An accurate representation of molecular clusters in liquid mixtures using Khasare's equation of state

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ABSTRACT

The equation of state has been applied to the binary liquid mixture system of Cinnamaldehyde in methanol , p- dioxane & cyclohexane. It has been discussed in the domain of Khasare's theory.It is observed that there is close agreement with experimental one. The thermodynamic picture built up in this formulation could be consider as a good representation of molecular cluster in liquid state.

Keyword: The Khasare's equation of state , binary liquid mixture, Cinnamaldehyde, methanol , cyclohexane, p- dioxane, compressibility, molar volume.

INTRODUCTION

In recent year many attempts have been mode [1-3] to study molecular interactions in pure and binary liquid mixtures and various [4-5] equation of state for hard sphere fluid have come forward. Bhatti[6] has made ultrasonic study and calculated acoustical parameter of liquid and hard sphere model . Sharma [7] tested the validity of an equation of state of real fluids and derived the expressions for various acoustical parameter to relate them with Gruneisen parameter . Gopala Rao [8] formulated an equation for a square well fluid and obtained some thermodynamic parameters by extending the flory's equation to mixtures of unrelated type of molecule .Subensan[9] calculated excess enthalphy, activation energy of viscous flow and found experimental results in good agreement suggesting that flory's equation could be extended to mixtures of unrelated type. Khasare's theory has been tested by M.Kalidas [10-11] & et.al , to explain the properties of pure liquids, binary liquid and ternary liquid mixtures. Recently Khasare[12-16] developed an equation of state and found close agreement with computer simulation results. The present paper reports the results of the application of the approach based on Khasare's[17] model equation of state to the binary liquid mixture system of Cinnamaldehyde in methanol , p- dioxane & cyclohexane .

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2. Fomulation of model fluid mixture :

The precise picture of active molecular aggregate such as dimmer , trimer etc. is expressed in a generalized manner in well known thermodynamic relation. These are described using model equation of state corresponding to assumed potential . The experimental data viz ultrasonic velocity (u) , density (ρ) and expansion coefficient (αare used with suitable choice of hard sphere diameter of molecule or molecular aggregates regarding the size of the molecule in pure liquid and liquid mixtures.

Starting with one mole of real fluid as a working substance , the equation of state may be written as,

$$PV / RT = 1 / (1-\eta) + 3 e \eta / (1-\eta)^2 + 3 f \eta^2 / (1-\eta)^3 + 7w_x [\eta + \log(1-\eta)] / \eta \ldots\ldots.1.$$

$$e = r_{ab} \, s_{ab} / v_{ab} \; ; \quad f = s^3_{ab} / v_{ab} \; ; .$$

$$w_x = (w_v + 3 w_s \, r_{ab} + 3 w_r \, s_{ab}) / (7 v_{ab}) = \beta\varepsilon_i.$$

Here we have microscopic additive rules for binary liquid mixture as follows;

$$r_{ab} = \Sigma x_i \, R_i \, , \quad s_{ab} = \Sigma x_i \, R_i^2 \; \& \quad v_{ab} = \Sigma x_i \, R_i^3 \; ;$$

$$w_r = \Sigma x_i \, \beta \, \varepsilon_i \, R_i \, , \quad w_s = \Sigma x_i \, \beta \, \varepsilon_i \, R_i^{2,} \; \& \quad w_v = \Sigma x_i \, \beta \, \varepsilon_i \, R_i^3 \; ;$$

$$2R_i = \sigma, \quad w_x = \beta\varepsilon, \text{ and } (\sigma , \varepsilon) \text{ are the potential parameter ;}$$

$$\eta = (v_{ab} \, N_A) / V.$$

Where V_{ab} , N_A and V are the hard sphere volume, avagradro's and molar volume (bulk volume), η is space filling ratio (model parameter–1) and, $w_x = \beta\varepsilon =$ Reduced depth of potential (model parameter–2).

