

THERMODYNAMIC BEHAVIOR OF TETRAHYDROFURON IN P-DIOXANE, METHYLCYCLOHEXANE AND CYCLOHEXANOL

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Abstract

The liquid state is intermediate in its properties of solid and gas. There are many attempts to develop a theory of liquid state based on simple consideration of molecular behavior like hard sphere having attractive forces as perturbative forces. The equation of state for Lennard-Jones fluid has been derived in the form of an expression for work, obtained from partition function through perturbation approach and found faithful reproduction of ultrasonic velocity and density data, theoretically at the given temperature. It has been applied to the binary liquid mixtures of tetrahydrofuron in p-dioxane, methylcyclohexane and cyclohexanol. There is a close agreement with experimental values. The thermodynamic picture built up in this formulation could be considered as a good representation of molecular cluster in liquid state.

Keywords: Ultrasonic velocity, tetrahydrofuron, p-dioxane, methylcyclohexane, cyclohexanol, adiabatic compressibility, molar volume

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1. INTRODUCTION

A large majority of liquid is complex and consists of polyatomic nonspherical molecule in which some additional molecular forces exist. Various equations of state [1-3] for hard sphere fluids have come forward. Bhatti [4] has reported ultrasonic investigation on acoustical parameters of liquid on a hard sphere model; Sharma [5] tested the validity of an equation of state for real fluids and several expressions for the various acoustical parameters to relate them with Gruneisen parameters. Gopalrao [6] formulated an equation of state for square well fluid and derived some thermodynamic parameters for it by extending Flory's [7] equation to mixture of unrelated type of molecules. Khasare [8-9] modified an equation of state; it has been observed that Khasare's theory is the extension of perturbation theories of the past. The equation of state for Lennard-Jones fluid has been derived in the form of an expression for work, obtained from partition function through perturbation approach and found faithful reproduction of ultrasonic velocity and density data, theoretically at the given temperature. The thermodynamic properties of liquids are intimately related to the intermolecular forces [10-11]. This dependence can be used for precise understanding of molecular cluster in the light of Lennard-Jones potential parameters. These parameters show the attractive and repulsive forces resulting in strong and weak association [12]. The present paper reports the results for application of the approach based on Khasare's model equation of state to the binary liquid mixture of tetrahydrofuron in p-dioxane, methylcyclohexane and cyclohexanol.

2. THEORETICAL AND COMPUTATIONAL APPROACH

Khasare's theory is a two scaling parameter model i.e. hard core diameter and depth of potential, the choice of the perturbing potential decides the nature of molecular interaction in binary liquid mixture. The earlier partition theories used an approach on obtaining expression of free energy functions. This faced with different problems of divergency and convergency and as such could not give better results. Better results could only be obtained when second order perturbation was applied. The deciding factor has been the level at which perturbation is applied. Khasare's [13-15] approach deals with the work done defined in scaled particle theory reference frame and expanding the work function using perturbation technique. The single order perturbation is found to be suitable for obtaining best results. The most important aspect of Khasare's theory is its provision of concentration dependence effect on basic parameter and therefore it is capable of predicting thermodynamic parameters i.e. ultrasonic velocity and density simultaneously for logical input parameters. The relations outlined are found to give transformation of thermodynamic data to interaction potential energy parameter, this transformation could be considered as applicable to construct of molecule cluster. Using the described model of equation of state corresponding to an assumed potential. The experimental data, i.e. ultrasonic velocity, density and thermal expansion coefficient were used with a suitable choice for the hard sphere diameter of a molecule or molecule aggregates in a pure liquid and a binary liquid mixture. Starting with a one mole of a real fluid as working substance the equation of state is written as,

$$\frac{\beta P}{\rho} = \frac{1}{(1-n)} + \frac{3En}{(1-n)^2} + \frac{3Fn^2}{(1-n)^3} + \frac{W}{n} [n + \log(1-n)]$$

