Thermoacoustical Excess Properties of Binary Liquid Mixtures — A Comparative Experimental and Theoretical Study

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Specific heat ratio (γ), pseudo-Grüneisen parameter (Γ), heat capacity (C_p) and effective Debye temperature (θ_D) for binary system of tetrahydrofuran with o-cresol and methanol respectively, were calculated using the experimentally measured densities, velocities and viscosities of the pure liquids and their mixtures over the whole composition range and at $T = 293, 303, 313$ K. The excess pseudo-Grüneisen parameter (Γ^E), excess molar isentropic compressibility (K_s^E) and excess acoustic impedance (Z^E) were also calculated. The excess deviation functions have been correlated using Redlich–Kister polynomial equation. The observed values of the excess parameters plotted against the mole fraction of tetrahydrofuran have been explained on the basis of intermolecular interaction suggesting strong interaction in tetrahydrofuran + o-cresol than in tetrahydrofuran + methanol. Partial molar isentropic compressibility at infinite dilution and their excess values were calculated for each component. Sanchez theory, Goldsach–Sarvas volume fraction statistics, Sudgen's relation, Flory–Patterson–Rastogi and Brock and Bird model were used with the Aurebach relation to compute theoretically the values of ultrasonic velocities at varying temperatures. The velocity deviations were estimated in terms of average percentage deviations. Internal pressure for both the systems were calculated theoretically and discussed on the basis of relative applicability of the models in theoretical estimations. The isothermal compressibility (k_T), for these binary mixtures were theoretically evaluated by using the Flory statistical theory and five hard sphere models and compared with the experimental values.

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1. Introduction

The present work is a continuation of systematic experimental studies on thermodynamic and transport properties of binary mixtures of tetrahydrofuran (THF) with o-cresol and methanol, as these solvents have important application in chemical industry and molecular technology.

Tetrahydrofuran is used as a solvent for polyvinyl chloride in printing inks, lacquers and adhesives, as well as an intermediate in the preparation of many industrial chemicals [1]. Tetrahydrofuran is an exceptionally useful solvent for reactions with organoalkali compounds [2].

o-cresol is mostly used as an intermediate for the production of pesticides, epoxy resins, dyes and pharmaceuticals, also as a component of disinfectants and cleaning agents. o-cresol is readily biodegradable and has a low bio- or geo-accumulation potential. In 90% of the uses, cresols are organic intermediates in manufacturing of phenolic and epoxy resins, plasticizers, herbicides, rubber and plastic antioxidants, dyes, deodorizing and odor-enhancing compounds, fragrances and pharmaceuticals [3].

Methanol, also known as methyl alcohol, carbinol, wood alcohol, wood naphtha or wood spirit, is a polar liquid at room temperature and is used as an antifreeze, solvent, fuel and as a denaturant for ethyl alcohol. It is also used for producing biodiesel via transesterification reaction. Methanol is a common laboratory solvent. The largest use of methanol by far, is in making other chemicals. About 40% of methanol is converted to formaldehyde and from there into products as diverse as plastics, plywood, paints, explosives and permanent press textiles.

The derived parameters such as specific heat ratio (γ), pseudo-Grüneisen parameter (Γ), heat capacity (C_p) and effective Debye temperature (θ_D) which can be estimated from the experimental data give more comprehensive information about the structural and interactional aspects of the mixture at the microscopic level. The values of excess parameters have been estimated to study the possibilities and extent of the disruption of self association among the methanol and o-cresol molecules and the breaking of dipole–dipole interaction in THF along with hydrogen bonding between oxygen of THF molecule and hydrogen of –OH group of the alcohol and cresol molecule in the binary mixtures of THF with methanol and o-cresol, respectively. The estimated values of excess pseudo-Grüneisen parameter (Γ^E), excess molar isentropic compressibility (K_s^E) and excess acoustic impedance (Z^E) are fitted into Redlick–Kister type polynomial equation to estimate the binary coefficient and standard deviations.

The study of ultrasonic velocity in liquids is well established forexamining the nature of intermolecular and

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intramolecular interactions in liquid system. Therefore, the ultrasonic measurements in liquids and its variation with temperature provide detailed information regarding the properties of the medium such as absorption, compressibility, intermolecular forces, molecular interactions, chemical structure and the energies of the molecules in motion. Here ultrasonic velocities of liquid mixtures of tetrahydrofuran with o-cresol and methanol have been theoretically estimated by Aurebach relation in which the surface tension values have been theoretically calculated by various empirical, semiempirical and statistical models and theories such as Sanchez theory, Goldsach–Sarvas volume fraction statistics, Sudgen's relation, Flory–Patterson–Rastogi model and Brock and Bird model and are compared with the experimental values. The results have been discussed on the basis of average percentage deviation.

Internal pressure is the fundamental liquid property, which is the resultant of forces of attraction and repulsion between the constituents of liquids. As degree of cohesion differs from liquid to liquid, internal pressure provides useful information about the molecular interactions in the liquid systems. In the present work, various relations for estimation of internal pressure of liquids and liquid mixtures, e.g. thermodynamic relation, relation using empirical equations for α and k_T, relation based upon Buehler–Hirschfelder–Curtiss equation of state and relation based upon Flory statistical theory have been used. Thermodynamic relation has been considered as an experimental method because the parameters used in the equation have been calculated with the help of experimental values of density. Estimated values of internal pressure have been analyzed in light of various theories involved and compared in terms of average percentage deviation.

The isothermal compressibility (k_T) of these binary mixtures were theoretically calculated in terms of pure components data by using Flory's theory and hard sphere models and the results were compared with the experimental values in terms of average percentage deviations.

2. Theoretical analysis

The previously measured experimental values of ρ, u and η [4] were used to calculate the values of different parameters.

2.1. Thermoacoustical parameters

The effective Debye temperature θ_D can be evaluated by using the following expression [5]:

$$\theta_D = \frac{h}{k} \left\{ \frac{9N}{4\pi V_m \left[\left(\frac{1}{u_l^3} + \frac{2}{u_t^3} \right) \right]} \right\}^{1/3}, \tag{1}$$

where u_l and u_t are the propagation velocities for longitudinal and transverse modes, respectively. V_m is the molar volume and h, k and N are the Planck constant, Boltzmann's constant and Avogadro's number, respectively.

The two wave velocities may be expressed in terms of density (ρ_m), the instantaneous adiabatic compressibility (k_s) and Poisson's ratio (σ) for liquids exhibiting the quasi-crystalline properties, as follows:

$$\frac{1}{u_l^3} + \frac{2}{u_t^3} = (k_s \rho_m)^{3/2} \left\{ \left[\frac{1+\sigma}{3(1-\sigma)} \right]^{3/2} \right.$$
$$\left. + 2 \left[\frac{2(1+\sigma)}{3(1-2\sigma)} \right]^{3/2} \right\}, \tag{2}$$

where

$$k_s = k_T - \frac{T\alpha^2 V_m}{C_p} \tag{3}$$

and α, k_T, C_P represent the coefficient of linear expansion, the isothermal compressibility and the specific heat at constant pressure, respectively.