Now related thermodynamic equation can be obtained as.,

$$Mu^2/\gamma RT = 1/(1-\eta)^2 + 6 e \eta / (1-\eta)^3 + 9 f \eta^2 / (1-\eta)^4 - 7 w_x \eta / (1-\eta) \ldots\ldots\ldots.2$$

Where M is molecular weight , u is the u.s. velocity, γ is the ratio of specific heat (for liquid state $\gamma = 1.3$)for a given value of c_P , R is the universal gas constant and T is the temperature.

$$Mu^2 \propto /\gamma R = 1 / (1-\eta) + 3 e \eta / (1-\eta)^2 + 3 f \eta^2 / (1-\eta)^3 \ldots\ldots\ldots\ldots \ldots 3$$

Where, the thermodynamic variable α is the volume expansion coefficient

Above equation shows different variables such as mean radius of curvature , surface area and hard core volume etc. are additive.

For calculating molecular cluster size , one has to assume that , λ times monomers are forming homo-molecular cluster . These may be assumed as in first order of approximation of having analog molecular weight. However density does not depend upon the scaling factor λ as,

$$\text{Density } (\rho) = \frac{\lambda * \text{molecular weight of monomer}}{\lambda * \text{molecular volume of monomer}} \quad ....4$$

3. Computational Aspect.

The observed thermodynamic parameter such as , $(Mu^2/\gamma RT)$ and $(Mu^2\alpha T/\gamma RT)$ of the two components in the binary mixture can be given as in put data to calculated the values of potential parameters for the two component liquids. The only variable factor in liquid is the assumed molecular weight. In case the value of ε comes to be negative , then one has to used integral value of molecular weight , such that ε becomes positive . In the liquid mixture the potential parameters for one component molecular clusters gets perturbed in the presence of other component . Hence the correction[12] are applied in the form of the following set of equation employing minimum numbers of interaction parameters (concentration dependent concepts).

$$v^c_i = v_i [1+ a_i \ x \ (1\text{-}x)] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..5$$

Where v^c_i for corrected molar volume (perturbed) and v_i is for uncorrected molar volume (unperturbed) for i^{th} species. Similarly for model parameter-1, R^c_i is the corrected mean radius of curvature for hard core parameter and R_i is unperturbed mean radius of curvature for i^{th} species. Hence we have,

$$.R^c_i = R_i \ [1+ b_i \ \ x \ (1\text{-}x]; \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots6$$

$$\text{and } \varepsilon^c_i = \varepsilon_i [1+c_i \ x(1\text{-}x)] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 7$$

Where ε^c_i is the perturbed model parameter–2 (depth of minimum potential parameter) , a_i, b_i and c_i are minimum number of interaction parameters corresponding to molar volume (v_i) , hard core diameter ($2R_i$) and depth of minimum potential (ε_l) & the x is mole fraction .Using the concept[12] of concentration dependant parameter for molar volume, we have,

$$v = x \ (v_1{}^c) + (1\text{-}x) \ v_2{}^c$$

$$= x \ [v_1 (1+a_1 x \ (1\text{-}x))] + (1\text{-}x) \ [v_2(1+a_2 \ x \ (1\text{-}x))] \ \ldots\ldots\ldots 8$$

Therefore we have expression for excess molar volume as ,

$$V_{excess} \ = x \ (1\text{-}x) \ [\ a_2 v_2 + (a_1 v_1 \text{-} a_2 v_2) \ x \ ]$$

$$= x \ (1\text{-}x) \ [\ A + Bx \ ] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.9$$

If, $\quad x_1 = \text{-} A / B = 1 / [\ 1 \text{-} (a_1 / a_2) \ (v_1 / v_2) \ ] \ \ldots\ldots\ \ldots\ldots\ldots\ldots.10$
then $V_{excess} = 0$.

