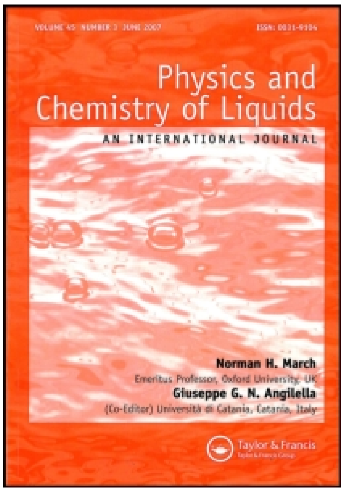

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Computation of various thermodynamic properties of binary liquid mixtures of nitrobenzene and benzene using equation of state modified for high pressures and varying temperatures

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A reduced equation of state, modified for high pressures has been employed to compute the density, ultrasonic velocity, the thermal expansion coefficient and heat capacities ratio of binary liquid mixtures of nitrobenzene and benzene at elevated pressures and varying temperatures. Computed values are compared with experimental findings, and results are presented graphically.

Keywords: Reduced equation of state; High pressure; Thermodynamic properties; Binary liquid mixture

1. Introduction

The thermodynamic behaviour of binary and multicomponent systems is of considerable interest. Knowledge of the density and ultrasonic velocity data offers convenient methods for determining certain thermodynamic properties of liquid mixtures, which are not easily accessible through direct measurement. Successful attempts have been made in recent past [1–11] on the theoretical evaluation of ultrasonic velocity and its correlation with the other thermodynamic properties of liquid mixtures using various empirical, semi-empirical and statistical theories at normal pressure. Very recently [11,12], the density and ultrasonic velocity of binary and multicomponent liquid mixtures have been computed through Flory theory at normal pressure. Some work has also been reported in literature [13,14] for the theoretical prediction of ultrasonic velocity in binary liquid mixtures at elevated pressures by means of empirical and semi-empirical relations. Moreover, to the best of our

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knowledge, a reduced equation of state [15] has yet not been used to predict thermodynamic properties of the liquid mixtures at high pressures. Therefore, in this communication, we have tried to modify a reduced equation of state given by Flory *et al.* [15] for high pressures to compute various thermodynamic properties viz. the density, ultrasonic velocity, the thermal expansion coefficient and heat capacities ratio of the binary liquid mixture, nitrobenzene + benzene, at high pressures and at different temperatures. The necessary data needed for the computation of above-mentioned properties for the binary liquid mixture at high pressures have been taken from literature [16].

2. Theoretical

To derive the expressions of $\tilde{P}$ and $\tilde{V}$ at high pressure, we start with the reduced equation of state given by Flory *et al.* [15]

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{\tilde{V}^{1/3}}{(\tilde{V}^{1/3} - 1)} - \frac{1}{\tilde{V}\tilde{T}}, \tag{1}$$

where the reduced parameters ($\tilde{V}$, $\tilde{T}$, $\tilde{P}$) are defined as [15]

$$\tilde{V} = \frac{V}{V^*}, \quad \tilde{T} = \frac{T}{T^*}, \quad \tilde{P} = \frac{P}{P^*}, \tag{2}$$

here, V^*, T^* and P^* are the characteristic parameters.

The thermal expansion coefficient (α), isothermal compressibility (β_T) and thermal pressure coefficient (γ_P) may be expressed as,

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \tag{3}$$

$$\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{4}$$

$$\gamma_P = \left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\beta_T} = \left(\frac{\tilde{T}P}{T\tilde{P}}\right)\left(\frac{\partial \tilde{P}}{\partial \tilde{T}}\right). \tag{5}$$

The partial derivatives and reduced parameters required in equations (3)–(5) have been obtained from equations (1) and (2), and the resulting equations have been simplified to obtain the expressions for α and β_T in terms of reduced parameters as given below,

$$(\alpha T)^{-1} = \left[\frac{1}{3(\tilde{V}^{1/3} - 1)} - 1 + \frac{2\tilde{P}\tilde{V}^2}{(\tilde{P}\tilde{V}^2 + 1)}\right] \tag{6}$$

$$(\beta_T P)^{-1} = \left[\frac{1}{3(\tilde{V}^{1/3} - 1)} - 1\right]\left[1 + \frac{1}{\tilde{P}\tilde{V}^2}\right] + 2. \tag{7}$$