And thermodynamic relation yield the following set of equation,

$$\frac{Mu^2}{YRT} = \frac{\{1+6E\left(\frac{n}{1-n}\right)+9F\left(\frac{n}{1-n}\right)^2\}}{(1-n)} - \frac{WN}{(1-n)}$$

$$\alpha t = \frac{\frac{1}{(1-n)} + \frac{3En}{(1-n)^2} + \frac{3Fn^2}{(1-n)^3}}{\frac{Mu^2}{YRT}}$$

Where

$$Y = 1 + \frac{R}{Cp} (\alpha t)^2 \frac{Mu^2}{RT}, \quad \alpha = \frac{1}{V} \left\{ \frac{dv}{dt} \right\}$$

$$E = \frac{3y_1y_2}{y_3}, \quad F = \frac{3y_2^2}{y_3^2}, \quad G = \sum_{j=1}^3 X_j (4\beta\epsilon_j) \frac{4\pi R_j^3}{3}$$

$$W = \frac{G}{gy_3}, \quad y_n = \sum_{j=1}^2 X_j R_j^n, \quad g = \frac{4\pi}{3}, \quad \sigma = R_j,$$

$$n = g\rho y_3, \quad \rho = \frac{N}{V}, \quad X_j = \frac{N_j}{N} = \text{mole fraction},$$

For calculating the molecular cluster size, one has to assume that, λ -monomers from homomolecular cluster. These may be assumed, in a first order of approximation to have analogues. Molecular weight which is λ -times the molar volume for a cluster, and thus λ -times the specific heat at constant pressure at monomer. However the density does not depend upon the scaling factor λ as,

$$\text{Density} = \frac{\lambda \text{ molecular weight of monomer}}{\lambda \text{ molecular volume of monomer}}$$

The observed thermodynamic parameters such as $\frac{Mu^2}{YRT}$ and $\frac{Mu^2\alpha t}{YRT}$ of two components in the binary mixture has been given as input data to calculate the value of potential parameter σ_1, ϵ_1 , and σ_2, ϵ_2 for the two component liquids. The only variable factor is the assumed molecular weight in the liquid state. In case the value of ϵ turns out to be negative, then one has to use an integral

value of molecular weight such that ϵ become positive. In a liquid mixture the parameters for one component liquid molecule are perturbed in the presence of other component. Hence the corrections are applied in the form of the following set of equations, employing minimum number of interaction parameter.

$$V_1^c = V_1 [1 + \alpha_1 X(1-X)], \quad [CP]_1 = [CP]_1 [1 + d_2 x(1-x)]$$

$$\sigma_1^c = \sigma_1 [1 + b_1 x(1-x)], \quad \epsilon_1^c = \epsilon_1 [1 + c_1 x(1-x)]$$

$$V_2^c = V_2 [1 + \alpha_2 X(1-X)], \quad [CP]_2 = [CP]_2 [1 + d_2 x(1-x)]$$

$$\sigma_2^c = \sigma_2 [1 + b_2 x(1-x)], \quad \epsilon_2^c = \epsilon_2 [1 + c_2 x(1-x)]$$

$$\text{And, } V = x_1 V_1^c + X_2 V_2^c$$

$$V = (1-X)V_1 + X_2 V_2 + (1-X)x[A+Bx]$$

$$x_1 = 1-x; \quad X_2 = x; \quad q_2 = \frac{A}{V_1}; \quad a_1 = \frac{(A+B)}{V_2}$$

Where the subscript 1,2 denote the component molecules in the binary liquid mixtures, and a, b, c and d are the minimum numbers of interaction parameters in the mixture corresponding to molar volume V, a hard core diameter σ , a depth of minimum potential ϵ , and specific heat CP respectively while x is the mole fraction. These corrected values of interaction parameters have been used to generate thermodynamic parameters in pure liquids & binary liquid mixture. In case the calculated value do not match with those of experimental ones, then one had to change the value of molecular weight by selecting the value of scaling factor λ in equation (A) the integral value of λ denote the state of molecule, namely monomeric, dimeric, trimetric etc. A computer program developed to generate theoretical thermodynamic parameters for very small concentration ranges to 0.1 to 0.2, 0.2 to 0.3, 0.3 to 0.4, ... 0.9 to 1.0 of the two pure liquid component in a given binary liquid mixture of the two liquids.