Thus for cinnamaldehyde-methanol system, after substituting the values of interaction parameter a_1, a_2 and molar volume v_1, v_2, the value of x_1 from equation(10) comes out to be 0.017 .i.e. $0 < x < x_1$ and $x_1 < x < 1.0$, are the intervals where behavior of liquid mixtures is different .

Now, these corrected values of interaction parameter are used to generate thermodynamic parameter in liquid mixture. In case the calculated value do not match with those of experimental ones, then one has to select the new values of molecular weight by using the equation(4). Thus the integral value of λ denote the state of molecule viz. monomer , dimmer etc. and can be worked out easily.

4. Experimental Details.:-

The liquid cinnamaldehyde (solute), methanol, p-dioxane and cyclohexane (solvents) were of Analar grade and redistilled before use . The binary mixture of different mole fraction of the two components in systems cinnamaldehyde-methanol, cinnamaldehyde-p-dioxane (here after p-dioxane refered as dioxane only), and cinnamaldehyde-cyclohexane were prepared immediately before use. The velocity of ultrasonic wave (u) of frequency 10 MHz and density (ρ) in these mixtures were measured by employing Ultrasonic Time inetervelometer, UTI-10 (Innovative instruments , Hyderabad) , and hydrostalic sinker method in the temperature range $10\text{-}40^o$ C. Ultrathermostat U-10 maintained temperature of samples, constant to 0.1^o C . A specially designed[22] and fabricated double walled , metallic ultrasonic cell and glass cell along with 6-digit monopan balance permitted to achieve accuracy of 1 in 10^4 m/s in velocity and 1 in 10^4 gm in density measurement . The u and ρ in these mixture were found to be linear with temperature and hence method of least squares was applied and the values of u and ρ at different temperature were calculated from the equation.

$$u = u_o + \partial u / \partial T \mid_{T=0} \cdot T \text{ and } \rho = \rho_o + \partial \rho / \partial T \mid_{T=0} \cdot T$$

RESULT

The computational results of u ., ρ, ∞ and adiabatic compressibility β_a employing the new approach on the basis of model equation of state for fluid mixture are given in table 1 to 3 . Table - 4 contains the values of the outputs v, σ & ϵ. The values of percentage mean deviation of u , ρ , α,and β_a from observed values are given in table 1 to 3 . Table - 5 contain the values of theremodynamic parameter for pure liquids (inputs) at T= 303.15 ^{o} k . Table - 6 represent variation, of excess thermodynamic parameter % V^E & % β_a^E with . respect to composition (x) of the binary liquid mixtures, dioxane & Cinnamaldehyde, methanol-Cinnamaldehyde & cyclohexane-Cinnamaldehyde.

DISCUSSION

Form excess molar volume and excess adiabatic compressibility, which leads to following classification as given in the table. Accordingly broad classification of molecular interaction[20-21].

Sr.No.	β_a^E	V^E	Nature
1	Negative	Negative	Association
2	Positive	Positive	Dissociation
3	Negative	Positive	Ordering
4	Positive	Negative	Concealing

The thermodynamic properties of liquids intimately related to the inter molecular forces . This dependenance can be used for precise understanding of molecular cluster in the light of L-J. potential parameter viz.σ & ε. After the application of interaction parameters (a_1,a_2), (b_1,b_2) and (c_1,c_2) (Table–4) to,molar volume(v) , hard sphere diameter (σ) & depth of potential (ε) respectively , it is observed that values of measured parameters viz ultrasonic velocity (u), and density (ρ) and expansion coefficient (α) are reproduced accurately. This conclusively exhibits the validity of thermodynamic mixture built up in the formulations. This become evident, when different values such as 1,2, and etc. , are assigned to λ in equation(4), as such we find that the agreement between evaluated thermodynamic parameters and experimental values are very close for a particular numerical value of λ. For value λ =1, the formation of monomer in the mixture is indicated. While the existence of dimmer and trimer would be indicated for the values of λ =2 and λ =3 , etc. Another important aspect of this approach is that , the value of the interaction parameters $((a_1, a_2)$, (b_1, b_2) and (c_1, c_2) are directly related to molar volume , hard sphere diameter and depth of potential of liquid component in the mixture. Thus for example the value of $a_1 > a_2 > 0$ would imply the increase in the molar volume of the component-1 than component-2. Similarly we can relate the other interaction parameters to relatively increase or decrease in hard sphere diameter and depth of potential of two component in the mixture.