Poisson's ratio can be obtained from the knowledge of the bulk modulus K_T and the modulus of rigidity G_T, which arise from the change in lattice spacing corresponding to the solid-like character of the liquid. The Poisson ratio [6, 7] is given by

$$\sigma = \frac{3A - 2}{6A + 2} \tag{4}$$

and

$$A = \frac{K_T}{G_T} = \frac{4}{3\gamma}, \tag{5}$$

where γ is specific heat ratio defined as

$$\gamma = \frac{k_T}{k_s}. \tag{6}$$

The pseudo-Grüneisen parameter has been defined in terms of specific heat ratio as

$$\Gamma = \frac{\gamma - 1}{\alpha T}. \tag{7}$$

2.2. Excess parameters

In order to substantiate the presence of interaction between the molecules, it is essential to study the excess parameters. Excess parameters, associated with a liquid mixture, are a quantitative measure of deviation in the behavior of the liquid mixture from ideality. The literature survey [8–10] reveals that most common way to evaluate the excess value of a given thermodynamic parameter is to use the equation

$$A^E = A_{\text{expt}} - \sum_i x_i A_i, \tag{8}$$

where symbols have their usual meaning.

2.3. Redlich–Kister polynomial equation

The composition dependences of the excess properties are correlated by the Redlich–Kister polynomial equation [11]:

$$Y^E = x_1 (1 - x_1) \sum_{i=1}^{5} a_i (2x_1 - 1)^{i-1}. \tag{9}$$

The values of the coefficient a_i were calculated by method of least squares along with the standard deviation $\sigma(Y^E)$. The coefficients a_i are adjustable parameters for a better fit of the excess functions.

The standard deviation values were obtained from relation

$$\sigma\left(Y^{\mathrm{E}}\right) = \left[\frac{\sum_{i=1}^{n}\left(Y_{\mathrm{expt}}^{\mathrm{E}} - Y_{\mathrm{cal}}^{\mathrm{E}}\right)^2}{n - p}\right]^{1/2}, \qquad (10)$$

where n is the number of experimental points, p is the number of parameters, Y_{expt} and Y_{cal} are the experimental and calculated parameters, respectively.

2.4. Partial molar isentropic compressibility

Molar isentropic compressibility was calculated by the relation

$$K_{\mathrm{s}} = -\left(\partial V/\partial P\right)_{\mathrm{s}} = V_{\mathrm{m}}k_{\mathrm{s}}. \qquad (11)$$

The partial molar compressibilities $\overline{K_{\mathrm{m},1}}$ of THF and $\overline{K_{\mathrm{m},2}}$ of o-cresol and methanol in these mixtures were calculated adopting the approach used earlier [12, 13] for the calculation of partial molar volumes. $\overline{K_{\mathrm{m},1}}$ and $\overline{K_{\mathrm{m},2}}$ are evaluated using the following relations:

$$\overline{K_{\mathrm{m},1}} = K_{\mathrm{s}}^{\mathrm{E}} + K_{\mathrm{m},1}^{*} + x_2\left(\frac{\partial K_{\mathrm{s}}^{\mathrm{E}}}{\partial x_1}\right)_{T,p}, \qquad (12)$$

$$\overline{K_{\mathrm{m},2}} = K_{\mathrm{s}}^{\mathrm{E}} + K_{\mathrm{m},2}^{*} - x_1\left(\frac{\partial K_{\mathrm{s}}^{\mathrm{E}}}{\partial x_1}\right)_{T,P}, \qquad (13)$$

where $K_{\mathrm{m},1}^{*}$ and $K_{\mathrm{m},2}^{*}$ are the molar isentropic compressibilities of pure components THF and o-cresol or methanol, respectively.

We are interested to evaluate the partial molar isentropic compressibility of THF at infinite dilution $(x_1 = 0)$ in o-cresol and methanol, respectively, and the partial molar isentropic compressibilities of o-cresol and methanol at infinite dilution $(x_2 = 0)$ in THF. Therefore, $\overline{K_{\mathrm{m},1}^{0}}$ is obtained by setting $x_1 = 0$, which leads to

$$\overline{K_{\mathrm{m},1}^{0}} = K_{\mathrm{m},1}^{*} + \sum_{i=0}^{n} a_i\left(-1\right)^{i}. \qquad (14)$$

Similarly, setting $x_2 = 0$, leads to

$$\overline{K_{\mathrm{m},2}^{0}} = K_{\mathrm{m},2}^{*} + \sum_{i=0}^{n} a_i. \qquad (15)$$

In Eqs. (14) and (15), $\overline{K_{\mathrm{m},1}^{0}}$ and $\overline{K_{\mathrm{m},2}^{0}}$ represent the partial molar isentropic compressibilities of THF at infinite dilution in o-cresol or methanol and the partial molar compressibilities of o-cresol or methanol at infinite dilution in THF, respectively.

Excess partial molar isentropic compressibilities at infinite dilution $\overline{K_{\mathrm{m},i}^{E,\infty}}$ for each component in binary liquid mixtures were evaluated through relations

$$\overline{K_{\mathrm{m},1}^{E,\infty}} = \overline{K_{\mathrm{m},1}^{0}} - K_{\mathrm{m},1}^{*}, \qquad (16)$$

$$\overline{K_{\mathrm{m},2}^{E,\infty}} = \overline{K_{\mathrm{m},2}^{0}} - K_{\mathrm{m},2}^{*}. \qquad (17)$$

2.5. Ultrasonic velocity

Here we have used five different models and relations for surface tension to predict the ultrasonic velocity theoretically. From the theoretically computed values of sur-

face tension, we have calculated the ultrasonic velocity using Aurebach relation [14].

$$u = \left(\frac{\sigma}{6.3 \times 10^{-4}\rho}\right)^{2/3}. \qquad (18)$$

Using the density measured over all composition range and ultrasonic velocity of pure liquids at 293, 303, and 313 K, surface tension of the system under investigation has been calculated by using following theories and relations.

Sanchez relation [15] has been applied successfully to binary liquid mixtures to deduce the values of surface tension of liquid mixtures

$$\sigma = \sum_{i}\left(x_i A_i^{1/2}\right)\left[\sum_{i}\frac{(\phi_i\rho_i)}{(\phi_i k_{Ti})}\right]^{1/2}, \qquad (19)$$

where k_{Ti}, ρ_i, ϕ_i and x_i are the isothermal compressibilities, densities of pure liquids volume fraction and the mole fraction of the i-th component. A_i is defined as

$$A_i = \sigma_i^2\left(\frac{k_{Ti}}{\rho_i}\right). \qquad (20)$$

Goldsach and Sarvas [16] used the mole fraction and volume fraction statistics to obtain the following expression for the surface tension of non-electrolyte solutions and applied this equation to obtain surface tension of various organic liquid mixtures.

$$\sigma = -\left(\frac{RT}{A}\right)\ln\left[x_1\exp\left(\frac{-\sigma_1 A}{RT}\right)\right.$$
$$\left. + x_2\exp\left(\frac{-\sigma_2 A}{RT}\right)\right], \qquad (21)$$

where A is the molar surface area.