Equations (6) and (7) are rearranged to get the final expressions for $\tilde{P}$ and $\tilde{V}$ at elevated pressures in terms of α and β_{T}, and are represented by equations (8) and (9), respectively.

$$\tilde{P} = \frac{\beta_{\mathrm{T}} P}{(\alpha T - \beta_{\mathrm{T}} P)} \frac{1}{[1 + \alpha T/3(1 - 2\beta_{\mathrm{T}} P + \alpha T)]^6} \tag{8}$$

$$\tilde{V} = \left[1 + \frac{\alpha T}{3(1 - 2\beta_{\mathrm{T}} P + \alpha T)}\right]^3. \tag{9}$$

By knowing values of the thermal expansion coefficient (α), isothermal compressibility (β_{T}) and the density (ρ), of pure components at different pressures, their reduced ($\tilde{P}$, $\tilde{V}$, and $\tilde{T}$) and characteristic (P^*, V^* and T^*) parameters have been calculated for different pressures with the help of equations (1), (2), (8) and (9). In the present work, density of nitrobenzene and benzene has been taken from literature [16], and their α and β_{T} are obtained with the help of equations (3) and (4).

The characteristic pressure, P^*, for the binary liquid mixtures has been calculated using the following expression [15]

$$P^*_{\mathrm{mix}} = \lfloor \psi_1 P_1^* + \psi_2 P_2^* - \psi_1 \theta_2 X_{12} \rfloor. \tag{10}$$

Here, ψ, θ and X_{12} are segment fraction, site fraction and the interaction parameter, respectively. Subscripts 1 and 2 stand for components 1 and 2, respectively.

Expressions of ψ and θ for a multicomponent system are given by [11]

$$\psi_i = \frac{x_i V_i^*}{\sum_{i=1}^{2} x_i V_i^*} \tag{11}$$

and

$$\theta_i = \frac{\psi_i}{\psi_i + \sum_{i,j=1,j\neq i}^{2} \psi_j (V_i^*/V_j^*)^{1/3}}. \tag{12}$$

Here, subscripts i and j represents the i^{th} and j^{th} components respectively.

In the case of a multicomponent system, an interaction parameter (X_{ij}) is defined as [11]

$$X_{i_j} = P_i^* \left[1 - \left(\frac{P_j^*}{P_i^*}\right)^{1/2} \left(\frac{V_i^*}{V_j^*}\right)^{1/6}\right]^2. \tag{13}$$

Ultrasonic velocity in liquid mixture, u_{mix} is obtained through the following well-known relation:

$$u_{\mathrm{mix}} = \sqrt{\left(\frac{1}{\beta_{\mathrm{s,mix}} \rho_{\mathrm{mix}}}\right)}. \tag{14}$$

The density of the liquid mixture, ρ_{mix} has been calculated as given below [11]

$$\rho_{\text{mix}} = \frac{\sum x_i M_i}{V_{\text{mix}}} \tag{15}$$

where

$$V_{\text{mix}} = \sum (x_i V_i^*) V_{\text{mix}}. \tag{16}$$

The expression of $\tilde{V}_{\text{mix}}$ is [11]

$$\tilde{V}_{\text{mix}} = \tilde{V}^E + \tilde{V}^0 \tag{17}$$

$\tilde{V}^E$ and $\tilde{V}^0$ are calculated as described in literature [11].

Isentropic compressibility of mixture, $\beta_{\text{s,mix}}$ in equation (14), has been evaluated from the thermodynamic relation

$$\beta_{\text{s,mix}} = \beta_{\text{T,mix}} - \frac{\alpha_{\text{mix}}^2 T V_{\text{mix}}}{C_{\text{p,mix}}} \tag{18}$$

α_{mix} and $\beta_{\text{T,mix}}$ for binary mixtures are obtained vide equations (6) and (7), respectively, using the calculated values of $\tilde{P}_{\text{mix}}$ and $\tilde{V}_{\text{mix}}$.