The potential energy parameter in the binary liquid mixture system Cinnamaldehyde–methanol , Cinnamaldehyde–dioxane and Cinnamaldehyde–cyclohexane shows the component Cinnamaldehyde to be the most tightly bound than methanol , dioxane and cyclohexane ,while the hard core diameter is appreciably larger than the component methanol but slightly smaller than dioxane and cyclohexane respectively.

The system Cinnamaldehyde – methanol ,
In this system the reduced energy parameter shows an increase in binding energy and hard core diameter of both the components ($c_1 > c_2 > 0$, $b_1 > b_2 > 0$) , the increase being greater for Cinnamaldehyde than methanol. The value of a_1 , a_2, A and B indicates a marginal contraction ($a_1 < 0$) and expansion ($a_2 > 0$) in bulk volume of methanol and Cinnamaldehyde molecule in the mixture . It further shows an overall contraction and expansion in molar volume of interacting molecular aggregate in the binary mixture in the composition range of ($0 < x < 0.017$) i.e. ordering in low concentration region and association in ($0.017 < x < 1.0$) respectively.

Cinnamaldehyde – dioxane system:
In this system the value of $c_1 < 0$, $c_2 < 0$ indicates a decrease in reduced binding energy of both the component in mixture than pure state value. The decrease being of the same order of magnitude . The value of $b_1 < 0$, shows a decrease and $b_2 > 0$, an increase in hard core diameter of both the component in mixture than pure state value. The value of $a_1 < 0$ indicates an expansion in bulk volume of component -dioxane and Cinnamaldehyde respectively. This along with the values of A and B shows and overall volume contraction of interacting molecular aggregates in the mixture over the complete composition range .

Cinnamaldehyde – cyclohexane system ,:
In this system, the reduced energy parameters shows the decrease binding energy of both the components in the mixture than pure state value, i.e. $c_1 < c_2 < 0$. This decrease being larger for component cyclohexane . The value of $b_1 < 0$ and $b_2 > 0$ shows, a decrease and increase in bulk volume of cyclohexane and Cinnamaldehyde respectively. The value of a_1, a_2 , A and B shows over all contraction in molar volume of interaction molecular aggregates in this mixture over the entire composition range .

The state of molecular cluster in liquid mixtures:
The percentege   mean deviation between the calculatd and observed values of ultrasonic velocity(u), density(ρ) , copressibility (β_a) and expansion coefficient(α) in all the system is very small for value of $\lambda = 3$ (trimer), for methanol , cyclohexane and dioxane ,while $\lambda = 1 \text{(monomer)}$ and 2(dimer) for Cinnamaldehyde in system cyclohexane–methanol , Cinnamaldehyde-dioxane and Cinnamaldehyde–cyclohexane respectively. This therefore conclusively exhibits the behavior of methanol , p-dioxane and cyclohexane in trimaric form while Cinnamaldehyde behaves in monomeric form in mixture with methanol and in dimeric form in the mixture with   cyclohexane and dioxane respectively .The earlier studies[18-19] have shown behavior of methonal in vapor and in acrolein as tetramer and dimmer , while the present investigation shows its trimeric behavior in the mixture.

