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Estimation of some important thermodynamic and thermophysical properties of ternary liquid mixtures from ultrasonic velocity and density data

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ABSTRACT

An attempt has been made to determine internal pressure and energy of vaporization and their corresponding excess parameters from experimentally determined values of ultrasonic velocity and density for four ternary liquid mixtures at 298.15 K. Furthermore, enthalpy of vaporization, pseudo Gruneisen parameter, cohesive energy density and solubility parameters for the four multicomponent liquid mixtures under investigation have also been computed to get a better understanding for the intermolecular interactions taking place thereof.

1. Introduction

The aspect of cohesive forces is of primary importance in the study of liquid state. One liquid system differs from the other essentially due to its relative degree of cohesion which produces a pressure directed inwards making a dissolved solute experience an inward pressure of 10^3 to 10^4 atmosphere. Thus, in a way, internal pressure is a resultant of forces of attraction and repulsion between the constituents in a liquid medium and provides an estimate of the pressure directed inwards by cohesion. The role of internal pressure in solution thermodynamics was recognized long by Hildebrand [1] following earlier work of van Laar [2]. Over the years, it has been found to be an important tool in the study of several chemical reactions and in the investigation of molecular interactions. Internal pressure data of liquid are highly useful in understanding molecular interactions, internal structure and the clustering phenomenon. Successful attempts have been made by several investigators [3–6] to calculate theoretically internal pressure of pure, binary and multicomponent liquid mixtures. Hildebrand et al. [1] proposed the concept of cohesive energy density, which is the energy of thermal vaporization from the liquid state to the ideal gas state per unit volume of fluid. The significance of solubility parameter (δ) and its correlation with internal pressure (P_{int}) have also been discussed by several workers [7–9]. Another equally important parameter, the energy of vaporization (ΔE_{vap}), can also be estimated directly from internal pressure [10,11].

In the theory of lattice dynamics, the Gruneisen parameter has also been found to be an important tool to study the thermodynamic and other properties of solid crystalline lattice [10,12]. The concept of anharmonicity of the lattice is characterized by Gruneisen parameter which is basically a diagnostic parameter. It is a well established fact that liquids support a quasi-crystalline model for their structure, the lattice nature being increased at high pressure and low temperature. Its pseudo counterpart, pseudo Gruneisen parameter (Γ) has been found to be suitable to investigate the internal structure, clustering phenomenon and other quasi-crystalline properties of liquids and liquid mixtures [10,12,13]. However, in order to get an in-depth picture of the various interactions between the components, especially in multicomponent systems, it is of utmost importance to also compute the corresponding excess parameters. In this regard, extensive work has been carried out on excess thermodynamic and thermophysical parameters like excess internal pressure (P^E_{int}) [3,4,10–12,14], excess enthalpy [15–20] and excess energy of vaporization [11] and is still in progress. Since data on sound velocity and density offers a convenient method for determining certain thermodynamic and thermophysical parameters not easily obtained by other means, extensive work has been done for investigating liquid state properties through analysis of ultrasonic propagation parameter

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Table 1
Thermodynamic parameters of the pure liquid components at 298.15 K.

Components	$a \times 10^{-3}$ K^{-1}	β_T T Pa^{-1}	ρ kg m^{-3}	C_P J mol^{-1} K^{-1}	P_i MPa	Γ	$\delta \times 10^{-2}$ $(KJ\ m^{-3})^{1/2}$	ΔE_{vap} KJ mol^{-1}	CED KJ m^{-3}	u m sec^{-1}
n-Heptane	1.2589	142.4	679.5	224.78	266.88	0.741	5.13	38.84	26.33	1131.0
n-Hexadecane	0.9020	85.7	770.1	500.21	317.96	0.402	5.60	92.27	31.38	1488.7
Cyclohexane	1.2150	114	773.8	156.84	321.98	1.010	5.63	34.56	34.56	1253.0
Isooctane	1.1920	151.2	687.8	242.49	238.16	0.667	4.84	39.03	23.50	1088.5
Chlorobenzene	0.9820	75.5	1100.9	153.78	392.93	1.160	6.22	39.64	38.77	1241.4
1-Chloronaphthalene	0.7020	48.8	1187.8	212.60	434.58	1.150	6.54	58.66	42.88	1414.6

and density and to correlate it with other physical and thermodynamic parameters like internal pressure (P_{int}), energy of vaporization (ΔE_{vap}), cohesive energy density (CED) and solubility parameter (δ). All these properties have been studied for binary liquid mixtures on the basis of statistical mechanical theories [21]. Due to scarcity of data on ternary and higher multicomponent liquid mixtures, an attempt has been made to determine the aforementioned parameters with the help of experimentally determined values of ultrasonic velocity (u) and density (ρ) at 298.15 K for four ternary mixtures viz.,

