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Investigation of molecular interactions & prediction of calorimetric potentials of a binary liquid system at T = 308.15 K: An insight from physicochemical parameters

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Abstract

Excess values of surface tension/isothermal compressibility/internal pressure/free volume/enthalpy/entropy and Gibbs energy are computed using the experimentally measured density (ρ) and ultrasonic speed (*u*) for the binary liquid mixtures of *dimethyl sulphoxide* with *acetophenone* at $T = 308.15$ K. Activity coefficients and excess chemical potential are estimated using Morgules, Porter, Van laar and Wilson equations. The studied system shows departure to the ideality indicating the presence of weak interactions. Further, PFP theory is tested to correlative the experimental excess molar enthalpy. Moreover, PFP theory is extended to compute different derivatives of thermodynamic potentials rather calorimetric measurements. The present investigation also encompass of assessment of the acoustic non-linearity parameter **(B/A)** along with computation of cohesive energy, **ΔA**, Van der Wall's constants (**a,b**), distance of closest approach (**d**).

Keywords: Molecular interactions; PFP theory; Thermodynamic potential derivatives; Activity coefficients; Excess chemical potentials

1. Introduction

For an adequate choice of binary mixture for the possible application, the knowledge of their interaction with each other is an indispensable feature for forecasting the reactivity and selectivity. The practical application of mixed solvents rather than single solvent in biological and industrial process has been established all over the world as they provide an extensive alternative of solutions with appropriate properties [1].

It is well known fact that ultrasonic speed, density and related thermodynamic factors are helpful as well as needed for characterizing thermodynamic and physicochemical features of binary liquid mixtures for instance molecular dissociation and association. These physicochemical investigations are used to grip the mixtures of hydrocarbons etc. In the chemical industry, knowledge of the thermodynamic properties of binaries is essential in the design involving chemical separation, heat transfer, mass transfer and fluid flow. Further, the advantage of knowledge of physicochemical properties over calorimetric experiments in binary liquid mixtures has relevance in theoretical and applied

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areas of research, and such results are frequently used in many chemical and industrial processes. Knowledge of the dependence of these properties on the composition, temperature and pressure is important in understanding the intermolecular interactions and phase behavior of fluids. Very large number of parameters can be computed with physicochemical properties and it show its impact in acoustics which goes from underwater acoustics to biology and medicine. These are used to compute microscopic to macroscopic level characteristic properties pertinent to binary liquid in study. In spite of many precautions, Calorimeters lost heat to surroundings which cannot be eradicated completely. This leads to an error in measurements.

In continuation of our research [2–6], an attempt has been made to (i) evaluate certain excess parameters (ii) testing of PFP statistical theory values of excess enthalpy with the experimental values (iii) Computation of differentials of thermodynamic potentials (iv) computation of non-linear parameters with molecular properties (v) prediction of activity coefficients/excess chemical potentials. Thus the aim of the article is to predict the above mentioned values with physicochemical properties rather calorimetric experiments. For this, experimental data from our paper [7] pertinent to the binary system *dimethyl sulphoxide* (DMSO) with *acetophenone* (*AP*) at $T = 308.15$ K has been taken. The liquids under investigation *DMSO* and *AP* have been chosen on the basis of their medicinal and industrial applications. These purposes have significantly motivated the requisite for extensive information on the thermodynamic, acoustic, and transport properties of these chemicals and their mixtures [8].

The study of DMSO is imperative because of its deployment in an extensive range of applications in medicine [9–11]. Acetophenone is generally used as flavoring in many cherry/almond/honeysuckle/jasmine/strawberry flavored sweets, chewing gum and drinks. Study on thermo physical properties data of binary liquid mixtures containing ketones has attracted considerable interest in the literature [12–15]. Literature survey reveals that Radhamma et al. reported speed of sound data and density for binary mixtures of DMSO and certain ketones at 303.15 K [16].

1.1. Experimental section and theory

The experimental details and the procedure for measuring u and ρ have been described in our earlier papers [2–6]. Specific heat (Cp) values for pure liquids [17,19]are taken directly from literature and experimental with literature values pertinent to density/speeds of sound for pure [18,20] are tabulated in Table 1. Experimental values with derived excess parameters are tabulated in Table 2 at $T = 308.15$ K. Various formulae used in this article are as follows.

Surface tension (σ_s) is given by

$$\sigma_s = \left(6.3{*}10^{-4}\right){*}u^{\frac{3}{2}} \Big/ \left(10^{-3}\mathrm{Nm}^{-1}\right) \tag{1}$$

Internal pressure (π_i) is a fundamental property of a liquid and it quantifies the change in the internal energy of liquid or liquid mixtures. It is a measure of cohesive or binding forces between the solute and solvent molecules. Mathematically,

$$\pi_i = \left(\frac{\partial U}{\partial V}\right)_T \tag{2}$$

where, U is the internal energy, V the volume and T the temperature.

By thermodynamic relation,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \tag{3}$$

where, P is the external pressure and

$$\left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_V = \frac{\alpha_\mathrm{P}}{k_\mathrm{T}}, \tag{4}$$

here, α_p and k_T are the isobaric thermal expansion coefficient and isothermal compressibility respectively.

Isobaric thermal expansion coefficients for pure liquids are computed from the data available from the literature [17,21] by

$$\alpha_p = \frac{1}{V_m}\left(\frac{\partial V_m}{\partial T}\right)_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p = -\left(\frac{\partial \ln \rho}{\partial T}\right) \tag{5}$$

Since the experiment is carried out at single temperature, the isobaric thermal expansion coefficient for pure (α_p) are computed from literature and for the mixtures $(\alpha_{p,mix})$ (as an approximation) at different mole fractions is evaluated by the formula $\alpha_{p,mix} = (\phi_i\alpha_{p,1} + (1-\phi_\mathrm{i})\alpha_{p,2})$ where $\alpha_{\mathrm{p},1}$ and $\alpha_{\mathrm{p},2}$ are the isobaric thermal expansion coefficients of pure

Table 1
Comparison of experimental values of density (ρ), ultrasonic speed (u) with the corresponding literature values and literature values of specific heat (C_P) of pure liquids at $T = 308.15$ K.

Liquid	C_P/ (J/K mol) Literature	ρ/(kg/m^3) Present work	Literature	u/(m/s) Present work	Literature
DMSO	152.90 [17]	1084.60	1084.7 [18]	1455.80	1456.0 [18]
AP	126.26 [19]	1013.35	1013.5 [20]	1441.10	1441.2 [20]

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