According to Sudgen, assuming that parachor $[P_i]$ is additive with respect to mole number [17], σ can be obtained for a binary mixture as

$$\sigma = \left\{[P_1]\frac{x_1}{M_1} + [P_2]\frac{x_2}{M_2}\right\}^4 \rho^4, \qquad (22)$$

where M_i is the molar mass of the pure component i and ρ is the density of mixture.

Patterson and Rastogi [18] have used Flory statistical theory (FST) to calculate surface tension which in turn is used to evaluate ultrasonic velocity in liquid mixtures. The following relation was used to calculate characteristic surface tension [14]:

$$\sigma^* = k^{1/3}P^{*2/3}T^{*1/3}, \qquad (23)$$

where k, P^* and T^* are the Boltzmann constant, characteristic pressure and temperature, respectively. Thus the surface tension of a liquid mixture is given by the relation

$$\sigma_m = \sigma^*\tilde{\sigma}\left(\tilde{V}\right). \qquad (24)$$

Starting from the work of Prigogine and Saraga the equation for reduced surface tension [19] is given by

$$\tilde{\sigma}\left(\tilde{V}\right) = M\tilde{V}^{-5/3} - \frac{\tilde{V}^{1/3} - 1}{\tilde{V}^2}\ln\left(\frac{\tilde{V}^{1/3} - 0.5}{\tilde{V}^{1/3} - 1}\right), \quad (25)$$

where M is the fraction of nearest neighbors that a

molecule loses on moving from the bulk of the liquid to the surface.

Another theoretical model we analyzed is due to Brock and Bird [17], which obtains the surface tension of pure components only from the values of critical parameters. Using a suggestion by Miller, Brock and Bird expression for a binary mixture is given by

$$\sigma = P_{\text{cm}}^{2/3} T_{\text{cm}}^{1/3} Q \left(1 - T_{\text{r}}\right)^{11/9}, \qquad (26)$$

where

$$Q = 0.1196 \left[1 + \frac{T_{\text{br}} \ln \left(P_{\text{cm}}/1.01325\right)}{1 - T_{\text{br}}}\right] - 0.279 \quad (27)$$

and P_{cm}, T_{cm}, T_{br} are the critical pressure, critical temperature and boiling temperature for the mixture.

2.6. Internal pressure

A number of relations can be utilized to estimate the internal pressure in pure liquids and liquid mixtures. Some of them are summarized here.

2.6.1. Thermodynamical relation

The relation among applied pressure (P), molar volume (V), temperature (T) and molar internal energy (U) is given by thermodynamic relation

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P. \qquad (28)$$

The isothermal internal energy–volume coefficient $(\partial U/\partial V)_T$ is often called internal pressure π_i. Since $\alpha = (1/V)\left(\partial V/\partial T\right)_p$ and $k_{\text{T}} = -(1/V)\left(\partial V/\partial P\right)_T$, the above equation, for the pressure limiting to zero, can be written as

$$\pi_i = \frac{\alpha T}{k_T}. \qquad (29)$$

2.6.2. Relation using empirical equations for α and k_T

From the empirical equations for thermal expansion coefficient α and isothermal compressibility k_T [20] we get

$$\pi_i = 44.2 T^{4/3} u^{3/2} \rho. \qquad (30)$$

2.6.3. Relation based upon Buehler–Hirschfelder–Curtiss equation of state

With the help of equation proposed by Buehler et al. [21, 22] the internal pressure can be given as

$$\pi_i = \frac{2^{1/6} R T}{2^{1/6} V - d N^{1/3} V^{2/3}}, \qquad (31)$$

where V is the molar volume, d is the molecular diameter, T is the absolute temperature and R is the gas constant.

2.6.4. Relation based upon Flory statistical theory

Knowing the thermal expansion coefficient α and isothermal compressibility k_T of pure liquid components, the values of α and k_T for liquid mixture can be evaluated as

$$(\alpha)_{\text{Flory}} = \frac{3\left(\tilde{V}^{1/3} - 1\right)}{\left[1 - 3\left(\tilde{V}^{1/3} - 1\right)\right] T} \qquad (32)$$

and

$$(k_T)_{\text{Flory}} = \frac{(\alpha)_{\text{Flory}} T \tilde{V}^2}{P^*}, \qquad (33)$$

where $\tilde{V}$ is the reduced volume, T is the absolute temperature and P^* is the characteristic pressure. Using the values of α and k_T thus obtained, one can evaluate the internal pressure of the liquid mixture using the relation

$$\pi_i = \frac{(\alpha)_{\text{Flory}} T}{(k_T)_{\text{Flory}}}. \qquad (34)$$

2.7. Isothermal compressibility

The values of isothermal compressibility k_T for the binary mixtures were predicted by the equation based on Flory's statistical theory [23, 24] and five rigid sphere equations [25] based on various hard sphere models which are Thiele–Lebowitz model [26, 27], Thiele model [26], Guggenheim model [28], Carnahan–Starling model [29] and Hoover–Ree model [30]. The experimental k_T values were calculated using the relation

$$k_T = k_{\text{s}} + T\alpha^2 V/C_p, \qquad (35)$$

where C_p is the heat capacity.

3. Results and discussion

The calculated values of specific heat ratio (γ), heat capacity (C_p), effective Debye temperature (θ_{D}) and pseudo-Grüneisen parameter (Γ) for THF + o-cresol and THF + methanol mixture with mole fraction of THF (x_1) at $T = 293$, 303, 313 K are given in Tables I and II, respectively. The values of coefficient a_i evaluated using the method of least squares for both the mixtures are given in Table III along with the standard deviations $\sigma\left(Y^{\text{E}}\right)$. The values of excess Γ^{E}, K_{s}^{E} and Z^{E} are plotted against the mole fraction of THF and are shown in Figs. 1 to 3, respectively.

Tables I and II reveal that the values of specific heat ratio (γ), pseudo-Grüneisen parameter (Γ) and effective Debye temperature (θ_{D}) decrease with increase in temperature for both the mixtures, whereas heat capacity (C_p) increases as temperatures increases. It is also observed that these parameters are affected by changing the mole fraction of THF. Γ, θ_{D} and C_p vary almost linearly with composition. The values of γ and Γ increase on increasing the mole fraction of the component having higher molecular weight. However, non-linear variation of γ with mole fraction has been observed for both the mixtures.