$\tilde{P}_{\text{mix}}$ is calculated from

$$\tilde{P}_{\text{mix}} = \frac{P}{P_{\text{mix}}^*}.$$

Heat capacity at constant pressure of mixtures, $C_{\text{p,mix}}$, is calculated from the expression

$$C_{\text{p,mix}} = C_{\text{p}}^E + C_{\text{p,idl}} \tag{19}$$

where $C_{\text{p,idl}}$ is the ideal heat capacity of mixture, expressed as,

$$C_{\text{p,idl}} = \sum x_i C_{\text{p},i}.$$

$C_{\text{p},i}$ is heat capacity of the i^{th} component and is computed from equation (18), substituting the values of all thermodynamic properties for pure components.

In the present work, expression for C_{p}^E given by Khanwalkar *et al.* [17] for normal pressure is modified at high pressures. The resulting expression is

$$C_{\text{p}}^E = \frac{P^* V^*}{T^*}\left[\frac{1}{(\tilde{P}\tilde{V}^2 - 2/3\tilde{P}\tilde{V}^{5/3} + 4/3\tilde{V}^{-1/3} - 1)} - \sum_i \left\{\frac{x_i}{(\tilde{P}_i\tilde{V}_i^2 - 2/3\tilde{P}_i\tilde{V}_i^{5/3} + (4/3\tilde{V}_i^{-1/3} - 1))}\right\}\right]. \tag{20}$$

Heat capacities ratio (γ) for the mixture can be calculated using the following relation:

$$\gamma = \frac{\beta_{\text{T}}}{\beta_{\text{s}}}. \tag{21}$$

3. Results and discussion

The density, ultrasonic velocity, the thermal expansion coefficient and heat capacities ratio of a binary liquid mixture nitrobenzene + benzene at three temperatures viz. 293.15, 303.15 and 313.15 K, and pressures 0.1, 5 and 10 MPa have been computed over the entire composition range using a reduced equation of state developed for high pressures, vide equations (8) and (9). Experimental values of the density and ultrasonic velocity for the pure components and a binary mixture have been taken from the study of Takagi and Teranishi [16]. The thermal expansion coefficient (α), isothermal compressibility (β_T) and heat capacity (C_P) values of pure components have been calculated using experimental values of density and ultrasonic velocity, and are reported in table 1. Theoretical results obtained from the employed method have been compared with the experimental findings.

A reduced equation of state, developed for high pressures has been employed for the theoretical prediction of the density of system under the present study. Variations of experimental and theoretical values of the density vs. pressure are presented graphically in the figure 1 at three temperatures 293.15, 303.15 and 313.15 K. The theoretical values of the density increase with an increase in concentration of the first component of liquid mixture following the similar trend shown by the experimental density values.

Table 1. Various thermodynamic properties for pure components at different pressures and temperatures.

Pressure (P) (MPa)	u (m s^{-1})	ρ (g cm^{-3})	$\alpha \times 10^3$ (K^{-1})	$\beta_T \times 10^{12}$ (cm^2 dyne^{-1})	C_p (J K^{-1} mol^{-1})
Benzene					
$T = 293.15$ K					
0.1	1321.7	0.8792	1.154	93.07	124.21
5.0	1345.9	0.8831	1.142	89.22	128.36
10.0	1369.9	0.8869	1.131	85.63	132.55
$T = 303.15$ K					
0.1	1271.1	0.8685	1.178	100.77	131.50
5.0	1300.4	0.8727	1.163	95.66	134.84
10.0	1327.4	0.8768	1.149	91.24	137.94
$T = 313.15$ K					
0.1	1231.0	0.8578	1.198	107.67	136.46
5.0	1259.4	0.8623	1.182	102.15	139.98
10.0	1281.2	0.8667	1.170	98.03	142.77
Nitrobenzene					
$T = 293.15$ K					
0.1	1471.6	1.2031	0.986	49.42	263.89
5.0	1486.7	1.2060	0.980	48.26	269.30
10.0	1502.4	1.2089	0.974	47.11	274.89
$T = 303.15$ K					
0.1	1438.1	1.1939	0.996	51.50	281.53
5.0	1453.8	1.1969	0.990	50.23	285.25
10.0	1470.1	1.1999	0.983	48.96	289.10
$T = 313.15$ K					
0.1	1403.2	1.1822	1.008	54.03	299.09
5.0	1419.1	1.1853	1.001	52.64	303.24
10.0	1435.6	1.1884	0.995	51.26	307.55

