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Analytical study of temperature variation of some real binary liquid mixtures using khasare formulation

M.S. Deshpande

Department of Physics, Anand Niketan College, Anandwan, Dist. Chandrapur (M.S.), India

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ABSTRACT

We have used Khasare's formalism, to compute thermodynamic behaviour of structurally related real fluid mixtures under consideration, in terms of, temperature variation within permissible limits for temperature for liquids. The code developed in C is extensively used for theoretical computations. The temperature is varied from 293.16 K to 318.16 K in equal steps of 5K. Effect of temperature change is studied for Geometric packing fraction (η) and reduced depth of potential ($\beta\epsilon$) for equal concentration of each liquid component in mixtures. Excess Helmoltz Energy, Excess bulk energy, Excess adiabatic compressibility. Ultrasonic wave velocities are computed using Khasare EOS.

Keywords: Khasare's EOS, Depth of Potential, Space filling ratio, compressibility.

INTRODUCTION

Liquids have immense significance to physics, chemistry and chemical engineering. There are two viewpoints in understanding the liquid properties: One proposes a gas like behaviour and second one a solid like behaviour. The properties are basically statistical in nature. Mainly noticeable resemblance in liquids and gases is their lack of rigidity. Several features of liquids are shown by collection of rigid spheres. The approach to an understanding of liquid state is to realize molecular interactions, manifesting itself through multiplicity of phenomena such as molecular association etc. Statistical thermodynamics is extensively used in study of liquids, as thermodynamic properties of liquids reveal nature and strength of interactions. The precise picture of active molecular aggregates is expressed in a generalized manner in well known thermodynamic relations. When two structurally related liquids are mixed in different proportions to form a mixture, homo and hetero molecular interactions take place. Hetero-molecular interactions introduce new kind of configuration in a liquid. Space filling factor (η) throws light on intermolecular geometry (micro geometry) and cluster geometry (macro geometry). In binary liquid mixtures, presence of the intermolecular interactions is reflected through the excess parameters such as excess adiabatic compressibility and excess molar volume.

A number of workers presented theories[1-7] and equations of state (EOS) (Gibbons [8] and Boublik[9] , Percus-Yevick[10-11], Carnahan-Starling (CS)[12], Barker-Henderson (*et al*) to comprehend the liquids and liquid mixtures. The development in fundamental formulation of Gibbs and Boltzmann, integral equations, perturbation theories, and computer simulations in statistical mechanics provides key to further insight in perception of intermolecular forces.

Ultrasonic study is comprehensively used by large number of workers to grasp the molecular behaviour of liquids. Propagation of the ultrasonic waves in liquid mixtures depends upon molecular geometry and on intermolecular interactions. In a liquid, the space filling factor (η) changes with temperature and composition of the mixture. The variation in the sound velocity for mixture reflects the variation of (η) . Thus change in ultrasonic wave velocity can be related with the excess thermodynamic properties.

Recently B Sathyanarayana (*et al*)[13] determined the ultrasonic velocity and density for the mixtures of 1,2 dichloromethane, 1,1,2 trichloroethane, 1,1,2,2 tetracholoroethane, trichloroethane and tetrachloroethane with N-methyllacetamide, over the entire range of composition at fixed temperature 308.15 K. and found that maximum interactions are present at equal mole fraction of components in every system under study. Thermo-acoustic study of cobalt(III) complexes in aqueous and binary aqueous media at the temperature 303.15K and 313.15K is conducted by U N Dash *et al*[14] and concluded that the temperature has diminutive effect on the compressibility. V Kannappan and R Jaya Santhi [15] conceded the study of dipole dipole-induced interactions in binary liquid mixtures of benzene, *n*-hexane, carbon tetrachloride and *p*-xylene with Cyclohexane by ultrasonic velocity measurements, to estimate experimental values of compressibility, free volume *etc* and found that strength of interaction depends on the polarisibilty of the molecules of the components present in the mixtures. Rita Mehra and Minakshi Pancholi[16] examined molecular interactions in mixtures of benzene-butanol and toluene-butanol systems from acoustic and thermodynamic parameters, for different concentration and temperature of binary mixtures of methanol and pyridine and found that sound speed decreases with high mole fraction. The decrease in the sound speed is attributed to sound polarization of polar alcohols originated by the addition of non-polar benzene. Study of molecular interactions and ultrasonic velocity in mixture of some alkanols with aqueous propylene glycol by D Sravana Kumar and D Krishna Rao[17] revealed that non-ideal behaviour is predominant in low alkanol concentration region is due to strong specific interactions. M Selvakumar and D Krishna Bhat [18] conducted study of polymethyl methacrylate and polyetheleneglycol solutions in Tetrahydrofuran using ultrasonic velocities at 293K and 313K to calculate Gibb's free energy and heat of mixing. Relative study of liquid models in the prediction of excess thermodynamic properties of ternary systems is carried out by R K Shukla *et al* [19] and found that strength of interaction between components is weakened by addition of third component. Ultrasonic study of molecular interactions and compressibility behaviour of strontium soaps in chloroform-propylene glycol mixture is used to envisage the ultrasonic velocity, intermolecular free length, adiabatic compressibility by M K Rawat and Sangeeta [20]. A K Srivastava and B K Gupta [21] studied Temperature dependence of thermal expansivity and volume thermal expansion making use of ultrasonic measurements to use Singh and Gupta Equation for theoretical predications. S R Kanherkar *et al* [22] investigated thermodynamic properties of electrolytes in aqueous solution of glycine at different temperatures by measuring ultrasonic velocity, density and viscosity and precisely stated result as, increase in ultrasonic velocity depend upon structural properties of Solutes. J Ishwara Bhat *et al* [23] studied acoustic behaviour of citric acid in water, dimethylformide, dimetylsulphoxide at 303K and established that compressibility decreases with increase in concentration which in turn indicates increase in ion-solvent interaction. Robles and de Haro [24] used CS as a reference system, Wu and Sadus [25] conducted extensive comparative studies of EOS for hard-sphere (HS) Compressibility. Mulero, Gulan and Cuadros [26] reviewed accuracy of the established EOS. Mustafa Vatandas *et al* [27] conducted analytical study of ultrasonic velocity measurement for determination of the type of alcohol. J. M. Resa *et al* [28] studied influence of temperature on ultrasonic velocity measurement of ternary mixtures. Kalidoss *et al* [29-30] and Bhandakkar *et al* [31-32] have applied Khasare EOS[33-34] to binary and ternary liquid mixtures and established the aptness of the formulation. Recently, Khasare *et al*[35-36] have used extended scaled particle approach to establish thermodynamic properties of liquids.