The nature and sign of excess functions can be explained in terms of the molecular interactions considering both the positive and negative contributions. It can be seen from Fig. 1 that the values of excess pseudo-Grüneisen parameter (Γ^{E}) are negative for both the binary mixtures which indicate the presence of specific intermolecular interaction through hydrogen bonding between the oxygen atom of tetrahydrofuran and hydrogen atom of o-cresol and methanol. The values of Γ^{E} increase with temperature, which suggests that there is an increase in strength of interaction with temperature in both the mixtures. The values are more negative for

Specific heat ratio (γ), pseudo-Grüneisen parameter (Γ), heat capacity (C_p) and effective Debye temperature (θ_{D}) for THF + o-cresol mixture with mole fraction of THF (x_1) at $T = 293, 303, 313$ K.

x_1	γ	Γ	C_p [cal mol^{-1}]	θ_{D} [K]
		$T = 293$ K		
0.0000	1.347	1.1803	222.091	79.175
0.1434	1.351	1.1862	208.835	79.669
0.2735	1.355	1.1873	195.246	79.451
0.3921	1.359	1.1876	182.807	79.111
0.4999	1.365	1.1927	171.010	78.554
0.5999	1.373	1.2017	159.701	77.775
0.6923	1.382	1.2115	149.068	76.809
0.7778	1.393	1.2227	139.272	75.765
0.8571	1.403	1.2354	130.314	74.693
0.9310	1.413	1.2436	121.977	73.478
1.0000	1.422	1.2452	113.738	71.848
		$T = 303$ K		
0.0000	1.328	1.0724	236.845	77.632
0.1434	1.330	1.0702	222.007	77.789
0.2735	1.333	1.0674	207.170	77.409
0.3921	1.335	1.0628	193.791	76.957
0.4999	1.342	1.0672	180.513	76.168
0.5999	1.349	1.0739	167.678	75.092
0.6923	1.359	1.0832	155.724	73.891
0.7778	1.369	1.0942	144.814	72.655
0.8571	1.381	1.1091	135.004	71.491
0.9310	1.397	1.1296	125.473	70.049
1.0000	1.407	1.1359	117.181	68.669
		$T = 313$ K		
0.0000	1.313	0.9705	245.530	74.219
0.1434	1.313	0.9625	229.917	74.189
0.2735	1.313	0.9548	215.633	74.056
0.3921	1.317	0.9532	201.199	73.528
0.4999	1.321	0.9546	188.179	73.019
0.5999	1.328	0.9592	175.037	72.094
0.6923	1.338	0.9702	162.089	70.868
0.7778	1.349	0.9837	150.453	69.685
0.8571	1.361	0.9994	139.843	68.481
0.9310	1.376	1.0184	130.155	67.267
1.0000	1.391	1.0396	121.309	66.032

Specific heat ratio (γ), pseudo-Grüneisen parameter (Γ), heat capacity (C_p) and effective Debye temperature (θ_{D}) for THF + methanol mixture with mole fraction of THF (x_1) at $T = 293, 303, 313$ K.

x_1	γ	Γ	C_p [cal mol^{-1}]	θ_{D} [K]
		$T = 293$ K		
0.0000	1.478	1.2558	41.283	77.511
0.0471	1.472	1.2515	44.359	77.142
0.1000	1.466	1.2469	47.815	76.664
0.1599	1.460	1.2427	51.789	76.156
0.2285	1.455	1.2392	56.392	75.583
0.3075	1.449	1.2360	61.803	74.993
0.3998	1.443	1.2343	68.230	74.347
0.5090	1.438	1.2341	76.002	73.667
0.6399	1.432	1.2335	85.709	73.072
0.7995	1.427	1.2388	97.831	72.428
1.0000	1.422	1.2452	113.738	71.848
		$T = 303$ K		
0.0000	1.457	1.1470	43.119	75.295
0.0471	1.451	1.1421	46.282	74.828
0.1000	1.446	1.1381	49.856	74.293
0.1599	1.440	1.1342	53.971	73.737
0.2285	1.435	1.1307	58.710	73.087
0.3075	1.430	1.1278	64.283	72.426
0.3998	1.425	1.1261	70.876	71.690
0.5090	1.420	1.1254	78.844	70.921
0.6399	1.415	1.1254	88.735	70.194
0.7995	1.411	1.1301	101.098	69.438
1.0000	1.407	1.1359	117.181	68.669
		$T = 313$ K		
0.0000	1.441	1.0560	44.662	72.668
0.0471	1.434	1.0483	47.971	72.224
0.1000	1.428	1.0430	51.690	71.698
0.1599	1.423	1.0384	55.967	71.146
0.2285	1.417	1.0343	60.934	70.550
0.3075	1.412	1.0306	66.722	69.886
0.3998	1.407	1.0277	73.575	69.153
0.5090	1.402	1.0273	81.829	68.380
0.6399	1.398	1.0282	92.043	67.633
0.7995	1.395	1.0331	104.731	66.817
1.0000	1.391	1.0396	121.309	66.032

THF + o-cresol as compared to THF + methanol which implies that the intermolecular interaction is stronger in THF + o-cresol which may be due to the reason that phenoxide ion of o-cresol is stabilized to a greater extent through resonance as compared to hydroxide ion of methanol thus making the phenol more acidic in nature.

The values of excess molar isentropic compressibilities (K_s^{E}) (Fig. 2) for THF + o-cresol mixture are found to be negative over the entire composition range, which indicates that the mixture is less compressible than the corresponding ideal mixture.
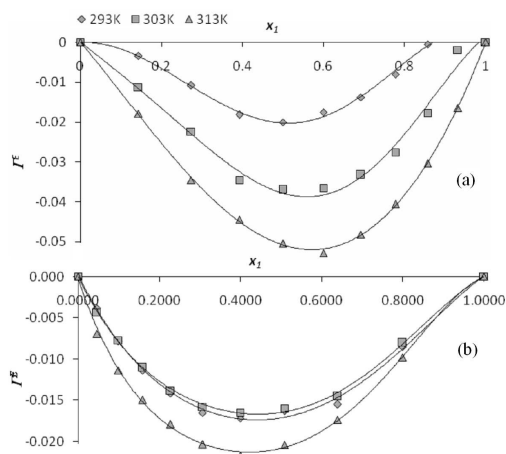
Fig. 1. (a) Excess pseudo-Grüneisen parameter (Γ^E) vs. mole fraction of THF (x_1) for binary mixture of THF + o-cresol at $T = 293, 303, 313$ K. (b) Excess pseudo--Grüneisen parameter (Γ^E) vs. mole fraction of THF (x_1) for binary mixture of THF + methanol at $T = 293, 303, 313$ K.
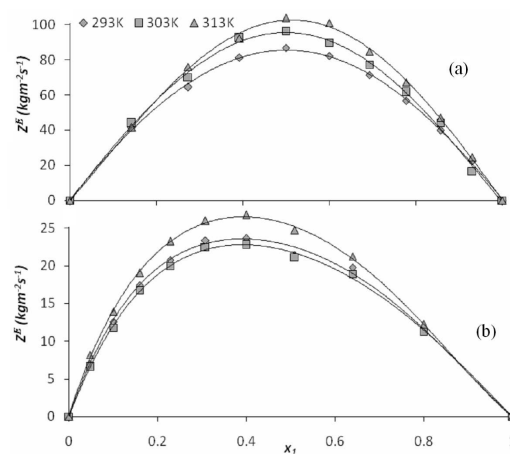

Fig. 2. (a) Excess acoustic impedance (Z^E) vs. mole fraction of THF (x_1) for binary mixture of THF + o-cresol at $T = 293, 303, 313$ K. (b) Excess acoustic impedance (Z^E) vs. mole fraction of THF (x_1) for binary mixture of THF + methanol at $T = 293, 303, 313$ K.