As velocity of ultrasonic waves is a sensitive function of space filling factor , small changes in volume cause significant changes in velocity of ultrasonic waves . The volume of dioxane-Cinnamaldehyde liquid mixture depends upon the structural arrangement in liquid as well as on inter–molecular interactions . The forces between molecules and also their geometry would decide the structural arrangement . Thus geometry of molecules has a vital role in deciding the volume of liquid . In a binary liquid mixture of dioxane and   Cinnamaldehyde the shape of the molecule i.e. cluster geometric or macro geometric , would therefore predominantly decide an excess of molar volume. An increase in strength of dioxane- Cinnamaldehyde   , hetero molecular forces manifesting in a decrease in adiabatic   compressibility β_a of the mixture would tends to reduced the size of the cluster of dioxane , Cinnamaldehyde   and dioxane–Cinnamaldehyde, hence the decrease in total volume of the mixture .

Relative strength of interactions:
The variation both $\beta_a{}^E$ and V^E is non linear [22] with one minimum (Table –6). Such smooth variation with minimum at certain composition is known to indicate an attractive hetero-molecular dioxane–Cinnamaldehyde interaction , leading to association of the molecules . Pure liquids dioxane and Cinnamaldehyde suppose to exists in monomer , dimmer and trimmer etc. with , number of monomers > no. of dimmers > no.of. trimmers . Due to associative hetero-molecular, dioxane-Cinnamaldehyde interaction**,** the (dioxane–Cinnamaldehyde) liquid mixture can be imagined as ,(dioxane- cinnamaldehyde   a dimmer, dioxane–Cinnamaldehyde-Cinnamaldehyde , a trimmer and dioxane - dioxane-Cinnamaldehyde a trimmer etc.

Above association would occur due to the presence of an active sub group of p-dioxane i.e. lone pair of oxygen at 1 and 4th position in p-dioxane , which plays vital role in association mechanism and active subgroup of - CHO(aldehyde) in Cinnamaldehyde molecule . As minima is closer to higher concentration of p-dioxane , thus, p-dioxane –p-dioxane interaction is greater than Cinnamaldehyde - Cinnamaldehyde   interaction .

In the dioxane-Cinnamaldehyde system both $\beta_a{}^E$ and V^E are negative. Thus this system has more strength of interaction (large value of $\beta_a{}^E$ at x = 0.4). Therefore dioxane–Cinnamaldehyde interaction is stronger than dioxane- dioxane and Cinnamaldehyde-Cinnamaldehyde interaction . Since dip is concentrated on dioxane side of molar concentration , dioxane-dioxane interaction seems to be stronger than dioxane–Cinnamaldehyde and Cinnamaldehyde-Cinnamaldehyde interaction .

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Table – 1. Measured and theoretically evaluated value of u, ρ, β_a and α in Methanol - cinnamaldehyde at T = 303.15^0 K

		Observed					Theoretical		
x	u m/s	$\alpha*10^{-3}$	$\rho*10^3$ gmcm^{-3}	$\beta_{a*}10^{-12}$ cm^{2}dyne^{-1}		u m/s	$\alpha*10^{-3}$	$\rho*10^3$ gmcm^{-3}	β_a*10^{-12} cm^{2}dyne^{-1}
0.0	1086	1.183	0.7760	109		1086	1.183	0.7760	109
0.1	1110	1.793	0.7906	102		1076	1.536	0.7982	108
0.2	1130	1.850	0.8216	95		1102	1.913	0.8196	100
0.3	1155	2.850	0.8402	89		1159	2.236	0.8404	86
0.4	1188	2.170	0.8602	83		1221	2.420	0.8604	77
0.5	1205	2.320	0.8602	78		1254	2.424	0.8803	72
0.6	1230	2.322	0.9003	73		1256	2.474	0.9003	70
0.7	1260	2.042	0.9205	68		1257	2.031	0.9206	68
0.8	1295	2.071	0.9405	63		1274	1.757	0.9414	65
0.9	1335	2.099	0.9604	58		1314	1.491	0.9632	60
1.0	1375	1.253	0.9861	53		1375	1.253	0.9862	53