I. Chlorobenzene (1) + cyclohexane (2) + n-heptane (3).
II. Chlorobenzene (1) + cyclohexane (2) + isooctane (3).
III. Chlorobenzene (1) + isooctane (2) + n-heptane (3).
IV. Chloronaphthalene (1) + isooctane (2) + n-heptane (3).

The present investigation is a continuation of our earlier work [22], whereby ultrasonic velocity and density of the four aforementioned liquid mixtures were determined at 298.15 K and excess thermodynamic properties were calculated along with excess volume. The idea behind the selection of the aforementioned systems lies in studying the influence of a polar component (chlorobenzene or chloronaphthalene) on the mixture of alkanes (viz., components 2 and 3 of the ternary system). The results and discussions have been done taking into consideration the size, shape, polarity, chemical nature and flexibility of the polar molecule and the induced conformational changes in the alkane mixture. For a better picture, the excess parameters have also been computed viz., excess enthalpy and excess internal pressure. The main aim of the study is to provide information about the like and the unlike interactions by making use of the experimental and computed parameters and their excess counterparts. By taking into account the parameters computed in the present work together with the properties determined earlier [22], a very comprehensive picture emerges regarding the various interactions involved in the variation of the properties with the variation in the mole fractions.

2. Theoretical

Internal pressure has been computed with the help of the equation:

$$P_{int} = \left(\frac{\alpha T}{\kappa_T}\right) \tag{1}$$

where all the symbols have their usual meaning.

For the ternary liquid mixture, internal pressure has been evaluated by,

$$(P_{int})_{mix} = \left(\frac{\alpha_{mix} T_{mix}}{\kappa_{Tmix}}\right) \tag{2}$$

where α_{mix} and κ_{Tmix} represent coefficient of thermal expansion and isothermal compressibility of the ternary liquid mixtures respectively. The ideal internal pressure has been computed by employing the equation

$$P_{int}^{\ id} = \sum_{i=1}^{n} (P_{int})_i . x_i \tag{3}$$

where x_i is the mole fraction and $(P_{int})_i$, the internal pressure of the i^{th} component respectively in a n-component liquid mixture.

The excess internal pressure, $(P_{int})^E$ is given by,

$$P_{int}^{\ E} = (P_{int})_{mix} - P_{int}^{\ id} = (P_{int})_{mix} - \sum (P_{int})_i . x_i . \tag{4}$$

In order to extend the utility of Gruneisen parameter for structural studies of liquids, its pseudo counterpart is defined as

$$\Gamma = \frac{\alpha u^2}{C_p} \tag{5}$$

where u is the ultrasonic velocity, and C_p, the heat capacity at constant pressure. Suitable rearrangement gives

$$\Gamma = \frac{\gamma - 1}{\alpha T} \tag{6}$$

where γ is specific heat ratio.

The energy of vaporization can be obtained by the expression

$$\left(\Delta E_{vap}\right)_{mix} = \left(\frac{\alpha_{mix} T}{\kappa_{Tmix}}\right) . V = (P_{int})_{mix} . V \tag{7}$$

where V is the molar volume.

Thus excess energy of vaporization can be determined by

$$\left(\Delta E_{vap}\right)^E = \left(\Delta E_{vap}\right)_{mix} - \left(\Delta E_{vap}\right)_{id} \tag{8}$$

where $(\Delta E_{vap})_{id}$ is the ideal energy of vaporization given by

$$\left(\Delta E_{vap}\right)_{id} = (P_{int})_{id} . V_{id} \tag{9}$$

where V_{id} is the ideal volume of mixing which is additive over the mole fraction.

Further the cohesive energy density (CED) is given by

$$CED = n \left(\frac{\Delta E_{vap}}{V}\right) \tag{10}$$

where n approaches unity for non-polar liquids.

This parameter has been employed for correlation of the solubility parameter as

$$\delta = \sqrt{CED}. \tag{11}$$

In order to calculate heat of vaporization following equation has been used which involved energy of vaporization and is given by

$$\Delta H_{vap} = \Delta E_{vap} + RT \tag{12}$$

where all the symbols have their usual meaning.