TABLE III

Adjustable parameters a_i with the standard deviations $\sigma(Y^E)$ for excess pseudo-Grüneisen parameter (Γ^E), excess acoustic impedance (Z^E), and excess molar isentropic compressibility for both the binary mixtures at temperature $T = 293, 303, 313$ K.

Parameters	Temp. [K]	a_1	a_2	a_3	a_4	a_5	$\sigma(Y^E)$
			THF + o-cresol				
Γ^E	293	−0.0869	0.0146	0.1673	−0.0696	−0.0427	0.0002
	303	−0.3575	−0.9616	−0.7325	1.9422	2.3316	0.0005
	313	−0.1995	0.0502	−0.0141	0.0406	0.0400	0.0003
$Z^E \times 10^{-3}$	293	346.8344	−16.5097	−143.2758	48.5663	225.4550	0.0813
[kg m^{-2} s^{-1}]	303	349.2720	−87.6560	224.0041	168.5739	−403.8437	0.5701
	313	438.3686	94.5512	−66.5609	−252.6640	−161.5987	0.9488
$K_s^E \times 10^{14}$	293	−243.4063	69.4389	64.0032	−11.3557	−149.3610	0.0482
[m^5 N^{-1} mol^{-1}]	303	−281.2110	163.1849	−279.7280	−127.0632	407.8124	0.4020
	313	−375.0642	122.1414	45.7887	26.7855	−59.3857	0.6200
			THF + methanol				
Γ^E	293	−0.0650	0.0030	−0.0485	−0.0773	0.1119	0.0001
	303	−0.0639	0.0038	0.0036	−0.0626	0.0107	0.0001
	313	−0.0822	−0.0191	0.0063	−0.0524	−0.0306	0.0001
$Z^E \times 10^{-3}$	293	86.1901	29.4571	144.3472	98.5734	−221.5526	0.1308
[kg m^{-2} s^{-1}]	303	85.0160	29.1736	90.0909	60.7908	−126.1915	0.1806
	313	99.1479	22.9216	10.0370	65.0723	8.1809	0.0428
$K_s^E \times 10^{14}$	293	21.1589	−5.1153	−125.9916	−88.0336	202.5821	0.1175
[m^5 N^{-1} mol^{-1}]	303	19.7142	−6.0429	−87.7291	−60.9595	134.0959	0.1803
	313	0.4054	0.5945	−4.7450	−74.6267	−6.1099	0.0497

The values of K_s^E increase with temperature, suggesting an increase in intermolecular interaction between the unlike molecules due to thermal energy. However, the excess molar isentropic compressibilities for THF + methanol mixture are slightly negative in methanol rich region, turning to small positive values in THF rich region in observed temperature range. This indicates that dispersive forces are also operating in case of THF + methanol, in THF rich region.

Specific acoustic impedance is a quantity, which depends on the molecular packing of the systems. Excess acoustic impedance (Z^E) is positive for THF + o-cresol and THF + methanol mixtures and the values increase with increase in temperature. The positive values of Z^E
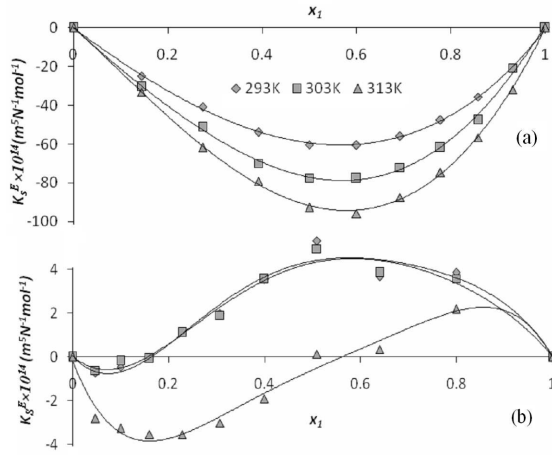
Fig. 3. (a) Excess molar isentropic compressibility (K_s^E) vs. mole fraction of THF (x_1) for binary mixture of THF + o-cresol at $T = 293, 303, 313$ K. (b) Excess molar isentropic compressibility (K_s^E) vs. mole fraction of THF (x_1) for binary mixture of THF + methanol at $T = 293, 303, 313$ K.

Fig. 4. (a) Comparison of the experimental and theoretically calculated velocities for the system THF + o-cresol at 293 K. (b) Comparison of the experimental and theoretically calculated velocities for the system THF + o-cresol at 303 K. (c) Comparison of the experimental and theoretically calculated velocities for the system THF + o-cresol at 313 K.

TABLE IV

Molar isentropic compressibility of pure liquids ($K_{m,i}^*$), partial molar isentropic compressibility ($\overline{K_{m,i}^0}$) and excess partial molar isentropic compressibility ($\overline{K_{m,i}^{E,\infty}}$) at infinite dilution of each component in THF + o-cresol and THF + methanol mixtures at varying temperatures.

Temperature	$K_{m,1}^*$	$K_{m,2}^*$	$\overline{K_{m,1}^0}$	$\overline{K_{m,2}^0}$	$\overline{K_{m,1}^{E,\infty}}$	$\overline{K_{m,2}^{E,\infty}}$
			THF + o-cresol			
293 K	5.3201	4.0475	1.4516	1.3407	−3.8685	−2.7068
303 K	5.9218	4.2281	4.0293	3.0580	−1.8925	−1.1700
313 K	6.4990	4.6857	1.1231	2.2884	−5.3759	−2.3973
			THF + methanol			
293 K	5.3201	4.0622	7.2291	4.1082	1.9090	0.0460
303 K	5.9218	4.3131	7.2526	4.3039	1.3308	−0.0092
313 K	6.4990	4.7064	7.1348	3.8616	0.6358	−0.8448

Fig. 5. (a) Comparison of the experimental and theoretically calculated velocities for the system THF + methanol at 293 K. (b) Comparison of the experimental and theoretically calculated velocities for the system THF + methanol at 303 K. (c) Comparison of the experimental and theoretically calculated velocities for the system THF + methanol at 313 K.

suggest the presence of strong interaction through hydrogen bonding between oxygen atom of THF molecules with its lone pair of electron and the hydrogen atom of –OH group of alcohol and cresol. The positive values of Z^E in THF + o-cresol mixture are found to be approximately four times greater than THF + methanol mixture. This reflects the strong interaction in THF + o-cresol in comparison with THF + methanol which increases with temperature. The results of Γ^E, K_s^E and Z^E also support each other.