3. EXPERIMENTAL DETAILS

The experimental data evolved in the laboratory was used for the present theoretical investigation. The liquid of tetrahydrofuron, cyclohexane, methylcyclohexane and methyl alcohol were analar grade & redistilled before use. The binary mixture of different mole fraction of two components in system tetrahydrofuron -p-dioxane, tetrahydrofuron - methylcyclohexane, tetrahydrofuron-cyclohexanol were prepared Immediately before use. The velocity of ultrasonic waves (u) at a frequency of 2MHz and density (ρ) in these binary liquids mixtures were measured by employing Ultrasonic interferometer and the hydrostatic sinker method in the temperature range 10-40°C and ultra Thermostat U-10 min of the samples constant to 0.1°C. The accuracy of one part in 10⁴ in the velocity and one part in 10⁴ in the density measurement is achieved. The variation of u and ρ in this mixtures were found to be linear with the temperature and hence method of least squares was applied and the values of u and ρ at different temperatures were calculated from the equation

$$u = u_0 + [du/dT]_{T=0} \cdot T, \quad \rho = \rho_0 + [d\rho/dT]_{T=0} \cdot T$$

The Cp value used for the calculation were taken from the literature [16-19]

4. RESULTS OF THEORETICAL INVESTIGATION

The result of ultrasonic velocity (U) density (ρ) depth of minimum potential for the mixture ($\beta\epsilon_{AB}$) the depth of minimum potential of liquid component A presence of liquid component B ($\beta\epsilon_{AA}$), the depth of minimum potential of liquid component B in presence of liquid component A ($\beta\epsilon_{BB}$) the hard sphere diameter of liquid component A in presence of liquid component B (σ_{AA}) the hard sphere diameter of component B in presence of liquid A (σ_{BB}) and

the packing fraction (n) at temperature 303.15°K employing the Khasare's theory on the basis of model equation of state for fluid mixture have been presented in table 1,2,and 3 for the respective binary liquid mixture system the value of experimental velocities and densities of these binary liquid mixture system have also been presented in table 1,2,and 3 for comparison with theoretically evaluate values at same temperature while the value of u & ρ are obtained at mole fraction ratio of 0.1,0.2,0.3.....1.0 the value parameter $\beta\epsilon_{AB}$, $\beta\epsilon_{AA}$, σ_{AA} , σ_{BB} have been obtained at mole fraction 0.05 ,0.15,0.25.....0.95 respectively the input parameter required for evaluating above thermodynamic data has been given in table 4.The variation of $\beta\epsilon_{AB}$, $\beta\epsilon_{AA}$, σ_{AA} , σ_{BB} verses molar concentration of two liquid component (C_m) in binary liquid mixture has been graphically presented in Fig 1 to 9.

4.1 Tetrahydrofuron + p-dioxane

In the system tetrahydrofuron +p-dioxane through THF is known to be more associative , the variation of potential parameter (Fig1-3) versus C_m in this mixture shows almost negligible molecular interaction between two molecules, this may be due to strength of homomolecular i.e. AA,BB and heteromolecular AB interaction being almost equal . A peak in $\beta\epsilon_{AA}$, σ_{AA} and deep in $\beta\epsilon_{BB}$, σ_{BB} would therefore indicate a partial loosening of p-dioxane cluster and THF molecules being consoled in the enlarge p-dioxane clusters.

4.2 Tetrahydrofuron+ methylcyclohexane and Tetrahydrofuron + cyclohexanol

The variation of potential parameter versus C_m (Fig 4-9) shows the presence of homomolecular AB interaction in this mixture. It appears that the volumes of the mixtures are mainly controlled by the volumes of the methylcyclohexane and cyclohexanol molecules which are appreciably larger as compared to those of tetrahydrofuron molecules it is worth while noting that the charge density in the ring decreases in the order methylcyclohexane and cyclohexanol . Thus this shows that AB interaction may be due to a ring –ring interaction only.

