, 29866.72024]):

$$Pol := 8597.17428934420 + 485.282814174745\ ts - 23.5918880108532\ ts^2 + 0.259754876416795\ ts^3$$

mol:= 0.2426; Xp:=Vector([20,30,40,50,60,70,80]):
Yp:=Vector([9480.544373, 8248.828880, 7043.362027, 5865.192231, 4716.466007, 3602.977868, 2540.660272]):

$$Pol := 11980.1201639315 - 125.902620610132\ ts + 0.0256628111950058\ ts^2 + 0.000912859194414958\ ts^3$$

mol:= 0.3280; Xp:=Vector([20,30,40,50,60,70,80]):
Yp:=Vector([8210.201109, 8354.679079, 6827.539016, 3862.927694, 495.1950683, 55.04449428, 30.44937486]):

$$Pol := -2731.21482884292 + 1004.17538071253\ ts - 26.4338807797101\ ts^2 + 0.179228522174571\ ts^3$$

mol:= 0.4509; Xp:=Vector([20,30,40,50,60,70,80]):
Yp:=Vector([9416.988515, 8221.588375, 7048.361323, 5899.225622, 4779.489784, 3704.906466, 2731.869866]):

$$Pol := 11736.2176095016 - 112.827952496943\ ts - 0.220402603449845\ ts^2 + 0.00278985552776122\ ts^3$$

mol:= 0.5444; Xp:=Vector([20,30,40,50,60,70,80]):
Yp:=Vector([9304.063252, 7985.192247, 6692.842154, 5429.588446, 4200.331713, 3016.004074, 1906.850374]):

$$Pol := 11940.5344228590 - 131.193770160058\ ts - 0.0714652398779795\ ts^2 + 0.00179127044442497\ ts^3$$

mol:= 0.6467; Xp:=Vector([20,30,40,50,60,70,80]):
Yp:=Vector([6303.876999, 6980.155302, 5814.268825, 2868.811842, 231.2642353, 39.11597866, 11.22380114]):

$$Pol := -5062.20235064946 + 1016.72415531926\ ts - 25.7303592356757\ ts^2 + 0.173094186532913\ ts^3$$

mol:= 0.7408; Xp:=Vector([20,30,40,50,60,70,80]):
Yp:=Vector([7062.069150, 5397.831649, 3794.561265, 2295.389820, 1058.765482, 405.2845449, 178.6762752]):

$$Pol := 9846.94529273073 - 107.940095173018\ ts - 2.03703128874650\ ts^2 + 0.0234708336749770\ ts^3$$

mol:= 0.8424; Xp:=Vector([20,30,40,50,60,70,80]):
Yp:=Vector([3404.065688, 3224.670172, 1363.026397, 209.9302306, 59.87863610, 21.00924384, 7.452818713]):

$$Pol := 4592.57364533436 + 3.52211937708805\ ts - 3.20329728335584\ ts^2 + 0.0308387727714713\ ts^3$$

mol:= 0.9191; Xp:=Vector([20,30,40,50,60,70,80]):
Yp:=Vector([335.3715713, 604.3652743, 230.0483473, 68.18093635, 23.90688107, 9.466921127, 4.117126291]):

$$Pol := -399.809358447336 + 72.3114694126763\ ts - 1.87852786266161\ ts^2 + 0.0130495937331763\ ts^3$$

mol:=1.0000;Xp:=Vector([20,30,40,50,60,70,80]):
Yp:=Vector([89.65199656, 117.3202698, 84.20777714, 41.92349369, 18.82006362, 8.521451251, 4.054385291]):

$$Pol := -75.0733892488222 + 14.9038453470466\ ts - 0.370102120927058\ ts^2 + 0.00246080335555731\ ts^3$$

DISCUSSION

Mathematical analysis: Normally data is presented in terms of numerical formats. Numerical format is a discrete representations of physical data in which continuity is loosed. Liquid region is as such narrow domain in terms of temperature variable. Therefore experimental data is represented in terms of cubical polynomial, so that hidden physical information in terms of first and second derivative could be extracted. In this thermo dynamical physical word basic data in terms of cubical polynomial has great importance. It is observed from table 1-3-5, density is conveniently represented by straight line in liquid region, whereas wave velocity is represented by parabolic curve. In the present calculations however ratio of specific heat is assumed to be constant! Now we have continuous input data for density and wave velocity which could be now freely used to compute model two parameters such as η and τ□which are related to geometry and binding energy of a molecules□□Interaction potential is also relates to these reduced variable η and τ□We can concentrate any derived equation of state which must contain maximum two model parameter and this model parameter are related to density and temperatures.

In the present analysis we used accurate equation of state [24-25] containing two parameters. It is easy to solve set of equation [12] which does not involve third variable. Solutions set of equations [12] is used to evaluate third variable [ζ =□n] with the help of equation [9].Situations can be analyzed in any domain of temperature in small steps, so that effect on model parameters is suitable and some predictions could be possible.