% deviation of u   =   2.8 %
% deviation of α. = 10.8 %
% deviation of ρ =   0.18 %
% deviation of β_a =   4.2 %

Table – 2. Measured and theoretically evaluated value of u ,ρ ,β_a and α in p-dioxan- cinnamaldehyde at T = 303.15^0 K

		Observed					Theoretical		
x	u m/s	$\alpha*10^{-3}$	$\rho*10^3$ gmcm^{-3}	$\beta_{a*}10^{-12}$ cm^{2}dyne^{-1}		u m/s	$\alpha*10^{-3}$	$\rho*10^3$ gmcm^{-3}	β_a*10^{-12} cm^{2}dyne^{-1}
0.0	1324	0.932	1.0270	58		1324	0.932	1.0270	58
0.1	1339	0.859	1.0269	54		1341	0. 857	1.0244	54
0.2	1349	0.853	1.0200	53		1351	0.847	1.0243	53
0.3	13 57	0.884	1.0256	53		1355	0.879	1.0256	53
0.4	1362	0.946	1.0250	52		1356	0.940	1.0272	52
0.5	13 67	1.014	1.0248	52		1359	1.019	1.0281	52
0.6	1370	1.069	1.0390	52		1365	1.105	1.0272	52
0.7	1373	1.191	1.0235	52		1375	1.184	1.0235	51
0.8	13 76	1.277	1.0227	51		1384	1.241	1.0160	51
0.9	1378	1.264	1.0222	51		1385	1.267	1.0037	51
1.0	1375	1.253	0.9860	53		1375	1.253	0.9862	53

% deviation of u   =   0.35 %
% deviation of α. =   0.53 %
% deviation of ρ =   0.99 %
% deviation of β_a =   0.41 %

In the methanol–Cinnamaldehyde and cyclohexane– Cinnamaldehyde system, $\beta_a^E < 0$ and $V^E > 0$. The observed negative β_a^E denote the decrease in adiabatic compressibility than observe one . This indicates the presence of hetero–molecular methanol-Cinnamaldehyde , cyclohexane–Cinnamaldehyde interaction in both the systems resulting in formation of cluster. . In methanol-Cinnamaldehyde , the dip concentrated towards methanol side indicates methanol-methanol interaction   is stronger than methanol-Cinnamaldehyde and Cinnamaldehyde– Cinnamaldehyde interaction.   In methanol active subgroup is - OH which plays important role in association . On the other hand in the system cyclohexane- Cinnamaldehyde the dip is

concentrated towords Cinnamaldehyde side , indicates Cinnamaldehyde- Cinnamaldehyde interaction is stronger than cyclohexane- Cinnamaldehyde and cyclohexane–cyclohexane interaction . In cyclohexane there is no chemical active group but its polar geometric has vital role for its association .

Table- 3. Measured and theoretically evaluated value of u, ρ, β_a and α in cyclohexane - cinnamaldehyde at T = 303.15^0 K

	Observed				Theoretical			
x	u m/s	$\alpha*10^{-3}$	$\rho*10^{3}$ gmcm^{-3}	$\beta_{a*}10^{-12}$ cm^{2}dyne^{-1}	u m/s	$\alpha*10^{-3}$	$\rho*10^{3}$ gmcm^{-3}	β_a*10^{-12} cm^{2}dyne^{-1}
0.0	1240	1.077	0.7723	84	1240	1.077	0.7722	81
0.1	1255	1.203	0.7691	79	1253	1.082	0.7961	80
0.2	1265	1.615	0.8107	77	1267	1.100	0.8214	75
0.3	1288	1.132	0.8477	71	1284	1.126	0.8417	71
0.4	1299	1.315	0.8707	68	1303	1.555	0.8743	67
0.5	1326	1.297	0.8962	63	1325	1.184	0.9004	63
0.6	1346	1.241	0.9214	59	1348	1.208	0.9252	59
0.7	1398	1.226	0.9473	56	1368	1.226	0.9473	56
0.8	1373	1.381	0.9605	55	1382	1.240	0.9657	54
0.9	1377	1.330	0.9974	52	1385	1.249	0.9791	53
1.0	1375	1.253	0.9862	53	1375	1.253	0.9862	53