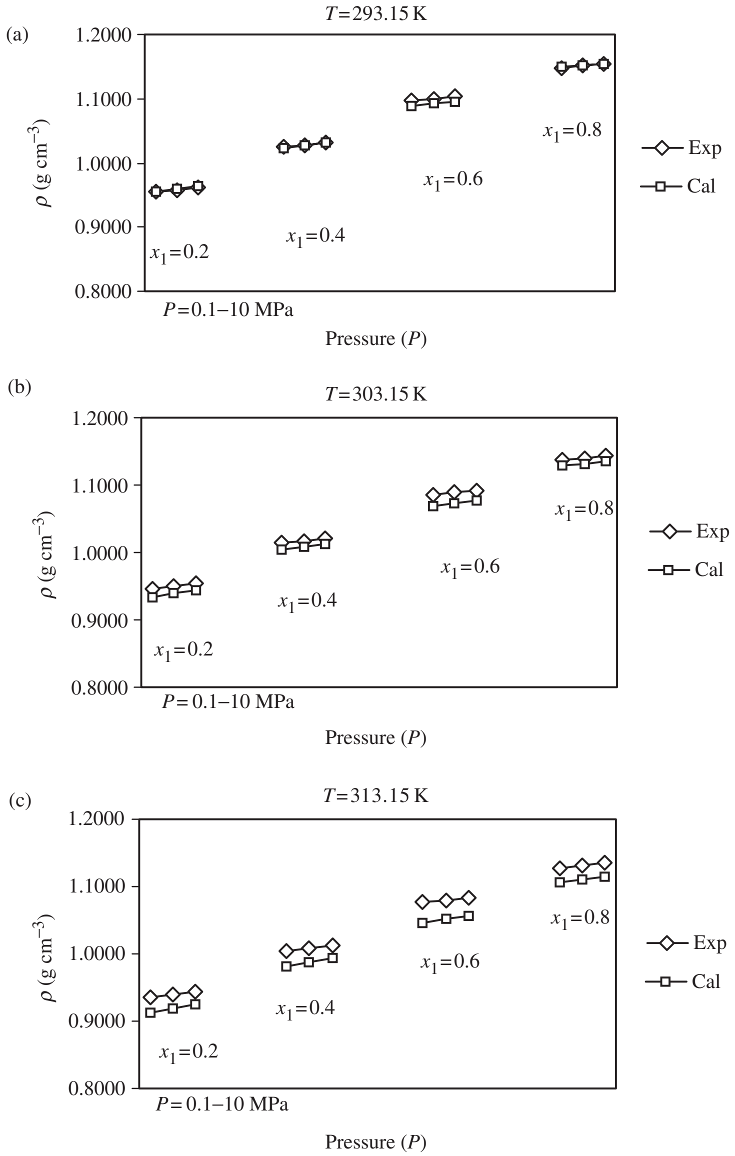

Figure 1. Variation of the density (ρ) of nitrobenzene + benzene with pressures at different temperatures as well as different compositions of nitrobenzene (x_1). (a) $T = 293.15\,\mathrm{K}$; (b) $T = 303.15\,\mathrm{K}$; (c) $T = 313.15\,\mathrm{K}$.

At constant temperature, the values of density increase with an increase in pressure, whereas density decreases with an increase in temperature at constant pressure. Furthermore, deviation between theoretical and experimental values of the density also increase on increasing the temperature. Excellent agreement has been observed at temperature 293.15 K out of the three temperatures under study.