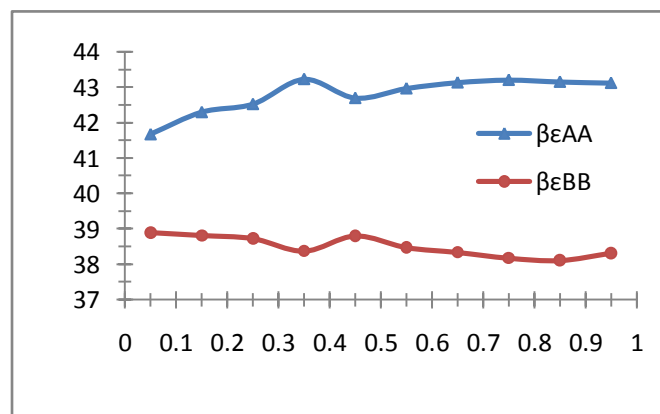


Fig 1: variation of $\beta\epsilon_{AA}$ & $\beta\epsilon_{BB}$ versus C_m in Tetrahydrofuron+p-dioxane

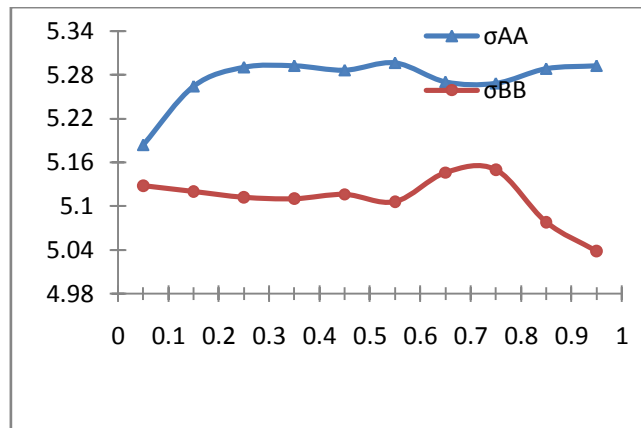


Fig 2: variation of σ_{AA} & σ_{BB} versus C_m in Tetrahydrofuron+p-dioxane

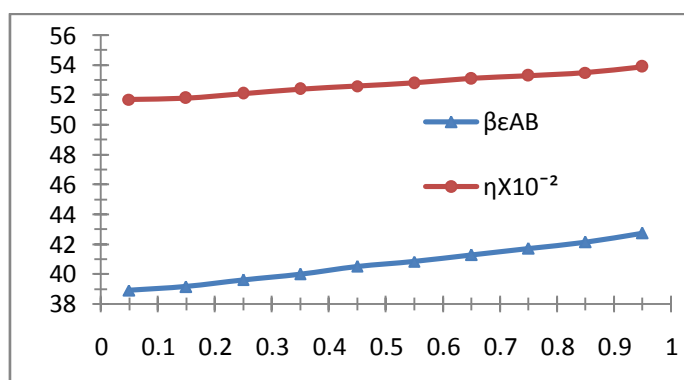


Fig 3: variation of $\beta\epsilon_{AB}$ & η versus C_m in Tetrahydrofuron+p-dioxane

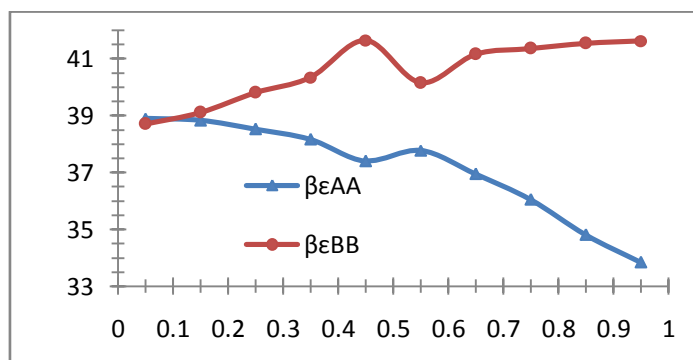


Fig 4: variation of $\beta\epsilon_{AA}$ & $\beta\epsilon_{BB}$ versus C_m in Tetrahydrofuron+methylcyclohexane