% deviation of u = 0.26 %

% deviation of α. = 10.70 %

% deviation of ρ = 0.60 %

% deviation of β_a = 0.83 %

Table – 4. Values of relatives interaction parameters in cinnamaldehyde liquid. (Output)

System	v_1	v_2	σ_1	σ_2	$\in_1$	$\in_2$
Cinnamaldehyde -methanol	a_1 =-0.8110^{-4}	a_2= 0.0432	b_1= 4.71	b_2= 1.557	c_1= 0.076	c_2= 0.051
cinnamaldehyde -p-dioxane	a_1= -0.0705	a_2= 10.2281	b_1= -0.26	b_2= 0.527	c_1= -0.020	c_2= -0.048
cinnamaldehyde -Cyclohexane	a_1= -0.42910^{-3}	a_2= -0.1669	b_1 = -2.70	b_2 = 0.755	c_1= -0.028	c_2= - 0.295

Table – 5. Values of Thermodynamic parameters for pure liquids at T=303.15^{O}K

Liquids	u.m/s	$\alpha.10^{-3}$	$\rho.10^3$
Cinnamaldehyde	1375	1.253	0.9860
Methanol	1086	1.183	0.7760
p-Dioxane	1324	0.9320	1.0270
Cyclohexane	1240	1.077	0.7723

Table-6 Variation of excess thermodynamic parameters % V^E & %β_a^E with respect to composition (x) of p-dioxane- cinnamaldehyde, methanol- cinnamaldehyde & cyclohexane - cinnamaldehyde systems.

Mole	p-dioxane- cinnamaldehyde		methanol-cinnamaldehyde		cyclohexane-cinnamaldehyde	
x	% V^E	%β_a^E	% V^E	%β_a^E	% V^E	%β_a^E
0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.1	-0.18	-1.52	3.62	-2.65	0.54	-0.21
0.2	-0.29	-2.20	4.53	-4.52	0.95	-0.42
0.3	-0.35	-2.52	4.91	-6.63	1.32	-0.61
0.4	-0.42	-2.54	5.22	-6.71	1.35	-0.85
0.5	-0.40	-2.53	4.72	-5.62	1.36	-0.82
0.6	-0.38	-2.25	4.05	-4.51	1.22	-0.62
0.7	-0.30	-2.00	3.51	-4.05	1.15	-0.43
0.8	-0.28	-1.50	2.32	-2.82	0.86	-0.35
0.9	-0.20	-1.00	1.05	-1.24	0.56	-0.22
1.0	0.0	0.0	0.0	0.0	0.0	0.0
Nature	Association		Ordering		Ordering	

CONCLUSION

The theoretical approach outline earlier[12-16] and elaborated   in this paper is found to be applicable to the system investigated . The thermodynamic picture built up in formulation therefore could be considered as correct representation of molecular cluster . The important aspects of this representation is its capability to reproduce u.s. velocity data with added flexibility of reproducing density and expansion coefficient of liquid mixture to a high degree of accuracy . This representation of fresh approach towards understanding the thermodynamic picture and properties of liquid mixture seems to be quite new and fascinating .It is observed that   this approach is capable of predicting all experimental thermodynamic data for logical input parameters. The formulation of molecular cluster viz. weak monomer , dimmer in pure liquid state of constituent liquid molecule in binary liquid mixture can be predicted satisfactory. This is possible on the simple assumption that degree of association factor for a liquid is important parameter for reproducing experimental thermodynamic parameters.

The theory has added   provision of concentration dependent effect[12] on basic parameter which is not available in any other theory.

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