Here, efforts are made to develop general mathematical outline based upon Khasare EOS (three parametric) with additive rules (Equ.7 and 9) to predict thermodynamic properties of real binary liquid mixtures, fitting experimental data.

Khasare Equation of State for Real Fluid Mixtures

Khasare [34] used perturbation approach to develop formulations for fluids using a strong repulsive potential and a weak attractive potential together, based upon Scaled Particle Theory (SPT). To begin with, liquids are considered as hard sphere (HS) liquids. They can be treated as simple three-dimensional ideal liquid systems for study.

Khasare formulation is applied to compute values of three model parameters (1) hard sphere diameter (σ), (2)reduced depth of potential ($\beta\varepsilon$) and (3)temperature variation of depth of potential ($\delta(\beta\epsilon T)$) Theses are used to estimate theoretical values of Geometric packing fraction (eta) , reduced depth of potential ($\beta\epsilon T$), Excess Helmholtz Energy, Excess bulk energy, Excess adiabatic compressibility factor and ultrasonic wave velocity to predict the behaviour of the real binary liquid mixtures. Initially values for $\left(\frac{PV}{RT}, \frac{Mu^2}{\gamma RT}, \frac{Mu^2\alpha}{\gamma R}\right)$

(Where P-pressure, V-Volume, R- Universal gas constant, T-Temperature in Kelvin, u - Ultra sonic wave velocity, M -Molecular Weight, γ-specific heat ratio, α -volume expansion coefficient) are calculated for pure liquid from experimental data[35] of 15 real binary systems for ultrasonic velocities and densities. From these values three model parameters (σ, ($\beta\epsilon T$), ($\delta(\beta\epsilon T)$) are predicted for pure liquids using computer code developed in "C". These values are further used in computation of model parameters (σ, ($\beta\epsilon T$), ($\delta(\beta\epsilon T)$) for liquid mixtures at different temperatures. With the help of these model parameters for the liquid mixtures, values for

$\left(\frac{PV}{RT}, \frac{Mu^2}{\gamma RT}, \frac{Mu^2\alpha}{\gamma R}\right)$liquid mixtures are computed. They are further used in predicting the thermodynamic parameters of liquid mixtures at entire concentration and in permissible temperature range. The temperature variation used for computation is 293.16 K to 313.16 K in equal steps of 5K.

Data for real 15 binary systems used are arranged in five groups as.

Group I	Group II
Methyl Cyclohexane + Cyclohexane	Tetrahydrofuran + Cyclohexane
Methyl Cyclohexane + Benzene	Tetrahydrofuran + MethylCyclohexane
Methyl Cyclohexane + 1,4 Dioxane	Tetrahydrofuran + Cyclohexanol
Group III	**Group IV**
Tetrahydropyrrol + Cyclohexane	1,4 Dioxane + Tetrahydrofuran
Tetrahydropyrrol + MethylCyclohexane	1,4 Dioxane + Benzene
Tetrahydropyrrol + Cyclohexanol	1,4 Dioxane + Carbon tetrachloride
Group V	
Cyclohexanol + Carbon tetrachloride	
Cyclohexanol + Benzene	
Cyclohexanol + Methyl alcohol	

For a fluid of hard sphere molecules each of diameter d, compressibility factor Z, is defined as

$$Z = \frac{\beta P}{\rho};\ \beta = \frac{1}{(K_B T)};\ \eta = \frac{\pi \rho d^3}{6} \qquad (1)$$

where P is pressure, ρ is density, $K_B T$ is Boltzman Constant and T is temperature. The compressibility factor based on Scaled Particle Theory is

$$Z_{SPT} = \frac{(1+\eta+\eta^2)}{(1-\eta)^3} \qquad (2)$$

The factor $\left(\frac{\pi}{6}\right) d^3$ is the volume of hard sphere.

The precise picture of active molecular aggregate is expressed in a generalized manner in well known thermodynamic relations. Theories such as free length theory Scaled particle theory are using single adjustable parameters and depend upon geometry of molecules. As far as propagation of ultrasonic waves in liquid mixture is concerned it not only depends upon the molecular structure, but also on intermolecular interaction. With such idea Khasare[21, 22, and 23] introduced Equation of State for real binary fluid mixture which is expressed as

$$\frac{PV}{RT} = \frac{1}{(1-\eta)} + \frac{3e\eta}{(1-\eta^2)} + \frac{3f\eta^2}{(1-\eta)^3} + \frac{7\beta\epsilon\left(\eta + log(1-\eta)\right)}{\eta} \qquad (3)$$

$$\theta_a = \frac{1}{(1-\eta)} + \frac{3e\eta}{(1-\eta^2)} + \frac{3f\eta^2}{(1-\eta)^3} \qquad (4)$$

$$\theta_b = \frac{7\beta\epsilon\left(\eta + log(1-\eta)\right)}{\eta} \qquad (5)$$