Experimental and theoretical values of ultrasonic velocity increase with an increase in concentration of the first component of the binary liquid mixture. At constant pressure, the values of ultrasonic velocity decrease with an increase in temperature at all the mole

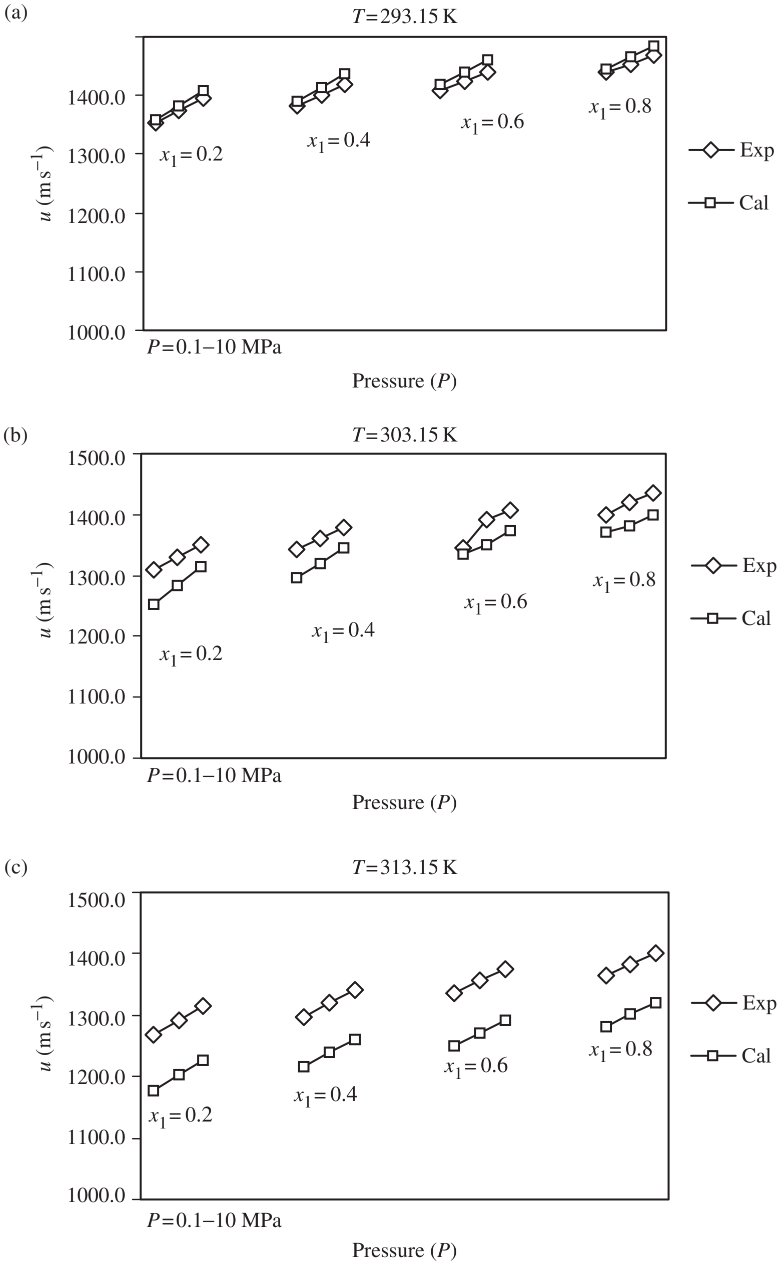

Figure 2. Variation of ultrasonic velocity (u) of nitrobenzene + benzene with pressures at different temperatures as well as different compositions of nitrobenzene (x_1). (a) $T = 293.15$ K; (b) $T = 303.15$ K; (c) $T = 313.15$ K.

fractions (x_1), whereas at constant temperature, the values of ultrasonic velocity increase with an increase in pressure, as observed experimentally. Comparison between theoretical and experimental values of ultrasonic velocity are presented in the figure 2 at three temperatures 293.15, 303.15 and 313.15 K. A close inspection of the figures shows