The values of $K_{m,1}^*$, $K_{m,2}^*$, $\overline{K_{m,1}^0}$, $\overline{K_{m,2}^0}$, $\overline{K_{m,1}^{E,\infty}}$ and $\overline{K_{m,2}^{E,\infty}}$ are listed in Table IV. These values can be interpreted in terms of structural compressibility, which results from the breakdown of associated structure on mixing of THF in alcohol and cresol as well as geomet-
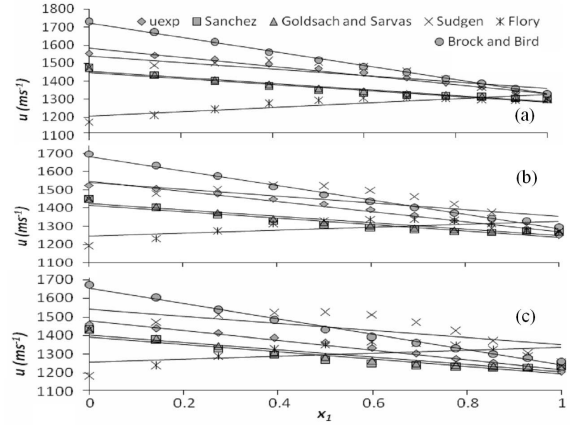
TABLE V

Value of critical parameters for pure components.

Parameters		THF	o-cresol	methanol
σ [m N m^{-1}][a]	293 K	26.40	37.41	22.46
	303 K	25.12	36.40	21.69
	313 K	23.84	35.39	21.69
T_c [K][b]		540.1	697.6	512.64
P_c [MPa][b]		5.19	5.01	8.09
T_b [K][b]		338	464.19	337.7
C_p [J mol^{-1} K^{-1}][c]	293 K	141.4	–	81.30

[a]calculated from the surface tension of Ref. [34]; [b][34]; [c][35]

<table>
<tr><td colspan="7" align="center">TABLE VI
Measured ultrasonic velocity and theoretical ultrasonic velocity of THF + o-cresol mixture from various methods and their average percentage deviations at $T = 293, 303, 313$ K.</td></tr>
</table>

		u_{theo} [m s^{-1}]				
x_1	u_{exp}	Sanchez	G–Sarvas	Sudgen	Flory	B–Bird
T=293
0.0000	1554.5	1471.9	1471.9	1471.9	1175.5	1728.2
0.1434	1543.6	1433.2	1438.8	1489.8	1208.8	1669.8
0.2735	1520.3	1399.8	1408.5	1503.1	1242.1	1614.8
0.3921	1496.1	1370.7	1380.8	1512.9	1275.5	1562.8
0.4999	1471.6	1349.5	1359.9	1504.7	1296.0	1519.0
0.5999	1446.2	1334.6	1344.4	1481.1	1304.7	1481.3
0.6923	1419.3	1323.6	1332.2	1449.9	1307.8	1447.3
0.7778	1392.8	1316.0	1323.0	1412.2	1305.3	1416.7
0.8571	1367.4	1311.6	1316.4	1369.0	1297.9	1389.3
0.9310	1339.1	1306.4	1308.9	1332.0	1296.0	1360.9
1.0000	1303.0	1300.5	1300.5	1300.5	1299.2	1331.8
APD		5.80	5.37	0.11	11.23	−4.07

The table continues for $T = 293, 303, 313$ K.

T = 293 K (Table VII)

<table>
<tr><td colspan="7" align="center">TABLE VII
Measured ultrasonic velocity and theoretical ultrasonic velocity of THF + methanol mixture from various methods and their average percentage deviations at $T = 293, 303, 313$ K.</td></tr>
</table>

		u_{theo} [m s^{-1}]				
x_1	u_{exp}	Sanchez	G–Sarvas	Sudgen	Flory	B–Bird
T=293
0.0000	1116.0	1261.4	1261.4	1261.4	919.4	2012.6
0.0471	1127.4	1287.4	1270.1	1260.2	954.2	1925.0
0.1000	1138.6	1304.0	1277.3	1260.7	996.4	1842.5
0.1599	1150.8	1313.8	1283.0	1263.0	1038.4	1765.5
0.2285	1164.1	1318.8	1287.5	1266.5	1078.2	1694.8
0.3075	1178.9	1320.6	1291.5	1270.6	1118.6	1623.8
0.3998	1195.8	1319.9	1294.8	1274.7	1156.0	1559.1
0.5090	1215.2	1316.9	1296.4	1281.1	1190.8	1502.6
0.6399	1238.7	1311.3	1297.5	1290.3	1232.4	1438.2
0.7995	1267.6	1307.1	1299.8	1293.2	1263.6	1385.5
1.0000	1303.0	1300.5	1300.5	1300.5	1299.2	1331.8
APD		−9.89	−8.32	−7.26	6.74	−39.21

T = 303 K

THF + o-cresol:

x_1	u_{exp}	Sanchez	G–Sarvas	Sudgen	Flory	B–Bird
0.0000	1525.0	1447.9	1447.9	1447.9	1191.3	1696.3
0.1434	1505.6	1400.9	1408.7	1481.4	1234.0	1631.9
0.2735	1478.4	1362.6	1374.7	1504.2	1272.2	1573.6
0.3921	1450.7	1328.2	1342.3	1527.3	1314.3	1517.3
0.4999	1422.6	1306.0	1320.4	1519.2	1331.9	1473.3
0.5999	1392.0	1289.8	1303.3	1497.3	1339.1	1434.7
0.6923	1361.6	1278.5	1290.4	1464.4	1337.5	1400.8
0.7778	1332.5	1271.0	1280.6	1424.0	1329.6	1370.5
0.8571	1307.0	1268.1	1274.8	1373.9	1312.6	1344.5
0.9310	1280.3	1272.8	1276.3	1304.6	1277.3	1326.2
1.0000	1250.0	1268.4	1268.4	1268.4	1272.9	1298.1
APD		5.15	4.54	−3.42	6.67	−4.85

THF + methanol:

x_1	u_{exp}	Sanchez	G–Sarvas	Sudgen	Flory	B–Bird
0.0000	1084.0	1233.1	1233.1	1233.1	922.7	1938.8
0.0471	1093.6	1256.4	1240.1	1234.1	955.4	1855.9
0.1000	1103.8	1271.6	1246.5	1234.6	994.8	1778.8
0.1599	1115.0	1280.2	1251.2	1237.7	1035.1	1706.1
0.2285	1126.7	1284.3	1255.0	1241.6	1072.9	1639.5
0.3075	1140.1	1285.8	1258.5	1245.5	1110.8	1572.7
0.3998	1155.0	1285.0	1261.5	1249.3	1145.6	1511.7
0.5090	1172.2	1281.8	1262.8	1255.8	1178.4	1458.1
0.6399	1193.1	1277.3	1264.5	1262.1	1214.8	1398.0
0.7995	1219.0	1273.7	1266.9	1263.9	1242.6	1348.4
1.0000	1250.0	1268.4	1268.4	1268.4	1272.9	1298.1
APD		−10.82	−9.31	−8.65	4.24	−39.37