Hence equation (3) can be rearranged as

$$\frac{PV}{RT} = \theta_a + 7\beta\epsilon\theta_b \qquad (6)$$

The Khasare additive rules are

$$\varphi(p,q) = \sum_{i=1}^{m} x_i\,(\beta\varepsilon_i)^p \left(\frac{\sigma_i}{2}\right)^q \qquad (7)$$

Where $\psi(0,1), \psi(0,2), \psi(0,3)$ signifies mean radius of curvature, surface area and volume of molecule respectively, p= 0,1; q = 1,2,3 and i=1, m

$$e = \frac{\psi(0,1), \psi(0,2)}{\psi(0,3)};\ f = \frac{\psi(0,2)^3}{\psi(0,3)^2} \qquad (8)$$

The additive rules for mixture are

$$(\beta\epsilon) = \frac{\psi(1,3) + 3\psi(1,2)\psi(0,1) + 3\big(\psi(1,1)\psi(0,2)\big)}{7\psi(0,3)} \qquad (9)$$

Where $\eta = \psi(0,3)N_A/V$ = Space filling ratio

N_A is Avogadro's Number

The related thermodynamic relations can be obtained as

$$\frac{Mu^2}{\gamma RT} = \frac{1}{(1-\eta)^2} + \frac{6e\eta}{(1-\eta)^3} + \frac{9f\eta^2}{(1-\eta)^4} - \frac{7\beta\epsilon\eta}{(1-\eta)} \qquad (10)$$

We define

$$\theta_c = \frac{1}{(1-\eta)^2} + \frac{6e\eta}{(1-\eta)^3} + \frac{9f\eta^2}{(1-\eta)^4} \qquad (11)$$

And

$$\theta_d = \frac{\eta}{(1-\eta)} \qquad (12)$$

So equation (10) takes the form

$$\frac{Mu^2}{\gamma RT} = \theta_c - 7\beta\epsilon\theta_d \qquad (13)$$

Where M = is molecular weight, u = ultrasonic velocity, γ = ratio of specific heat.

Computational Aspect

Experimental data for ultrasonic wave velocity (at 2MHz) and density of liquids at fixed temperature is taken from literature. For pure liquids, we have e=f=1.0. The numerical value of eta (a space filling ratio)for each liquid component is found out by finding the root of the equation (14) by subroutine of the main computer code presented here. The theoretical computations are carried out by using computer code developed in C (Appendix).

$$\frac{Mu^2}{\gamma RT} = \theta_c - \frac{\left(\frac{PV}{RT} - \theta_d\right)\theta_d}{\theta_b} \qquad (14)$$

mean radius of curvature(σ/2), reduced depth of potential and its temperature dependence worked out as

$$\left(\frac{\sigma}{2}\right)^3 = \frac{3\eta v}{4\pi N_A} \qquad (15)$$

$$(\beta\epsilon) = \theta_c - \frac{\left(\frac{PV}{RT} - \theta_a\right)\theta_d}{7\theta_b} \qquad (16)$$

$$\delta(\beta\epsilon T) = \frac{\left(\frac{Mu^2\alpha}{R}\right)\theta_a}{7\theta_b} \qquad (17)$$

As a result the temperature variation for depth of potential can be stated as

$$\epsilon(T) = (\beta\varepsilon)K_B T \qquad (18)$$

The general scheme for developing model parameters is given here for pure liquid which is further used for determining the model parameters for liquid mixtures.

$$\left(\frac{PV}{RT}, \frac{Mu^2}{\gamma RT}, \frac{Mu^2\alpha}{R}\right)_{pure} \longrightarrow [\sigma, \beta\epsilon, \delta(\beta\epsilon T)]_{pure} \qquad (19)$$

Model parameters for liquid mixture could be obtained by assuming values for pure liquids. They are as

$$[\sigma, \beta\epsilon, \delta(\beta\epsilon T)]_{pure} \longrightarrow [\sigma, \beta\epsilon, \delta(\beta\epsilon T)]_{mixture} \qquad (20)$$

$$[\sigma, \beta\epsilon, \delta(\beta\epsilon T)]_{mixture} \longrightarrow \left(\frac{PV}{RT}, \frac{Mu^2}{\gamma RT}, \frac{Mu^2\alpha}{R}\right)_{mixture} \qquad (21)$$

Thus thermodynamic properties of liquid mixtures obtained using above formulation. The values computed for real binary mixtures are presented in the subsequent tables. Tables 1.1 to 1.5 show effect of temperature variation on$(\eta), (\beta\varepsilon)$. In Tables 2.1 to 2.5 computed values of Excess Helmoltz Energy, Excess bulk Volume, Excess adiabatic compressibility and Experimental, and Calculated Ultrasonic Velocities are shown.