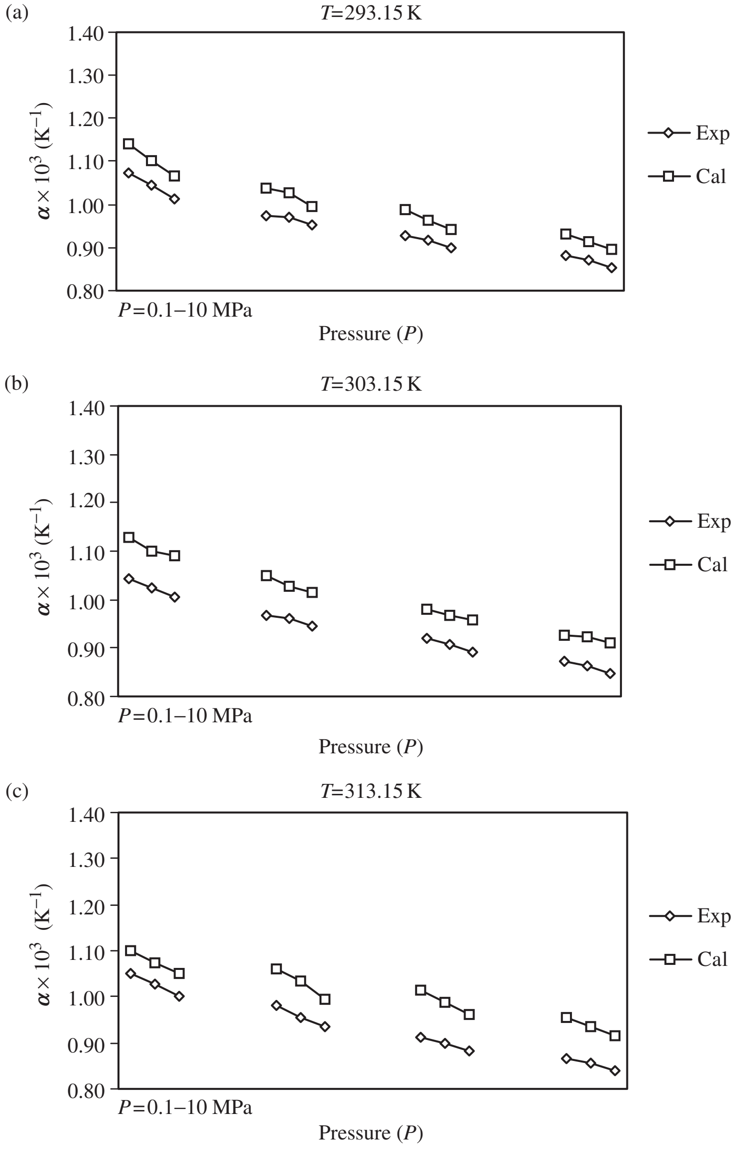

Figure 3. Variation of the thermal expansion coefficient (α) of nitrobenzene + benzene with pressures at different temperatures as well as different compositions of nitrobenzene (x_1). (a) $T = 293.15$ K; (b) $T = 303.15$ K; (c) $T = 313.15$ K.

that there is good agreement between experimental and theoretical results. Here, once again, an increase in deviations between theoretical and experimental values of ultrasonic velocity has been observed with an increase in temperature. The minimum and maximum deviations in ultrasonic velocity have been found at $T = 293.15$ K and $T = 313.15$ K, respectively. Though the deviation is higher at $T = 313.15$ K, the identical graphical trend in experimental and theoretical values of ultrasonic velocity shows the validity of the present approach.