T = 313 K

THF + o-cresol:

x_1	u_{exp}	Sanchez	G–Sarvas	Sudgen	Flory	B–Bird
0.0000	1462.0	1429.7	1429.7	1429.7	1185.7	1671.4
0.1434	1437.8	1376.5	1384.9	1472.5	1237.4	1601.4
0.2735	1413.4	1330.9	1343.9	1510.4	1289.8	1536.0
0.3921	1386.2	1296.9	1312.2	1524.0	1324.9	1481.5
0.4999	1362.0	1269.4	1285.1	1526.8	1353.1	1432.5
0.5999	1333.4	1249.2	1264.0	1511.5	1367.1	1390.4
0.6923	1303.7	1238.0	1251.0	1471.3	1358.8	1357.2
0.7778	1276.8	1230.8	1241.3	1423.2	1343.4	1327.8
0.8571	1251.4	1227.5	1234.9	1367.8	1321.1	1302.0
0.9310	1228.0	1228.7	1232.6	1303.6	1290.0	1280.4
1.0000	1205.9	1233.7	1233.7	1233.7	1252.6	1262.2
APD		3.64	2.95	−7.69	1.83	−6.53

THF + methanol:

x_1	u_{exp}	Sanchez	G–Sarvas	Sudgen	Flory	B–Bird
0.0000	1050.0	1213.2	1213.2	1213.2	928.1	1877.8
0.0471	1058.3	1232.0	1215.8	1219.5	959.6	1795.1
0.1000	1067.6	1244.4	1219.3	1221.0	997.2	1720.2
0.1599	1078.0	1250.8	1222.0	1223.5	1035.4	1650.2
0.2285	1089.5	1252.9	1223.6	1227.5	1072.3	1585.8
0.3075	1101.9	1252.5	1225.3	1230.7	1109.2	1521.4
0.3998	1115.6	1249.8	1226.3	1234.9	1144.0	1462.2
0.5090	1132.0	1246.2	1227.2	1238.0	1173.8	1411.6
0.6399	1152.0	1241.9	1229.1	1238.5	1204.9	1355.5
0.7995	1176.1	1238.5	1231.8	1235.1	1227.9	1309.1
1.0000	1205.9	1233.7	1233.7	1233.7	1252.6	1262.2
APD		−11.89	−10.33	−10.72	1.21	−39.61

rical compressibility which is due to simultaneous compression of the molecules leading to contraction in volume and decrease in the average intermolecular distances due to the formation of hydrogen bond between unlike molecules. It is observed from Table IV that the partial molar isentropic compressibility of THF at infinite dilution $\overline{K^0_{\text{m},1}}$ in o-cresol and o-cresol at infinite dilution $\overline{K^0_{\text{m},2}}$ in THF are smaller than the corresponding molar isentropic compressibility $K^*_{\text{m},1}$ and $K^*_{\text{m},2}$ of THF and o-cresol, respectively. It can also be observed that

$\overline{K^{\text{E},\infty}_{\text{m},i}}$ have values in accordance with K^{E}_{s} values for both the mixtures at each temperature. This further supports the presence of strong intermolecular interaction between unlike molecules and more pronounced interaction is observed in the mixture of THF + o-cresol as is also reflected from Γ^{E}, K^{E}_{s} and Z^{E} values.

The parameters for pure components used in the estimation of velocity theoretically are listed in Table V.

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TABLE VIII

Internal pressure of THF + o-cresol mixture from various methods at $T = 293, 303, 313$ K.

x_1	Eq. (29)	Eq. (30)	Eq. (31)	Eq. (34)
$\pi_i\ [\times 10^{-5}\ \mathrm{N\ m^{-2}}]$				
$T = 293$ K				
0.0000	5544.7	5543.4	5544.7	364.2
0.1434	5437.7	5436.4	5360.6	3788.3
0.2735	5267.7	5266.4	5168.7	3928.2
0.3921	5096.8	5095.6	4976.3	4064.4
0.4999	4905.0	4903.9	4782.8	4175.5
0.5999	4693.5	4692.4	4586.3	4264.3
0.6923	4473.5	4472.4	4389.1	4339.4
0.7778	4255.6	4254.6	4193.4	4401.0
0.8571	4044.3	4043.4	3999.6	4449.8
0.9310	3838.1	3837.2	3807.8	4503.6
1.0000	3615.7	3614.8	3615.7	4560.9
APD		−0.02	−1.43	−12.69
$T = 303$ K				
0.0000	5619.2	5617.8	5619.2	375.1
0.1434	5488.5	5487.2	5416.6	3917.6
0.2735	5306.1	5304.8	5207.1	4071.6
0.3921	5131.2	5130.0	4997.9	4227.9
0.4999	4913.1	4911.9	4785.2	4340.3
0.5999	4671.6	4670.5	4569.0	4431.9
0.6923	4426.3	4425.3	4352.7	4504.5
0.7778	4188.3	4187.3	4138.6	4561.9
0.8571	3963.7	3962.8	3927.6	4599.2
0.9310	3716.6	3715.7	3715.6	4596.2
1.0000	3510.3	3509.5	3510.3	4644.4
APD		−0.02	−1.31	−8.81
$T = 313$ K				
0.0000	5457.5	5456.2	5457.5	382.5
0.1434	5322.1	5320.9	5261.8	4011.8
0.2735	5184.2	5183.0	5064.7	4195.0
0.3921	4997.8	4996.6	4862.0	4345.4
0.4999	4819.4	4818.3	4661.5	4481.0
0.5999	4599.1	4598.0	4455.4	4589.1
0.6923	4347.0	4346.0	4246.4	4655.6
0.7778	4109.2	4108.2	4040.3	4705.1
0.8571	3878.7	3877.7	3836.6	4736.3
0.9310	3654.4	3653.6	3635.4	4744.7
1.0000	3436.8	3435.9	3436.8	4733.4
APD		−0.02	−1.65	−4.16

TABLE IX

Internal pressure of THF + methanol mixture from various methods at $T = 293, 303, 313$ K.