(η)=Geometric packing fraction; $(\beta\varepsilon)$ =Reduced depth of potential; (ρ) =Density ; T =Temperature in Kelvin

GROUP I

Table 1.1.1

MethylCyclohexane + Cyclohexane

Temp(K)	(η)	$(\beta\varepsilon)$	$\eta\rho$	(ε/k)
293.16	0.5379	6.07	0.4130	1779.48
298.16	0.5338	5.96	0.4071	1777.03
303.16	0.5297	5.85	0.4048	1773.48
308.16	0.5255	5.74	0.3964	1768.83
313.16	0.5213	5.64	0.3911	1766.22
318.16	0.5171	5.54	0.3860	1762.60

Table 1.1.2

MethylCyclohexane + Benzene

Temp(K)	(η)	$(\beta\varepsilon)$	$\eta\rho$	(ε/k)
293.16	0.5384	6.04	0.4352	1770.68
298.16	0.5344	5.93	0.4298	1768.76
303.16	0.5305	5.83	0.4243	1767.42
308.16	0.5264	5.73	0.4190	1765.75
313.16	0.5224	5.63	0.4137	1763.09
318.16	0.5183	5.53	0.4060	1759.42

Table 1.1.3

MethylCyclohexane+1,4 Dioxane

Temp(K)	(η)	$(\beta\varepsilon)$	$\eta\rho$	(ε/k)
293.16	0.5448	6.21	0.4339	1820.52
298.16	0.5409	6.10	0.4684	1818.77
303.16	0.5370	6.00	0.4628	1818.96
308.16	0.5331	5.89	0.4573	1815.06
313.16	0.5292	5.79	0.4514	1813.19
318.16	0.5252	5.69	0.4458	1810.33

GROUP II

Table 1.2.1

Tetrahydrofuran + Cyclohexane

Temp(K)	(η)	$(\beta\varepsilon)$	$\eta\rho$	(ε/k)
293.16	0.5307	5.85	0.4346	1714.62
298.16	0.5265	5.74	0.4288	1711.43
303.16	0.5223	5.64	0.4230	1709.82
308.16	0.5181	5.54	0.4171	1707.20
313.16	0.5138	5.44	0.4114	1703.59
318.16	0.5095	5.35	0.4055	1702.15

Table 1.2.2
Tetrahydrofuran + MethylCyclohexane

Temp(K)	(η)	$(\beta\varepsilon)$	$\eta\rho$	(ε/k)
293.16	0.5352	5.92	0.4352	1735.50
298.16	0.5312	5.81	0.4296	1732.30
303.16	0.5271	5.70	0.4239	1728.01
308.16	0.5230	5.61	0.4183	1728.77
313.16	0.5189	5.51	0.4127	1725.51
318.16	0.5147	5.42	0.4070	1724.42

Table 1.2.3
Tetrahydrofuran + Cyclohexanol

Temp(K)	(η)	$(\beta\varepsilon)$	$\eta\rho$	(ε/k)
293.16	0.5554	6.54	0.5106	1917.26
298.16	0.5510	6.40	0.5047	1908.22
303.16	0.5465	6.27	0.4978	1900.81
308.16	0.5420	6.14	0.4915	1892.44
313.16	0.5374	5.02	0.4815	1885.22
318.16	0.5327	5.90	0.4788	1877.14

GROUP III
Table 1.3.1
Tetrahydropyrrol + Cyclohexane

Temp(K)	(η)	$(\beta\varepsilon)$	$\eta\rho$	(ε/k)
293.16	0.5347	5.96	0.4315	1747.23
298.16	0.5307	5.86	0.4261	1747.21
303.16	0.5267	5.76	0.4155	1746.20
308.16	0.5227	5.66	0.4189	1744.18
313.16	0.5181	5.56	0.4092	1741.16
318.16	0.5145	5.47	0.4043	1740.33

Table 1.3.2
Tetrahydropyrrol + MethylCyclohexane

Temp(K)	(η)	$(\beta\varepsilon)$	$\eta\rho$	(ε/k)
293.16	0.5390	6.03	0.4317	1767.75
298.16	0.5351	5.93	0.4264	1768.08
303.16	0.5312	5.83	0.4212	1767.42
308.16	0.5273	5.73	0.4160	1765.75
313.16	0.5233	5.63	0.4107	1763.09
318.16	0.5193	5.54	0.4055	1762.60

Table 1.3.3
Tetrahydropyrrol + Cyclohexanol

Temp(K)	(η)	$(\beta\varepsilon)$	$\eta\rho$	(ε/k)
293.16	0.5581	6.64	0.5045	1945.58
298.16	0.5538	6.50	0.4949	1938.04
303.16	0.5495	6.37	0.4929	1931.12
308.16	0.5452	6.24	0.4870	1922.91
313.16	0.5408	6.12	0.4878	1916.53
318.16	0.5363	6.00	0.4741	1908.96

GROUP IV
Table 1.4.1
1, 4 Dioxane + Tetrahydrofuran

Temp(K)	(η)	$(\beta\varepsilon)$	$\eta\rho$	(ε/k)
293.16	0.5376	6.07	0.5160	1779.48
298.16	0.5338	5.96	0.5097	1777.03
303.16	0.5299	5.86	0.5035	1776.51
308.16	0.5260	5.76	0.4970	1775.00
313.16	0.5221	5.67	0.4909	1775.61
318.16	0.5181	5.57	0.4836	1772.15

Table 1.4.2
1,4 Dioxane + Benzene

Temp(K)	(η)	$(\beta\varepsilon)$	$\eta\rho$	(ε/k)
293.16	0.5419	6.19	0.5419	1814.66
298.16	0.5379	6.08	0.5379	1812.81
303.16	0.5338	5.97	0.5338	1809.86
308.16	0.5297	5.86	0.5297	1805.81
313.16	0.5256	5.76	0.5236	1803.80
318.16	0.5214	5.65	0.5214	1800.78

Table 1.4.3
1,4 Dioxane + Carbon tetrachloride

Temp(K)	(η)	$(\beta\varepsilon)$	$\eta\rho$	(ε/k)
293.16	0.5409	6.16	0.5409	1805.86
298.16	0.5371	6.05	0.5371	1803.86
303.16	0.5333	5.95	0.5333	1803.80
308.16	0.5294	5.85	0.5294	1802.73
313.16	0.5255	5.75	0.5255	1800.67
318.16	0.5216	5.65	0.5216	1797.60

