

*Review Article*

A Review on Thermodynamics of Mixtures- Studies and Investigations

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ABSTRACT

The non-ideal liquid and gas mixtures need to be studied for extent of non-ideality. The measurements of excess properties can be carried out experimentally by utilizing various measurable properties. Also these can be estimated by various model equations. Density, excess molar volume and apparent molar volume for a binary mixture are major properties. Thermodynamics can be used as a tool to determine many volumetric properties like this. Factors such as temperature, pressure affect the thermodynamic and volumetric properties considerably. These are large number of properties of a mixture such as thermal expansion coefficients, excess thermal expansion coefficients, and isothermal coefficients of pressure excess molar enthalpy, partial molar volumes, partial molar volumes at infinite dilution, partial excess molar volumes, and partial excess molar volumes at infinite dilution which have thermodynamic significance. Current review summarizes research and studies on thermodynamics of mixtures

Key words: Infinite dilution, excess properties, enthalpy, partial properties.

INTRODUCTION

Thermodynamics of mixtures is very important in the processes involving large entropy change. The non-ideal liquid and gas mixtures need to be studied for extent of non-ideality. The measurements of excess properties can be carried out experimentally by utilizing various properties. Also these can be estimated by various model equations.

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A REVIEW ON THERMODYNAMICS OF MIXTURES- STUDIES AND INVESTIGATIONS

Radovia et. al. used experimental densities and excess molar properties to estimate thermal expansion coefficients, excess thermal expansion coefficients, and isothermal coefficients of pressure excess molar enthalpy, partial molar volumes, and partial molar volumes at infinite dilution, partial excess molar volumes, and partial excess molar volumes at infinite dilution. [1] They performed calculations for the binary systems of cyclohexylamine with 1-propanol or 1-butanol or 2-butanol or 2-methyl-2-propanol. From their studies, they also provided a volumetric data, which can be used to study influence of temperature, chain length and position of hydroxyl group in the alcohol molecule on the molecular interactions. Patil et. al. reported density, excess molar volume and apparent molar volume for a binary mixture of ethanol, propane 2-ol and 2-methyl propan-2-ol with

propan-2-amine. [2] In their investigation, they observed that with increase in the chain length of alkanols, there was increase in V^E values. They also observed that with increase in temperature, the V^E values become more negative. They observed considerable difference between the molar volumes of alkanol (1) + Propan-2-amine (2) systems at 298.15 and 308.15. It was also found that dissociation of self-associated alkanol decreased due to breaking of H-bonds.

Hus et. al. investigated the properties of methanol and water-methanol mixtures. [3] For this purpose, they used a simple isotropic water model and its coarse-grained extension. In their work, they also carried out Monte Carlo simulations, which showed that the model was able to correctly describe the thermodynamic properties of methanol. It was also adequate for describing the density dependence of water-methanol mixtures upon temperature and composition, and excess properties of mixtures. Maximo et.al. studied solid liquid equilibrium. [4] They carried out investigation on Triacylglycerols and fatty alcohols, which are widely used in the formulation of cosmetic, pharmaceutical and food products. In their investigation, they used differential scanning calorimetry (DSC) and optical microscopy for evaluating the solid-liquid phase diagrams of two binary systems composed of triolein + 1-hexadecanol and triolein + 1-octadecanol. In their work, they solved phase equilibrium equation by using MATLAB. For liquid-phase activity coefficients, they used Margules equation (two- and three-suffix) and the UNIFAC model (original and modified Dortmund model). Abrams and Prausnitz carried out an investigation on statistical thermodynamics of liquid mixtures. [5] Their investigation was aimed at deriving a new expression for the excess gibbs energy of partly or completely miscible systems. They found that the UNIQUAC equation adequately described both vapor-liquid and liquid-liquid equilibria for binary and

multicomponent mixtures containing a variety of nonelectrolyte components. Studies were carried out by Ganesh and Srinivas on thermodynamic properties of ammonia-water mixture. [6] Their studies were about ammonia-water mixture up to 100 bar for power application systems. In their work, they developed a new MATLAB code to calculate the thermodynamic properties. They prepared charts such as enthalpy-concentration, entropy-concentration, temperature-concentration and exergy-concentration charts.

Ibrahim et. al., in their work have carried out investigation on the accuracy of the extended corresponding states equation of state SPUNG. [7] They used various reference fluids for the density and vapour liquid equilibrium (VLE) calculations of the CO₂ - water system. They carried out evaluation by comparing the numerical prediction with experimental data. Their results also indicated that the heavier the reference fluid was, the larger the range of densities the EoS can represent. These studies indicated very small impact of the reference fluid selection on the predictions of the VLE solubilities.

The studies were carried out by Dhar et. al., for determination of properties such as transition temperature, transition enthalpy and transition entropy for the binary mixtures or heptyloxybenzoic acid (HOBA) and decyloxybenzoic acid (DORA) in different mole ratios. [8] They observed that the peak transition temperature depended on the scanning rates like pure samples. Their studies also indicated that the transition temperatures recorded in the heating cycles were higher than those recorded in the corresponding cooling cycles. According to Ganesh and Srinivas, binary mixtures additionally need mixture concentration to solve thermodynamic properties. [9] They developed a flowchart to understand the computations of the properties. They used MATLAB computer code for generating the thermodynamic properties for ammonia-water mixture. According to them, use of

these correlations reduced the need of tedious iterations used in fugacity method.

Privat et. al. carried out investigation on the thermodynamics of alcohols-hydrocarbons mixtures. [10] In their studies they discussed the methodology and the results of the multi-step. They carried out multistep studies. In the first step, they pointed out the strongly non-ideal behavior of ethanol-naphtha blends. In the second step they provided general guidelines for preparing mixtures of gas oils with industrial alcohols. Minimum Miscibility Temperature (MMT) data works as important guideline in this. Heintz studied recent developments in thermodynamics and thermo-physics of non-aqueous mixtures. [11] Their emphasis was on non-ionic mixtures. They found that there is lack of systematic knowledge of many properties and activities of ionic liquids. More results on gas solubilities at ambient and elevated pressures are required.

Studies were carried out by Karunakar et. al. on measurements of Ultrasonic velocity and density for binary solutions. [12] By using properties such as adiabatic compressibility, molar volume inter molecular free length, they explained the molecular interaction between the components of these mixtures. Their studies indicated that an increase in compressibility keeps the molecules to a large distance. This in turn results into an increase in intermolecular free length. Ternary liquid system containing toluene, 1-dodecanol and cyclohexane was studied by Mehra et.al. [13] They determined sound speed for this mixture as a function of composition and temperature. They used this data to evaluate parameters like molar volume, molar free volume, isentropic compressibility, intermolecular free length, acoustic impedance and internal pressure. Also these derived properties were used for evaluating excess properties. They fitted the excess property data into Redlich-Kister polynomial equation for obtaining smoothing coefficients and their standard deviations.

CONCLUSION

Thermodynamics can be used as a tool to determine many volumetric properties. Factors such as temperature, pressure affect the thermodynamic and volumetric properties considerably. These are large number of properties of a mixture such as thermal expansion coefficients, excess thermal expansion coefficients, and isothermal coefficients of pressure excess molar enthalpy, partial molar volumes, partial molar volumes at infinite dilution, partial excess molar volumes, and partial excess molar volumes at infinite dilution which have thermodynamic significance.

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