x_1	Eq. (29)	Eq. (30)	Eq. (31)	Eq. (34)
$\pi_i\ [\times 10^{-5}\ \mathrm{N\ m^{-2}}]$				
$T = 293$ K				
0.0000	2552.6	2552.0	2552.6	881.3
0.0471	2623.4	2622.8	2647.1	8443.1
0.1000	2694.9	2694.2	2743.2	8063.0
0.1599	2771.8	2771.2	2841.5	7672.0
0.2285	2853.1	2852.4	2941.2	7265.5
0.3075	2943.4	2942.7	3044.5	6851.0
0.3998	3040.8	3040.1	3150.6	6418.3
0.5090	3149.4	3148.7	3259.7	5970.6
0.6399	3284.2	3283.4	3374.0	5524.6
0.7995	3431.3	3430.5	3491.7	5045.8
1.0000	3615.7	3614.8	3615.7	4560.9
APD		−0.84	1.28	103.88
$T = 303$ K				
0.0000	2553.2	2552.6	2553.2	908.7
0.0471	2617.9	2617.3	2638.8	8702.3
0.1000	2683.9	2683.3	2725.9	8300.1
0.1599	2756.0	2755.3	2814.9	7891.2
0.2285	2830.1	2829.4	2905.0	7466.1
0.3075	2912.5	2911.8	2998.2	7031.7
0.3998	3000.2	2999.5	3093.6	6579.7
0.5090	3098.9	3098.1	3191.9	6115.4
0.6399	3217.7	3217.0	3294.1	5646.0
0.7995	3349.7	3348.9	3399.7	5149.2
1.0000	3510.3	3509.5	3510.3	4644.4
APD		−0.78	1.04	111.67
$T = 313$ K				
0.0000	2512.0	2511.4	2512.0	925.6
0.0471	2579.8	2579.1	2595.2	8889.9
0.1000	2645.7	2645.1	2679.4	8489.4
0.1599	2716.6	2715.9	2765.5	8074.8
0.2285	2792.5	2791.9	2853.0	7645.6
0.3075	2873.1	2872.4	2943.1	7204.0
0.3998	2959.4	2958.7	3035.4	6746.1
0.5090	3053.4	3052.7	3130.3	6264.9
0.6399	3164.7	3163.9	3228.7	5774.2
0.7995	3285.8	3285.0	3330.1	5257.7
1.0000	3436.8	3435.9	3436.8	4733.4
APD		−0.87	0.66	119.63

</div>

TABLE X

Experimental values and theoretically calculated values of isothermal compressibility k_T, by using Flory's theory and various hard sphere models at $T = 293$ K and average percentage deviations in the calculated values for binary mixture of THF + methanol mixture.

k_T [$\times 10^{-10}$ N^{-1} m^2]						
x_1	$k_{T\exp}$	Flory	Thiele–Lebowitz	Thiele	Guggenheim	Carnahen–Starling	Hoover–Ree
$T = 293$ K						
0.0000	12.038	14.912	8.439	10.025	7.755	8.909	9.581
0.0471	11.726	14.275	8.489	10.154	7.770	8.979	9.718
0.1000	11.431	13.682	8.537	10.289	7.781	9.051	9.866
0.1599	11.129	13.110	8.571	10.418	7.775	9.110	10.013
0.2285	10.829	12.563	8.595	10.546	7.755	9.160	10.167
0.3075	10.512	12.025	8.595	10.659	7.706	9.188	10.316
0.3998	10.190	11.505	8.574	10.765	7.633	9.198	10.470
0.5090	9.851	10.992	8.521	10.850	7.522	9.178	10.622
0.6399	9.457	10.451	8.389	10.867	7.330	9.079	10.735
0.7995	9.054	9.928	8.215	10.857	7.090	8.940	10.853
1.0000	8.592	9.374	7.926	10.743	6.735	8.685	10.921
APD		−15.21	18.39	−2.54	27.36	12.46	−0.17

A close perusal of Tables VI and VII reveals that Sudgen's and Goldsach–Sarvas's methods are in a fairly good agreement with the experimental values. Average percentage deviations in Flory, Brock and Bird and Sanchez methods are also within the limits of error. The parameter parachor [P_i], introduced by Sudgen, has been calculated by using density thereby follows the same behavior. Earlier workers [31–33] also arrived at the same conclusion about Sudgen's method for evaluation of surface tension. Brock and Bird theory is found to give large deviations in case of THF + methanol in methanol rich region. Figures 4 and 5 are the graphical depiction of the ultrasonic velocities evaluated by various theories which show the relative deviations from the experimental values.

Internal pressures in the two binary mixtures have been computed using Eqs. (28) to (34). The computed values of internal pressure are depicted in Tables VIII and IX. It can be seen from these tables that internal pressure of THF + o-cresol mixtures is greater than that for THF + methanol. As far as various methods for estimating internal pressure in pure liquids and liquid mixtures are concerned, Eq. (34), based upon Flory statistical theory is found to give satisfactory results in case of THF + o-cresol where as it is found to give large deviations in case of THF + methanol. This may be due to the relation derived which is based upon some adjustments and the approach uses more than one empirical relations, which are not adjusted for methanol. The relation using empirical equations for α and k_T, based upon Buehler–Hirschfelder–Curtiss equation of state, and the thermodynamic relation show good agreement with the experimental values for both the mixtures.
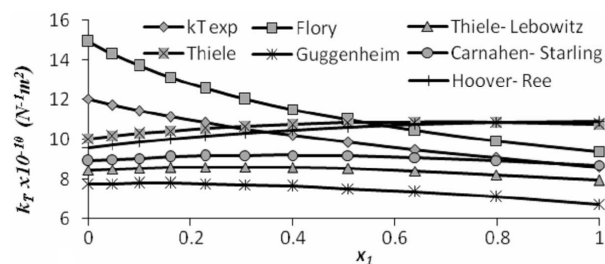

Fig. 6. Comparison of the experimental and theoretically calculated values of isothermal compressibilities for the system THF + methanol at 293 K.

The experimental and predicted values of k_T using Flory's statistical theory and five hard sphere models with average percentage deviations at 293 K are given in Table X. Flory's theory and five hard sphere models were compared with the experimental k_T values. It is clear from the table that out of five hard sphere models the Hoover–Ree model predicts k_T values the best in terms of average percentage deviations, followed by Thiele model, Carnahan–Starling model and Thiele–Lebowitz model while Guggenheim model could not predict k_T values well. Figure 6 shows the relative variation of k_T with the experimental values. It suggests that the values predicted by the Flory theory, Thiele model and Hoover–Ree model are near to the experimental values over the whole composition range.

4. Conclusions

The observed values of thermodynamic and excess parameters for both the mixtures show that the molecular

interaction is stronger in the binary mixture of THF + o-cresol. Further the theories used for estimation of velocities show good agreement with the respective measured values of ultrasonic velocity, except the Brock and Bird theory, which gives large deviations for THF + methanol mixture. Various empirical and semi-empirical relations for theoretically predicting the internal pressure for binary mixtures give reasonably good result for both the mixtures. However, Buehler–Hirschfelder–Curtiss equation of state and the relation using empirical equations for α and k_T are best suited for the prediction of internal pressure in both the mixtures. Models by Hoover–Ree and Thiele for evaluating the isothermal compressibility give very small deviations from the experimental values in comparison to the other models.

Acknowledgments

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