GROUP V
Table 1.5.1
Cyclohexanol + Carbon Tetrachloride

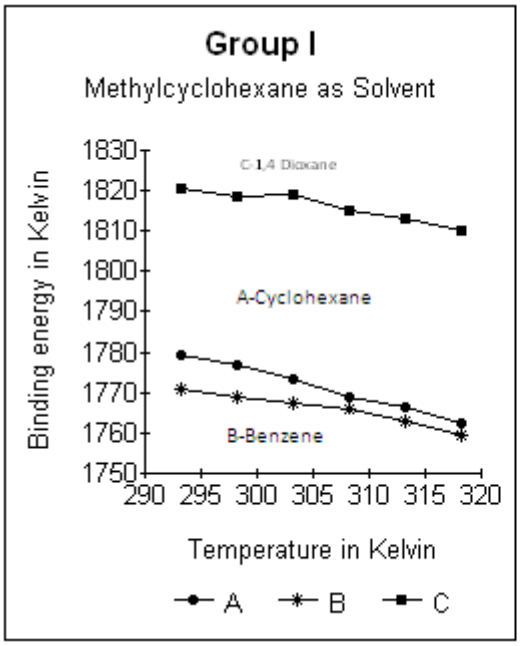
Temp(K)	(η)	$(\beta\varepsilon)$	$\eta\rho$	(ε/k)
293.16	0.5199	5.33	0.5199	1562.54
298.16	0.5163	5.25	0.5163	1565.34
303.16	0.5126	5.17	0.5126	1567.33
308.16	0.5088	5.09	0.5088	1568.53
313.16	0.5051	5.01	0.5051	1568.93
318.16	0.5013	4.90	0.5013	1558.98

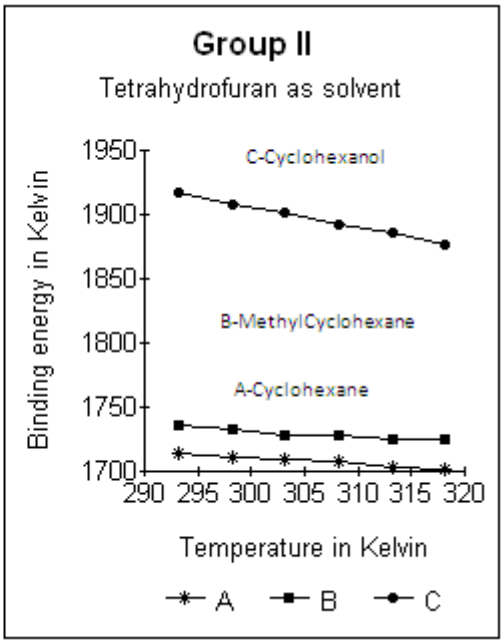
Table 1.5.2
Cyclohexanol + Benzene

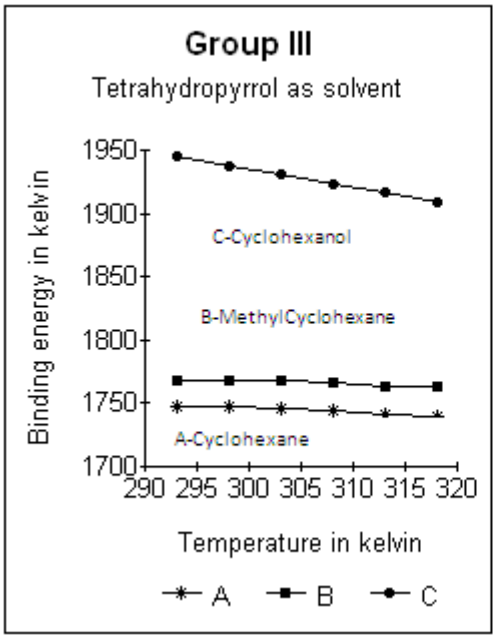
Temp(K)	(η)	$(\beta\varepsilon)$	$\eta\rho$	(ε/k)
293.16	0.5572	6.62	0.6860	1940.71
298.16	0.5528	6.49	0.5019	1935.05
303.16	0.5485	6.36	0.4958	1928.09
308.16	0.5411	6.23	0.8699	1910.83
313.16	0.5396	6.10	0.4834	1910.21
318.16	0.5350	5.98	0.4772	1902.59

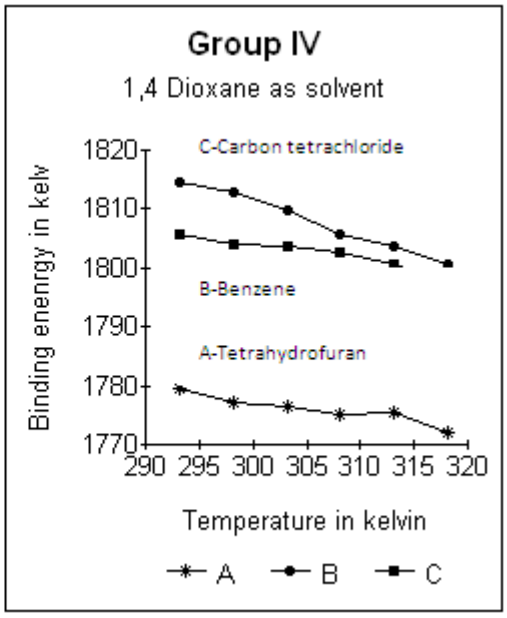
Table 1.5.3
Cyclohexanol + Methyl alcohol

