IN THE NAME OF GOD

DETERMINATION OF ISM EOS FOR LIQUIDS FROM SURFACE ENERGY: A SIMPLIFIED PROCEDURE FOR MIXTURES

BY

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Dedicated to

My dearest ones

My parents and my wife

ABSTRACT

Determination of ISM Equation of State for Liquids from Surface Energy: A simplified procedure for Mixtures.

BY

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To determine the ISM equation of state, we have established a new reduced temperature scale $T_{E^s}^* = T_{E^s}^*\left(T; E^s, \rho_f\right)$, where T is the absolute temperature, E^s and ρ_f are surface energy and the liquid density at the freezing temperature, respectively. Reduced second virial coefficient B_2^* follows a promising corresponding states correlation for a number of spherical, linear and long chain hydrocarbons liquids, allowing prediction of the ISM equation of state can be determined from only two scaling constants E^s and ρ_f.

The method we present is advantaged over previous methods in that E^s state independent and it can be used to simplify the application to mixtures. That is only two (rather than three) scaling constants E^s and ρ_f of the admixing partners must be combined. On the other hand, E^s

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involves the surface entropy and thus, T_E^*'s turns out to represent a real thermodynamic quantity that is concerned in theoretical investigation. The applications to the compressed and vapor-saturated liquids of wide range of accenteric factors and their mixture result in densities within 5% of the experimental values.

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1-1 Introduction

Reliable values of physical properties of materials are required for the design of industrial reactors at operating condition. An enormous amount of data has been collected and correlated over the years, but the rapid advance of technology into new field seems always to maintain a significant gap between demand and availability. The engineer is still required to rely primary and common sense experience, and a variety of methods for estimating physical properties. From over 100 years ago, many equation of states (EOS) have been used to estimate or predict the thermodynamic properties of compressed liquids [1-5]. An equation of state is a relation between pressure P, volume V, and temperature T which defines a surface in the P-V-T coordinate.

The equation of state plays a central role in the treatment of the thermodynamic properties of fluid, particularly of the mixture. An equation of state has several advantages: it permits interpolation of experimental data, it facilities thermodynamic calculation involving integration and differentiation, it provides a concise summary of large mass of data, and it provides a point of departure for the treatment of the thermodynamic

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properties of mixtures.

A suitable P-V-T equation of state can be used to evaluate many important properties of pure substances and mixtures, such as: 1) Densities of liquid and vapor phases, 2) Vapor pressure, 3) Critical properties of mixtures, 4) Vapor-liquid equilibrium relation, 5) Deviation of enthalpy and entropy from ideality.

An analytical equation of state is an algebraic relation between pressure, temperature, molar volume. Three analytical equations of state are virial equation, cubic equations of state, and Generalized Benedict-Webb-Rubin equations. The virial equation of state is a simple equation, and it can represent only modest deviations in the vapor phase from ideal-gas behavior. Over limited ranges of temperature and pressure, and they remain relatively simple form a computational point of view. The Benedict-Webb-Rubin equation, which is applicable over broader range of temperature and pressure than are the cubic equation, but it is also computationally more complex.

Every proposed equation of state has more or less sever limitations in regard to the kinds of substances that it could represent, the range of operating conditions, or the phases. Some equations are better for predicting volumetric properties, others for phase equilibrium, and others for enthalpy or entropy derivations. There is a little hope that a universal equation of state of moderate complexity ever will be discovered.

Equations of state for fluids can be broadly classified into two

categories: empirical and theoretical, although some equations, with a best modest claim to a theoretical basis, are sometimes called semiempirical.

Empirical equations are useful primarily for presenting experimental data in analytical form, thereby facilitating integration and differentiation of the data to obtain desired thermodynamic properties. They are quite accurate in making interpolative calculation of the data from which they have been evaluated. Such evaluations are usually made by regression techniques requiring a considerable amount of experimental data to minimize errors in interpolative calculations. These equations of state generally are specific to a given material. They are usually not easily generalized [6] such that accurate calculation can be made for expressing the compressive properties of liquids have been proposed. The well-known original one is Tait's equation [7].