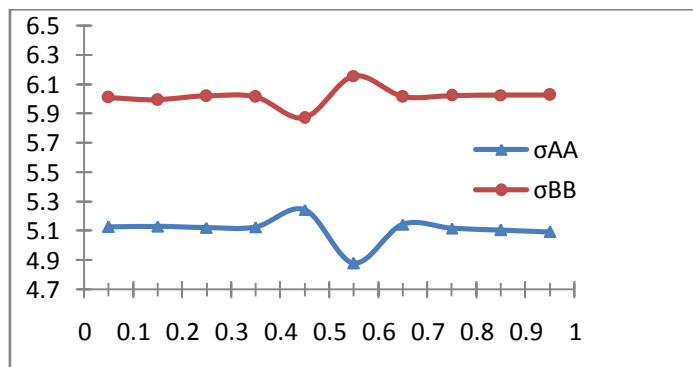


Fig 5: variation of σ_{AA} & σ_{BB} versus C_m in Tetrahydrofuron+methylcyclohexane

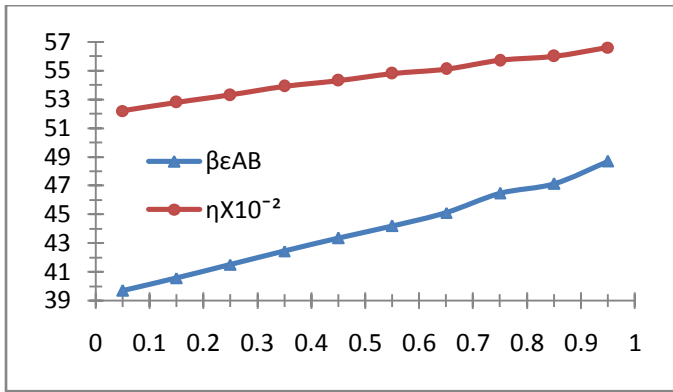


Fig 6: variation of $\beta\epsilon_{AB}$ & η versus C_m in Tetrahydrofuron+methylcyclohexane

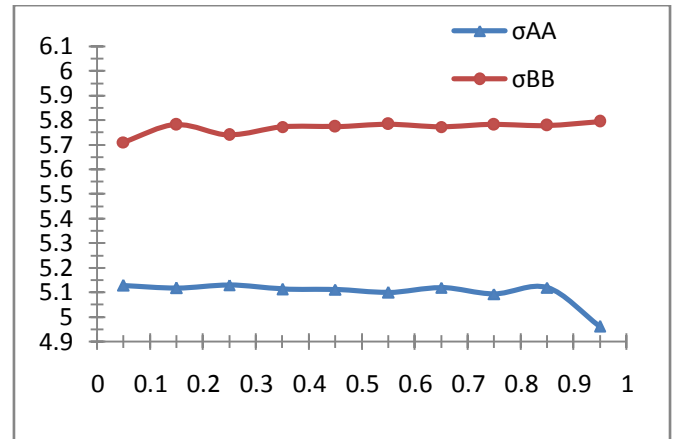


Fig 8: variation of σ_{AA} & σ_{BB} versus C_m in Tetrahydrofuron+cyclohexane

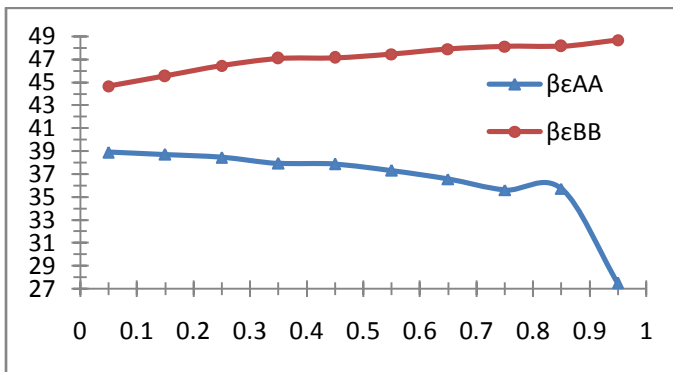


Fig 7: variation of $\beta\epsilon_{AA}$ & $\beta\epsilon_{BB}$ versus C_m in Tetrahydrofuron+cyclohexane