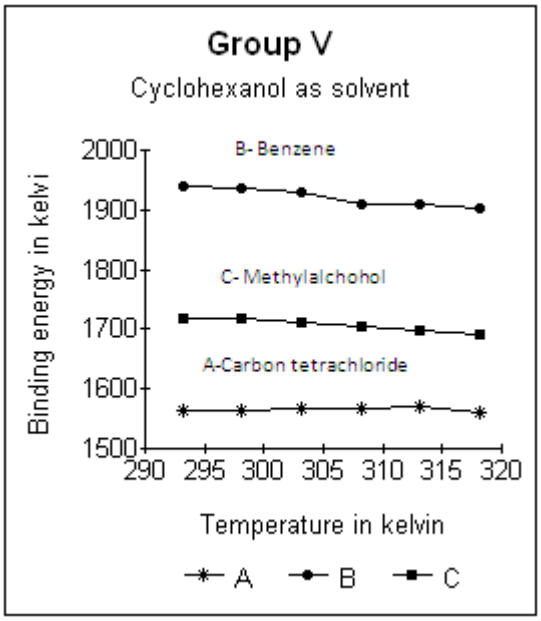
Temp(K)	(η)	$(\beta\varepsilon)$	$\eta\rho$	(ε/k)
293.16	0.5486	5.86	0.5025	1717.91
298.16	0.5441	5.76	0.4962	1717.40
303.16	05395	5.65	0.4898	1712.85
308.16	0.5349	5.53	0.4835	1704.12
313.16	0.5302	5.42	0.4771	1697.32
318.16	0.5254	5.32	0.4707	1692.61











Tables for Excess Helmoltz Energy (A^E), Excess bulk Volume (V^E), Excess adiabatic compressibility (Z^E), Experimental (u_{exp}) and Calculated (u_{cal}) Ultrasonic Velocity

GROUP I
Table 2.1.1
MethylCyclohexane + Cyclohexane

Temp K	(A^E) 10^{-5}	(V^E) 10^{-5}	(Z^E) 10^{-5}	(u_{exp}) m/s	(u_{cal}) m/s
293.16	6.2	-7.2	8.5	1245	1250
298.16	8.1	-7.2	8.1	1223	1228
303.16	10	-7.2	7.6	1202	1206
308.16	12	-7.2	7.1	1181	1184
313.16	14	-7.3	6.2	1159	1162
318.16	16	-7.4	5.9	1138	1140

Table 2.1.2
MethylCyclohexane + Benzene

Temp K	(A^E) 10^{-5}	(V^E) 10^{-5}	(Z^E) 10^{-5}	(u_{exp}) m/s	(u_{cal}) m/s
293.16	-2.3	-4.3	6.3	1246	1268
298.16	-2.4	-4.4	6.3	1224	1247
303.16	-2.4	-4.4	6.4	1202	1226
308.16	-2.5	-4.4	6.4	1180	1204
313.16	-2.6	-4.4	6.5	1159	1153
318.16	-2.6	-4.4	6.5	1137	1162

Table 2.1.3
MethylCyclohexane + 1,4 Dioxane

Temp K	(A^E) 10^{-5}	(V^E) 10^{-5}	(Z^E) 10^{-5}	(u_{exp}) m/s	(u_{cal}) m/s
293.16	-8.3	-1.6	-1.7	1239	1288
298.16	-8.6	-1.6	-2.2	1218	1265
303.16	-9.0	-1.7	-2.4	1197	1244
308.16	-9.1	-1.7	-3.0	1176	1224
313.16	-9.2	-1.8	-3.1	1155	1103
318.16	-9.3	-1.8	-3.5	1134	1182

GROUP II
Table 2.2.1
Tetrahydrofuran + Cyclohexane

Temp K	(A^E) 10^{-5}	(V^E) 10^{-5}	(Z^E) 10^{-5}	(u_{exp}) m/s	(u_{cal}) m/s
293.16	-9.2	-2.4	4.1	1267	1285
298.16	-9.7	-2.4	4.2	1244	1262
303.16	-9.0	-2.4	4.2	1121	1239
308.16	-10	-2.4	4.0	1198	1216
313.16	-11	-2.4	4.1	1175	1193
318.16	-12	-2.4	4.4	1152	1170

Table 2.2.2
Tetrahydrofuran + MethylCyclohexane

Temp K	(A^E) 10^{-5}	(V^E) 10^{-5}	(Z^E) 10^{-5}	(u_{exp}) m/s	(u_{cal}) m/s
293.16	-1.2	-5.6	9.1	1247	1263
298.16	-1.3	-5.5	9.1	1226	1242
303.16	-1.3	-5.4	9.2	1206	1220
308.16	-1.3	-5.3	9.2	1186	1298
313.16	-1.4	-5.2	9.3	1166	1277
318.16	-1.3	-5.1	9.1	1146	1155

Table 2.2.3
Tetrahydrofuran + Cyclohexanol

Temp K	(A^E) 10^{-5}	(V^E) 10^{-5}	(Z^E) 10^{-5}	(u_{exp}) m/s	(u_{cal}) m/s
293.16	8.9	-3.6	-6.9	1387	1434
298.16	8.6	-3.5	-6.7	1368	1405
303.16	8.3	-3.5	-6.5	1348	1377
308.16	8.0	-3.4	-6.3	1229	1248
313.16	7.7	-3.3	-6.1	1310	1320
318.16	7.3	-3.2	-5.2	1290	1291

GROUP III
Table 2.3.1
Tetrahydropyrrol + Cyclohexane

Temp K	(A^E) 10^{-5}	(V^E) 10^{-5}	(Z^E) 10^{-5}	(u_{exp}) m/s	(u_{cal}) m/s
293.16	-3.0	-4.9	1.9	1307	1324
298.16	-3.1	-5.2	1.7	1285	1302
303.16	-3.2	-5.5	1.5	1263	1280
308.16	-3.3	-5.8	1.2	1241	1257
313.16	-3.5	-6.2	8.6	1219	1235
318.16	-3.6	-6.6	5.1	1197	1213

