



Predicting solubility parameter of molecular fluids



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ABSTRACT

A molecular thermodynamic-based method has been previously developed by Mansoori-Oghaz et al., (J. Solution Chem., 42 (2013) 544–554) to predict the solubility parameters of normal alkanes from methane to decane. The novelty of the present method is to use the effective soft-sphere (d) diameter rather than the hard-sphere (σ) one to achieve a more realistic model for predicting the solubility parameter of molecular fluids. In the present study, the aim is to assess the performance of Lennard–Jones (12–6) parameters obtained from the second virial coefficients instead of transport properties using inversion method. Our predicted results revealed that, this work outperformed the preceding one. The calculated values of solubility parameter were used to predict several saturation properties including enthalpy of vaporization and saturated vapor–pressures with uncertainty equal to $\pm 5.24\%$. In this study, a new corresponding states correlation has also been developed for determining the second virial coefficients, B_2 of polar molecular fluids such as refrigerants by the help of liquid density and solubility parameter, both at normal boiling point. The uncertainty of the correlated values of B_2 was of the order of $\pm 15.64\%$.

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1. Introduction

The applications of the solubility parameter in chemical, petroleum and polymer engineering industries have been cleared up along the past 50 years. Selecting the best solvent for a particular industrial purpose is one of the most imperative concepts among the chemists and chemical engineers. Scatchard [1] was the first to introduce a parameter, later named as solubility parameter by Hildebrand and Scott [2] which resulted in defining a solvent affinity to solve a solute. This theory was then developed by Hansen [3,4] who stated the various applications of the solubility parameter varying from coating and paint technologies to complex extraction operations. For instance, the supercritical extraction of a solute from a solvent needs a careful and reliable measurement or calculation of the solute solubility [5]. The solubility parameter defines not only the solubility of a solute in solvents but also it demonstrates its affinity to different surfaces which contributes to a better dispersion and adhesion [6]. Under these circumstances the development of theoretical and empirical approaches for the estimation of the solubility parameters can be highly useful to achieve convenient and reliable methods for calculating the Hildebrand and Hansen solubility parameters and determine the effects of pressure and temperature on this property. So far, many efforts have been made to calculate the solubility

parameter. Fedors [7] has presented a correlation to estimate some liquid molar volumes along with their solubility parameters. An equation of state approach was provided by Lozada and Del Rio [8]. They used the Carnahan–Starling [9] EOS to estimate the one-component (Hildebrand) solubility parameter for five substances in their sub-critical regions.

Several studies have been done to show the applications of the group contribution [10,11] methods for calculating the solubility parameters. Further, a method based on lattice fluid theory was developed by Panayiotou [12] in order to estimate the hydrogen bonding component of the three-component (Hansen) solubility parameters.

Allada [13] also evaluated the Hildebrand solubility parameter (HSP) of some supercritical fluids by applying the internal energy of a supercritical gas. Gharagheizi et al. [14] modified the Hansen sphere model to omit the errors of the model predictions. They expressed the whole effects of this method on the values of the solubility parameter. A model based on an equation of state describing the partial solubility parameters was presented by Stefanis et al. [15]. The latest EOS approach was done by Zeng et al. [16] who used the PC SAFT (perturbed-chain statistical associating fluid theory) equation of state for calculation of the HSP of n-alkanes and 1-alcohols. In addition, the relations between the temperature and internal pressure (π_T) with the solubility parameter were studied by several authors [17,18].

In this work, solubility parameter of Lennard–Jones (LJ) fluids is calculated using integral equation method and employing pair correlation

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function. Further an inversion approach is employed to predict the molecular parameters of LJ model potential.

It should be mentioned that, recently, Khordad et al. [19] and Papari et al. [20] have predicted several properties of LJ fluids using integral equation approach.

2. Theory

2.1. Solubility parameter concept

The basic equation of Hildebrand and Scott designates the energy of vaporization as the cohesive energy density (CED) and its square root as the solubility parameter, (δ). The cohesive energy determines the energy needed to remove a molecule from its surrounding neighbors. This concept relates the solubility of a substance to its molecular structure. Thus, the solubility parameter is expressed as [2]:

$$(\text{CED})^{1/2} = \delta = \left(\frac{\Delta E_{\text{vap}}}{V_{\text{satd}}} \right)^{1/2} = \left(\frac{\Delta U_{\text{vap}}}{V_{\text{satd}}} \right)^{1/2} = \left(\frac{\Delta H_{\text{vap}} - RT}{V_{\text{satd}}} \right)^{1/2} \quad (1)$$

where δ represents the Hildebrand solubility parameter, ΔE_{vap} is the cohesive energy, V_{satd} is the saturated molar volume, ΔU_{vap} denotes the energy change upon isothermal vaporization of the saturated liquid to the ideal-gas state (energy of a complete vaporization) [21] and ΔH_{vap} is the enthalpy of vaporization. An exact experimental value for the enthalpy of vaporization of a component leads to a reliable value of its solubility parameter. Eq. (1) imply that the heat of vaporization ΔH_{vap} minus the volume work ($-RT$, where R = gas constant, T = absolute temperature) is the required energy to maintain the liquid state or cohesive energy. Dividing this value by molar volume V corrects for density leading to the term cohesive energy density. The values are reported in $\text{MPa}^{1/2}$ units. This equation is usually suitable for non-polar fluids (non-electrolytes). Generally, this concept relates the solubility of a substance with its molecular structure. By this we mean that the solubility can be influenced by polar, non-polar and hydrogen bonding effects.