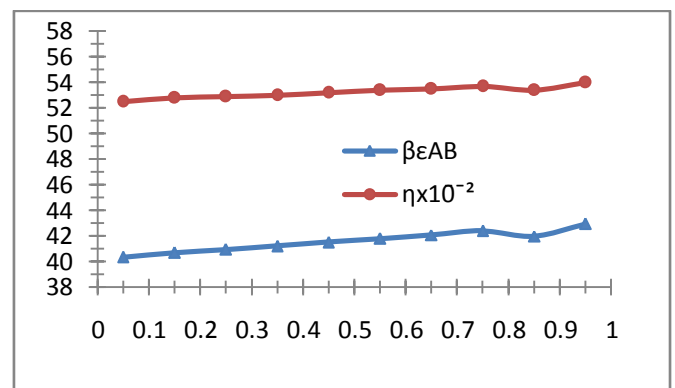


Fig 9: variation of $\beta\epsilon_{AB}$ & η versus C_m in Tetrahydrofuron+cyclohexane

Table 1: the values of experimentally measured u.s.velocity [u_{expt}] and density [ρ_{expt}] and theoretically calculated parameters U_{SBK} , ρ_{SBK} and corresponding reduced depth of potential, for mixture [$\beta\epsilon_{AB}$] and individual liquid component in presence of the other [$\beta\epsilon_{AA}$, $\beta\epsilon_{BB}$], hard sphere diameter for the individual liquid component molecules in presence of the other [σ_{AA} , σ_{BB}] at temperature 303.15^oK. {u x cm.se^cl⁻¹; ρ x gm.cc⁻¹; σ x 10⁸cm}

Table1: Tetrahydrofuron+p-dioxane

C_m	u_{expt}	u_{SBK}	ρ_{expt}	ρ_{SBK}	$\beta\epsilon_{AB}$	$\beta\epsilon_{AA}$	$\beta\epsilon_{BB}$	σ_{AA}	σ_{BB}	η
0.00	1255.2	1255.29	0.8759	0.8759						
0.05					38.906	41.680	38.906	5.184	5.128	0.517
0.10	1255.2	1255.18	0.8932	0.8932						
0.15					39.157	42.303	38.824	5.264	5.120	0.518
0.20	1260.4	1260.39	0.9130	0.9130						
0.25					39.620	42.530	38.736	5.290	5.112	0.521
0.30	1265.6	1265.60	0.9261	0.9261						
0.35					39.996	43.234	38.381	5.292	5.110	0.524
0.40	1275.9	1275.91	0.9410	0.9410						
0.45					40.507	42.701	38.811	5.286	5.116	0.526
0.50	1280.3	1280.25	0.9529	0.9529						
0.55					40.841	42.972	38.482	5.296	5.106	0.528
0.60	1287.6	1287.57	0.9661	0.9661						
0.65					41.295	43.139	38.345	5.270	5.146	0.531

0.70	1295.0	1294.99	0.9809	0.9809						
0.75					41.709	43.211	38.182	5.268	5.150	0.533
0.80	1303.4	1303.41	0.9970	0.9970						
0.85					42.155	43.158	38.116	5.288	5.078	0.535
0.90	1313.3	1313.31	1.0120	1.0120						
0.95					42.749	43.126	38.324	5.292	5.038	0.539
1.00	1324.0	1323.61	1.0145	1.0145						