Table 2.3.2
Tetrahydropyrrol + Methylcyclohexane

Temp K	(A^E) 10^{-5}	(V^E) 10^{-5}	(Z^E) 10^{-5}	(u_{exp}) m/s	(u_{cal}) m/s
293.16	-4.5	-7.5	8.7	1289	1300
298.16	-4.6	-7.6	8.7	1268	1279
303.16	-4.8	-7.8	8.7	1246	1257
308.16	-4.9	-7.9	8.7	1125	1236
313.16	-5.0	-8.1	8.7	1203	1215
318.16	-5.2	-7.5	8.1	1182	1149

Table 2.3.3
Tetrahydropyrrol + Cyclohexanol

Temp K	(A^E) 10^{-5}	(V^E) 10^{-5}	(Z^E) 10^{-5}	(u_{exp}) m/s	(u_{cal}) m/s
293.16	6.7	-2.3	-4.3	1449	1468
298.16	6.4	-2.2	-4.0	1430	1440
303.16	6.1	-2.1	-3.8	1412	1412
308.16	5.8	-1.9	-3.6	1393	1384
313.16	5.4	-1.8	-3.3	1375	1356
318.16	5.1	-1.7	-3.1	1357	1329

GROUP IV
Table 2.4.1
1,4 Dioxane + Tetrahydrofuran

Temp K	(A^E) 10^{-5}	(V^E) 10^{-5}	(Z^E) 10^{-5}	(u_{exp}) m/s	(u_{cal}) m/s
293.16	7.8	-1.0	-1.7	1325	1332
298.16	7.6	-1.0	-1.8	1303	1311
303.16	7.4	-1.1	-1.9	1280	1289
308.16	7.1	-1.2	-1.9	1256	1268
313.16	6.8	-1.2	-2.0	1235	1247
318.16	6.6	-1.3	-2.1	1213	1225

Table 2.4.2
1,4 Dioxane + Benzene

Temp K	(A^E) 10^{-5}	(V^E) 10^{-5}	(Z^E) 10^{-5}	(u_{exp}) m/s	(u_{cal}) m/s
293.16	-6.1	-5.8	-8.6	1341	1345
298.16	-7.1	-6.4	-9.4	1320	1321
303.16	-8.1	-7.1	-9.8	1299	1298
308.16	-9.2	-7.8	-11	1278	1275
313.16	-10	-8.6	-12	1258	1252
318.16	-12	-9.4	-13	1237	1229

Table 2.4.3
1,4 Dioxane + Carbon tetrachloride

Temp K	(A^E) 10^{-5}	(V^E) 10^{-5}	(Z^E) 10^{-5}	(u_{exp}) m/s	(u_{cal}) m/s
293.16	-2.3	-9.1	-1.1	1103	1106
298.16	-2.4	-9.3	-1.1	1086	1089
303.16	-2.4	-9.7	-1.1	1070	1071
308.16	-2.4	-10	-1.2	1053	1053
313.16	-2.5	-10	-1.2	1037	1037
318.16	-2.5	-11	-1.3	1020	1020

GROUP V
Table 2.5.1
Cyclohexanol + Carbon tetrachloride

Temp K	(A^E) 10^{-5}	(V^E) 10^{-5}	(Z^E) 10^{-5}	(u_{exp}) m/s	(u_{cal}) m/s
293.16	2.8	-3.2	-5.9	1152	1202
298.16	2.6	-3.1	-5.7	1136	1178
303.16	2.5	-3.1	-5.5	1120	1155
308.16	2.4	-3.0	-5.3	1103	1131
313.16	2.2	-2.9	-5.1	1087	1108
318.16	2.1	-2.8	-4.9	1071	1084

Table 2.5.2
Cyclohexanol + Benzene

Temp K	(A^E) 10^{-5}	(V^E) 10^{-5}	(Z^E) 10^{-5}	(u_{exp}) m/s	(u_{cal}) m/s
293.16	5.2	-2.8	-5.0	1367	1431
298.16	5.0	-2.7	-5.0	1348	1422
303.16	4.7	-2.6	-4.8	1328	1376
308.16	4.5	-2.5	-4.6	1309	1348
313.16	4.3	-2.4	-4.4	1289	1321
318.16	4.1	-2.3	-4.1	1270	1293

Table 2.5.3
Cyclohexanol + Methyl alcohol

Temp K	(A^E) 10^{-5}	(V^E) 10^{-5}	(Z^E) 10^{-5}	(u_{exp}) m/s	(u_{cal}) m/s
293.16	5.5	-1.9	-4.8	1364	1483
298.16	5.3	-1.8	-4.7	1348	1453
303.16	5.2	-1.8	-4.5	1331	1423
308.16	5.0	-1.8	-4.4	1315	1393
313.16	4.8	-1.8	-4.3	1298	1363
318.16	4.6	-1.7	-4.2	1281	1333

RESULTS AND DISCUSSION

Temperature variation plays an important role in the study of liquids. Linear variation is seen for geometric packing fraction and in binding energy (defined in Kelvin) for variation in temperature. A change in temperature causes change in the space filling factor. This change in space filling factor is indicative of the intermolecular interactions and change in structural geometry. These parameters are vital in deciding the volume of a liquid. Any small change in space filling factor induces significant change in the velocity of ultrasonic waves (table 2.1.1 to table 2.5.3) in liquid mixtures, which is primarily, an experimental tool in computing excess thermodynamic parameters of binary liquid mixtures. Intermolecular interactions and structural geometry decides the volume of a liquid. Thus geometry of molecules plays important role in determining volume of a liquid. Hence excess molar volume in binary liquid mixtures decide shape of a molecule i.e. cluster geometry or macro geometry.