One of the successful empirical equations of state is the Benedict-Webb-Rubin (BWR) equation [8,9], which contains eight adjustable parameters. This equation was used for P-V-T Properties of the gaseous or liquid phase, critical properties, vapor pressure, and latent heat of vaporization of hydrocarbons and their mixtures. Many empirical equations of state, in the form of modified versions of Tait's equation have been proposed for the correlation and prediction of the P-V-T properties of compressed liquids [1-3,5,10,11].

On the other hand, theoretical or semiempirical equations of state do not require vast amount of experimental data for their evaluations.

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Using only a few characteristic bits of experimental data (for example: critical pressure, critical temperature, critical compressibility factor, latent heat of vaporization at normal boiling point, etc.), these equations allow predictive calculations of properties at other temperatures and pressures. Such calculations naturally lack the accuracy of the regression-spawned equations of state. Yet, for calculating the properties of materials for which reliable experimental data are scarce, the theoretical and semiemperical equations are definitely useful.

Four main types of theoretical equation of state may be recognized: those obtained from the radical distribution function [12], statistical mechanics [13], the perturbation theories [14-17], or combination of the preceding three types [18].

In principle, the radial distribution theory is based on the many-body nature of the fluid. In this theory, the pair correlation function or the radial distribution function, $g(r)$ plays the key role. This function shows the distribution of molecules around a given molecule in terms of r, the distance from that molecule. If the potential between molecules of the fluid is assumed to be pairwise additive, then all thermodynamic quantities of the system can be obtained in terms of $g(r)$ [13]. A notable point is that, the radial distribution function can be determined by x-ray diffraction studies [19]. However, because of the complexity of the results obtained by using the radial distribution function, the use of such results is limited.

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1-2 Historical review

The best known example of an equation of state is ideal gas equation of state $P = \rho RT$ where P is the pressure, ρ is the density, T is the absolute temperature, and R is the gas constant. The above equation tells us that of the three state functions P, ρ, and T only two are independent.

Real gases, or vapors, approximate to ideal gases only if the density is low, i.e.; the volume is so great that the molecules are, on average, a long way apart from each other. As the gas is compressed this average distance decreases and the effects of the intermolecular forces become important. The ideal gas equation of state must then be replaced by an equation, which attempts to allow for these forces.

The earliest and most famous attempt to allow for the intermolecular forces is that of J.D.van der Waals [20], who modified the volume and pressure terms in the ideal gas equation to allow for the repulsive and attractive forces, respectively. van der Waals equation of state is

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \tag{1-2.1}$$

where a is a measure of the strength of the attractive force between a pair of molecules and b is the excluded volume. Since the time van der Waals put forward his equation, many other equations of state of state have been

proposed in attempt to improve general agreement with experiment.

The equations of state are raised directly from the analyses of the experimental data and are refered to empirical equation of state (EOS). Empirical equations of state are useful primarily for presenting experimental data in analytical form, thereby facilitating integration and differentiation of the data to obtain desired thermodynamic properties.

There have been many attempts over the years to produce modifications of the van der Waals equation having a greater accuracy; some of the better known ones are those of **Dieterici [21]**, **Bettie-Bridgman [22]**, **Bennedict-webb-Rubin [8]**, and **Redlich-Kwong [23]**. Such equations are widely used in engineering applications.

The equations of state that are raised from analysis of system, relying on a fundamental theoretical basis, are referred to as theoretical EOS. Among those via statistical mechanics are the virial equation of state [13], and those obtained from the radial distribution function [13], and the perturbation theories [18].

A number of modifications of the **van der Waals** equation have been made. A highly successful one is due to **Redlich and Kwong in (1949) [23]**, and more recent ones to **Soave in (1972) [24], Peng and Robinson in (1976) [25],** and **Peneloux et al. in (1982) [26]**. These equations are cubic in density whose parameters are basically expressible in terms of critical properties but include modification for temperature and another property such as critical compressibility or accentric factor.