From table2, it is observed that (Yp- vector) over entire temperature range size of cluster decrease uniformly as temperature increases except at mol fraction [0.2171,and 0.3356] where it posses minimum at 40 degree centigrade. From table4, it is observed that (Yp- vector) over entire temperature range size of cluster decrease uniformly as temperature increases when mol fraction is greater than [0.6770],whereas it possess minimum at 40 degree centigrade. From table6, it is observed that (Yp- vector) over entire temperature range size of cluster decrease uniformly as temperature increases except at mol fraction [0.1197] i.e. higher concentration of 1-Decanol where it posses minimum at 40 degree centigrade.

Temperature variation analysis: Following table7 shows fairly systematic variation of physical property [ζ^{-1} =□n^{-1}] over temperature. It shows decrease in magnitude of cluster size which is in accordance with breaking of bonds.

Table7: Comparative study of effect of temperature on [ζ^{-1} =□n^{-1}] related to a size of a cluster.

S.No	Temperature in Centigrade	Acetonitrile [ζ^{-1} =□n^{-1}]	1-Hexanol [ζ^{-1} =□n^{-1}]	1-Octanol [ζ^{-1} =□n^{-1}]	1-Decanol [ζ^{-1} =□n^{-1}]
1	20	89.65199656	9749.245487	12753.48548	8712.284987
2	30	117.3202698	8514.764734	8256.807801	7676.377449
3	40	84.20777714	7303.251235	7520.789464	6661.745622
4	50	41.92349369	6116.276644	10592.81524	5668.781431
5	60	18.82006362	4957.387502	21825.44529	4698.550637

Special temperature region analysis: Information in following table8 is in accordance with equation [13], showing that [α]and [n^{-1}] have a sharp correlations. Magnitude of [ζ^{-1}] can be associated to special process such phase transitions! This can be viewed as missing information of discrete data representations.

Table8: Molecular Cluster (ζ^{-1} at various temperatures in Acetonitrile-1-Octanol [Numerical Presentations, Xp = temperature in degree Celsius, Yp = ζ^{-1} = Polymerization] corresponding to mol:=0.1285.

S.No.	Temp.	[ζ^{-1} = n^{-1}]	η	τ	α
1	62.00	45556.86898	0.7404005620	1.317140388	0.000368127455609572
2	64.00	65544.90615	0.7404133879	1.317386194	0.000285327527162411
3	66.00	105944.0057	0.7404247985	1.317950895	0.000196347222508028
4	68.00	227777.6669	0.7404349365	1.319770281	0.000101222345585454
5	69.00	471034.8229	0.7404395724	1.323497453	0.0000513699523391376
6	69.20	592206.5616	0.7404404670	1.325372406	0.0000412171293064522
7	69.40	793445.9832	0.7404413512	1.328506480	0.0000310036610356530
8	69.60	0.1193135791 10^{7}	0.7404422250	1.334802022	0.0000207296083682561
9	69.80	0.2370230020 10^{7}	0.7404430885	1.353883906	0.0000103950333869798
10	69.90	0.4629669181 10^{7}	0.7404435164	1.392933145	0.520506977037030 10^{-5}
11	69.990	0.3131018719 10^{8}	0.7404438994	2.506000418	0.521186029020182 10^{-6}
12	69.999	0.7354575731 10^{8}	0.7404439376	1.572186264 *I*	0.521248770428703 10^{-7}
13	70.001	0.1050128117 10^{9}	0.7404439461	1.101220159 *I*	-0.521275432946773 10^{-7}
14	71.000	-511555.7223	0.7404480611	1.308513187	-0.0000528797505510619

Thermodynamic domain: Normally calculations show that local maxima at different mole fractions, corresponds to cluster formations activity increases. Thus we may assume that different specific structures are favored when concentrations of corresponding component of solute than solvent is more predominant. Conversely it is convenient to associate local minima at different mole fractions favoring cluster breaking activity of these formed structures. Structure diffusing process is associated when magnitude starts decreasing. As one goes from stable configurations

corresponding to certain temperature towards phase transitions point it is observed that increased temperature may changes the intensity of these activity and sometimes cease down which is a normal. All these imaginations are possible due to a thermodynamic parameter a mol□□ .Only calculating excess adiabatic compressibility in combinations with excess bulk volume one can expect either associations, dissociations, ordering or concealing process. It is observed that the excess adiabatic compressibility and excess volume both are positive, and indicates that a cluster loosens decreases. An increase in adiabatic compressibility in a mixture of two liquid, denotes a weakening of the intermolecular interactions. The hetero molecular interactions not only disturb the homo molecular interactions in component liquids, but also cause a 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 dissociations taking place in component liquid. The dissociation would predominantly occur in one of the component liquids in which homo molecular interactions 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. This dissociative process is exactly the inverse of an associative process, but here it is the homo molecular cluster which dissociates and not the hetero molecular clusters. No structural conclusions are possible. We have limited to qualitative results hence there is a scope for comparison with experimental data and other models in the literature.

CONCLUSION

Occurrence of physical parameter□ζ□[number of moles (the amount of gas)] gives□□unique solution of η and τ□ Association of mol□□□□to clustering can give a reasonable picture of thermodynamic parameters under studies. With the help of set of physical parameters, such as [ζ^{-1},η,τ] can throw light on hidden process taking place in liquid mixture.

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