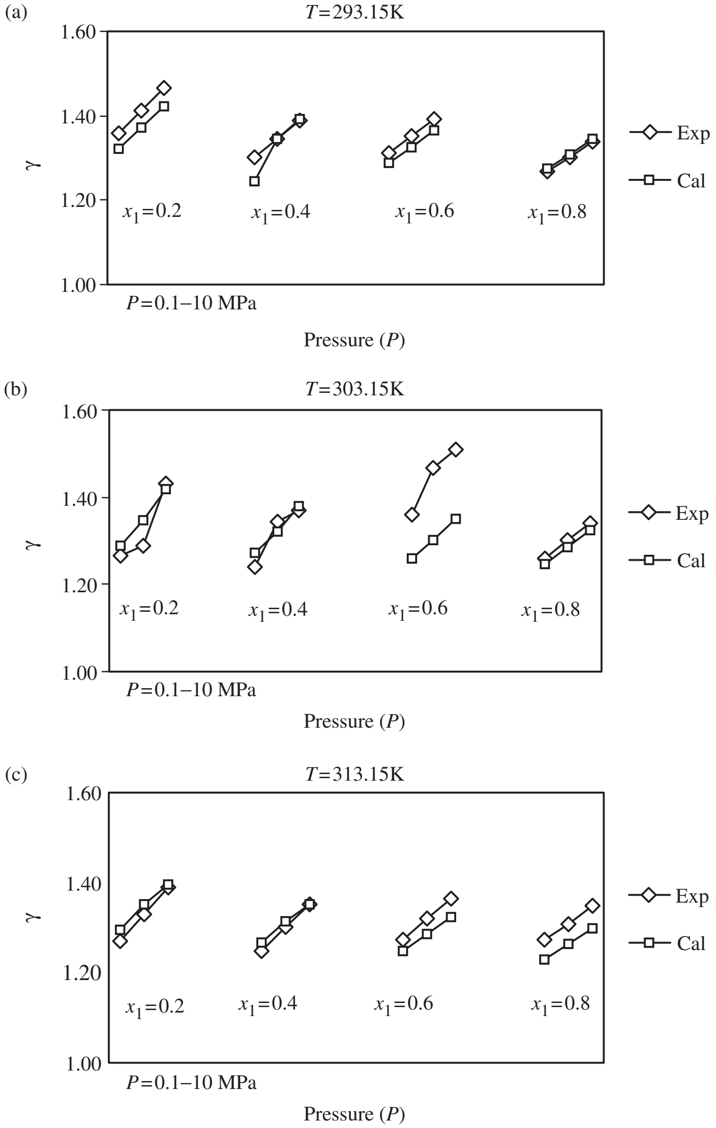

Figure 4. Variation of heat capacities ratio (γ) of nitrobenzene + benzene with pressures at different temperatures as well as different compositions of nitrobenzene (x_1). (a) T = 293.15 K; (b) T = 303.15 K; (c) T = 313.15 K.

The values of thermal expansion coefficient, α, of the binary liquid mixture have been computed using equation (6) for the entire mole fraction range, and are shown graphically along with experimental findings in figure 3. A close graphical observation shows that at constant temperature, values of α decrease with an increase in pressure, and a similar variation in the values of α have been observed with varying temperatures at constant pressure. At constant temperature and pressure, as the concentration of the first component is increased, thermal expansivity values are found to decrease. Identical graphical trends in experimental and theoretical values of α have been observed.

The values of heat capacities ratio increase with an increase in concentration of the first component at every temperature and pressure. Figure 4 shows the variation of heat capacities ratio vs. pressure at the three temperatures 293.15, 303.15 and 313.15 K. Graphical trend between experimental and theoretical values are identical and very close to each other at most points. On increasing the temperature, deviations in heat capacities ratio is observed in a similar manner, as obtained in the case of both density and ultrasonic velocity.

4. Conclusion

The results of the computation of the density, ultrasonic velocity, the thermal expansion coefficient and heat capacities ratio of a binary liquid mixture, obtained by the reduced equation of state derived for elevated pressures and varying temperatures, indicate that this reduced equation of state can successfully be used to predict various thermodynamic properties of liquid mixtures at elevated pressures and varying temperatures. Thus, this work is of great importance to predict theoretically various thermodynamic properties of liquid mixtures at elevated pressures in the light of the fact that data of thermodynamic properties of liquid mixtures at elevated pressures are rarely available.

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