Table 2: Tetrahydrofuron+methylcyclohexane

Cm	u _{expt}	u _{SBK}	□ _{expt}	□ _{SBK}	β _{AB}	β _{AA}	β _{BB}	□ _{AA}	□ _{BB}	η
0.05					38.874	38.906	38.713	5.128	6.010	0.518
0.10	1236.2	1236.17	0.8553	0.8553						
0.15					38.912	38.833	39.117	5.130	6.994	0.519
0.20	1223.5	1223.46	0.8424	0.8424						
0.25					39.061	38.530	39.816	5.122	6.020	0.521
0.30	1212.7	1212.73	0.8266	0.8266						
0.35					39.297	38.174	40.345	5.126	6.014	0.523
0.40	1205.6	1205.62	0.8144	0.8144						
0.45					39.836	37.408	41.654	5.244	6.872	0.524
0.50	1206.2	1206.21	0.8157	0.8157						
0.55					39.519	37.779	40.162	4.88	6.156	0.527
0.60	1196.1	1196.13	0.7920	0.7920						
0.65					40.273	36.949	41.171	5.144	6.016	0.527
0.70	1191.3	1191.34	0.7813	0.7813						
0.75					40.637	36.055	41.369	5.118	6.024	0.529
0.80	1188.9	1188.87	0.7728	0.7728						
0.85					41.601	34.810	41.554	5.106	6.026	0.530
0.90	1188.7	1188.72	0.7662	0.7662						
0.95					41.631	33.845	41.631	5.094	6.028	0.533
1.00	1189.0	1188.99	0.7560	0.7560						

Table 3: Tetrahydrofuron+cyclohexanol

Cm	u _{expt}	u _{SBK}	□ _{expt}	□ _{SBK}	β _{AB}	β _{AA}	β _{BB}	□ _{AA}	□ _{BB}	η
0.00	1255.2	1255.24	0.8759	0.8759						
0.05					39.687	38.906	44.660	5.128	5.710	0.522
0.10	1270.1	1270.07	0.8870	0.8870						
0.15					40.560	38.704	45.544	5.118	5.782	0.528
0.20	1289.5	1289.54	0.8936	0.8936						
0.25					41.496	38.458	46.459	5.130	5.740	0.533
0.30	1309.2	1309.24	0.9029	0.9029						
0.35					42.433	37.940	47.097	5.114	5.772	0.539
0.40	1330.5	1300.47	0.9097	0.9097						
0.45					43.350	37.870	47.153	5.112	5.774	0.543
0.50	1348.4	1348.35	0.9154	0.9154						
0.55					44.196	37.314	47.460	5.100	5.784	0.548
0.60	1364.5	1364.46	0.9193	0.9193						
0.65					45.108	36.562	47.911	5.120	5.772	0.551
0.70	1381.6	1381.55	0.9247	0.9247						
0.75					46.467	35.612	48.133	5.094	5.782	0.557
0.80	1406.5	1406.45	0.9301	0.9301						
0.85					47.135	35.726	48.156	5.120	5.778	0.560

0.90	1416.9	1416.85	0.9333	0.9333						
0.95					48.682	27.480	48.682	4.962	5.794	0.566
1.00	1451.5	1451.51	0.9338	0.9338						

Table 4: some physical parameters (input data) for pure liquids at 303.15K

Liquids	Molecular Weight	Density ρ Kg-m ³	U.S. Velocity m/s	β	α^0
Tetrahydrofuron	72.00	0.8759	1255.2	39.16	5.146
p-dioxane	88.11	1.0145	1324.0	42.85	5.291
Methylcyclohexane	98.00	0.7560	1189.0	41.41	5.575
Cyclohexanol	101.16	0.9338	1451.5	48.68	5.782

5. CONCLUSIONS

In the system tetrahydrofuron +p-dioxane shows almost negligible molecular interaction between two molecules, this may be due to strength of homomolecular i.e. AA, BB and heteromolecular AB interaction being almost equal. In the systems tetrahydrofuron+ methylcyclohexane and Tetrahydrofuron + cyclohexanol shows the presence of homomolecular AB interaction in this mixture may be due to a ring –ring interaction only. The Khasare's theory is capable of predicting thermodynamic parameters i.e. ultrasonic velocity and density simultaneously for logical input parameters at different concentration in variety of binary liquid mixtures having weak as well as strong intermolecular AB interaction to high degree of accuracy at a given temperature.

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