CONCLUSION

In all groups negative values of (V^E) and (Z^E) indicate the strong interaction between components while positive values of (Z^E) suggest weak interaction. The strength of interaction depends upon the mixture components.

Computational outline of Khasare EOS may be used to predict the behavior of real binary liquids in domain of the theory.

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Appendix

```
/*Root of a equation*/
void root()
double a,c,wt,magn,hk;
int l;
hk=1.0e-8;
for(a=0.10,c=1-hk,l=1;l<=36;l++)
n=(a+c)/2.0;
func();
ww=(ek1-fa)/(7.0*fb);
wt=(ek3-fa)/(7.0*fb);
magn=ek2-(fc-7.0*ww*fd);
if(magn>0.0)a=n;
else c=n;
etaa=n;ener=ww;tene=wt;
/*Calculations for pure components*/
void pure()
double velo,dens,gama,
valph,vol,xx,yy,av,aq;
double velc,denc,compric,volc;
int l;
for(l=1;l<=2;l++)
mwx=mw[l];velo=vel[l][lt];
dens=den[l][lt];
valph=valp[l][lt];
/*av=valph;
aq=(log(1.3)-1.00)*av*av;
gama=exp(av*temp+aq*temp*temp);
;*/
gama=1.3;
vol=mwx/dens;
ek1=pres*vol/(gasc*temp);
ek2=mwx*velo*velo/(gama*gasc*temp);
ek3=ek2*valph*temp;e=1.0;f=1.0;
root();
yy=1.0/3.0;xx=etaa*vol/(g3*avnu);
na[l][lt]=etaa;
ra[l][lt]=pow(xx,yy);
wa[l][lt]=ener;twa[l][lt]=tene;
ck1=fa+7.0*wa[l][lt]*fb;
ck2=fc-7.0*wa[l][lt]*fd;
ck3=fa+7.0*twa[l][lt]*fb;
ck4=fg+7.0*wa[l][lt]*fh;
ck5=fg+7.0*twa[l][lt]*fh;
ck6=fc-7.0*twa[l][lt]*fd;
are[l]=ck4;
gre[l]=are[l]+ck1;
sre[l]=-1.0*ck5;
ure[l]=(ck4-ck5);
fre[l]=ck6;
denc=pres*mwx/(ck1*gasc*temp);
velc=sqrt(ck2*gama*gasc*temp/mwx);
volc=mwx/denc;
compric=1.0/(velc*velc*denc);
comp[l]=compric;
volu[l]=volc;
if(ctable[7]==1)
gotoxy(25*l,3);
printf("Component=%dn",l);
gotoxy(25*l,4);
printf("PV/RT=%7.3en",ek1);
```

```
gotoxy(25*l,5);
printf("MU2/GRT=%7.3en",ek2);
gotoxy(25*l,6);
printf("MU2AV/GR=%7.3en",ek3);
gotoxy(25*l,7);
printf("Helmhoz Energy=%7.3en",are[l]);
gotoxy(25*l,8);
printf("Gibbs Energy=%7.3en",gre[l]);
gotoxy(25*l,9);
printf("Entropy=%7.3en",sre[l]);
gotoxy(25*l,10);
printf("Internal Energy=%7.3en",ure[l]);
gotoxy(25*l,11);
printf("MU2AU/GR=%7.3en",fre[l]);
gotoxy(25*l,12);
printf("Comprisibility=%7.3en",comp[l]);
gotoxy(25*l,13);
printf("Volume=%7.3en",volu[l]);
/*Different equation of state*/
void func()
if(sbkfun==1)
h=1.0-n;j=n/h;
fd=j;fa=(j+3.0*e*j*j+3.0*f*j*j*j)/n;
fb=(n+log(h))/n;
fc=(1.0+6.0*e*j+9.0*f*j*j)/pow(h,2.0);
fg=log(j)+3.0*e*j+1.5*f*j*j;
fh=log(h)-fb;
if(sbkfun==2)
fd=n;
fa=((1.0)/(1.0-4*n));
fb=-n/2.0;
fc=(1.0)/((1-4*n)*(1-4*n));
fg=(log(n)-log(1-4*n));
fh=-n/2;


if(sbkfun==3)
h=1.0-n;j=n/h;
fd=j;fa=j/n;
fb=(n+log(h))/n;
fc=1.0/pow(h,2.0);
fg=log(j);
fh=log(h)-fb;
if(sbkfun==4)
h=1.0-n;j=n/h;
fd=j;fa=j/n;
fb=-n/2.0-n*n/3.0-n*n*n/4.0;
fc=1.0/pow(h,2.0);
fg=log(j);
fh=log(h)-fb;
;
return;
/*Simultaneous linearequations */
void lequ()
double numx,numy,det,mmagn;
det=a11*a22-a21*a12;
numx=a12*a23-a13*a22;
numy=a21*a13-a23*a11;
solx=numx/det;soly=numy/det;
/*Root of a equation*/
void vroot()
```

```
double a,c,ww,wt,magn,vol,hk;
int l;
hk=1.0e-8;
for(a=0.10,c=1-hk,l=1;l<=36;l++)
n=(a+c)/2.0;
vol=g3*vab*avnu/n;
ek1=pres*vol/(gasc*temp);
func();
ww=(ek1-fa)/(7.0*fb);
magn=(wx-ww);
if(magn>0.0)a=n;
else c=n;
nx=n;
```

s