2.2. Molecular thermodynamic method

As we know, molecular thermodynamic models based on statistical mechanics are developing rapidly [22,23]. It is well known that, once the intermolecular pair potential energy and RDF of dense fluids are known, their thermodynamic properties of fluids can be predicted using an integral equation method [24]. Recently, emphasis has been placed on the development of molecular thermodynamic-based models which makes it feasible to separate and quantify the effects of molecular structure on the interactions [25].

An analytical equation for internal pressure based on the statistical mechanical integral equation theory has been previously proposed [26]:

$$\pi_T = -2\pi\rho^2 \int_0^\infty u(r) \left\{ g(r) + \rho \left(\frac{\partial g(r)}{\partial \rho} \right)_{r,T} \right\} r^2 dr. \quad (2)$$

The above equation was derived from the total energy equation, by simple differentiation with respect to the volume at constant temperature. Meanwhile, by combining these equations, it is possible to link the solubility parameter to molecular theory based on the statistical-mechanical expression for fluids.

Through a simple relation developed by Verdier and Andersen [17], one can easily find the solubility parameter via the above-mentioned analytical equation using the internal pressure. The internal pressure, π_T and the solubility parameter, δ are related based on the following equation, viz.:

$$\delta^2 = \pi_T + \frac{A}{\rho} \quad (3)$$

where, A is a constant determined for any reference condition and ρ is the liquid density, for which its value is usually estimated from an EOS. In this paper, the values of liquid densities are estimated from the modified Carnahan–Starling–vdW EOS by Papari et al. [27]. Inserting the relevant radial distribution function (RDF), dispersion forces and Lennard–Jones (LJ) (12–6) potential to Eq. (2), one can easily calculate the internal pressure of non-polar and slightly polar fluids. Their solubility parameters were evaluated according to the calculated values of the internal pressure.

The required RDF expression was taken from Xu and Hu [28]. This expression reads as:

$$g(r) = H(r-r^{**}) + (r^{**}-\sigma^3)D(r-r^{**})/3r^{*2} \quad (4)$$

where H is the Heaviside function, viz:

$$\begin{cases} H(x-a) = 1, & x > a \\ H(x-a) = 0, & x < a \\ H(x-a) = 1/2 & x = a \end{cases} \quad (5)$$

Here, $r^* = 1.150d$ is the distance between molecules in the first coordination shell [29], and $r^{**} = 1.575d$ is the outer radius of the first coordination shell [30]. D is Dirac delta function, viz:

$$\begin{cases} D(x-a) = 0, & x \neq a \\ D(x-a) = \infty, & x = a \end{cases} \quad (6)$$

The LJ (12–6) potential function of pure fluids to be used in Eq. (2) is defined as:

$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (7)$$

where ϵ and σ represent the dispersive energy parameter (or potential well-depth) and hard-sphere diameter of LJ fluid, respectively and r is the distance between the center of mass of two molecules.

Basically, it is believed that the cohesive energy depends on pressure (since the cohesion of a liquid is affected by pressure). This concept is contrary to the Barton's [31] definition in which the solubility parameter is pressure independent. Maloney and Prausnitz [32] considered that the cohesive energy is equal to the residual internal energy. The solubility parameters were estimated according to the calculated values of the internal pressure.

2.3. The revisited methods

The objective of the present work is to improve the previous method developed by Mansoori-Oghaz et al. [26]. The following revisions were taken into account:

- 1) Mansoori-Oghaz and his co-workers fixed the required LJ (12–6) parameters from transport properties such as self-diffusion coefficient [33] and hard-sphere equation of state (HS EOS) [34] method. The applicability of HS EOS approach is restricted to simple fluids like monatomic and non-polar fluids. Moreover, it is well-known that the estimated LJ parameters obtained from equilibrium properties such as second virial coefficients [35] are almost different from those estimated using transport properties such as self-diffusion coefficients. In the present study, the aim is to assess the performance of Lennard–Jones (12–6) parameters obtained from the second virial coefficients instead of transport properties using inversion method. Then this model potential was employed to predict other equilibrium properties including internal pressure and solubility parameters. The proposed idea can be performed in two ways: One way is the fitting of the second virial coefficient with the experimental ones, for which their values are available in the literature [35] and then obtaining the LJ parameters using Eq. (8). Generally,

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