Fluid Phase Equilibria 415 (2016) 42–50

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Determination of hydrocarbon-water interfacial tension using a new empirical correlation

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ARTICLE INFO

Article history:
Received 4 August 2015
Received in revised form
19 January 2016
Accepted 20 January 2016
Available online 22 January 2016

Keywords:
Interfacial tension
Estimation
Model
Pure hydrocarbons
Water

ABSTRACT

Interfacial tension is one of the very important parameters in pharmacology science, chemical engineering and petroleum engineering. The interfacial tension between pure hydrocarbons and water is widely used in chemical and petroleum engineering and so that it is highly desirable to find its accurate values. In this study a new unique correlation has been developed based on a comprehensive database of pure hydrocarbons-water interfacial tension values which contained both aliphatic and aromatic compounds (32 different hydrocarbons) with pressure ranges of 0.1–300 MPa and temperature ranges of 252.44–550 K. The proposed correlation uses the density difference between pure hydrocarbon and water, system temperature and critical temperature of hydrocarbon to estimate the interfacial tension value. The accuracy and estimation efficiency of the proposed model has been checked by comparing the model estimated values with the corresponding experimental values. Also, they have been compared to the estimated values using the other common correlations which showed the superiority of the proposed model. Also the trend estimation capability test against pressure and temperature changes has been conducted and compared for the proposed model and other common correlations which showed that the proposed model is more efficient in estimating interfacial tension between pure hydrocarbons and water.

1. Introduction

Interfacial tension is one of the thermophysical properties of fluids that determines the behavior of the interface between two immiscible fluids. Interfacial tension is less investigated related to the other thermophysical properties like viscosity, density, etc. This is because of that the other thermophysical properties are dealing with one phase and its properties while the interfacial tension is dealing with two evolved phases and their properties [1] so that it has diverse nature and is more complex related to the other thermophysical properties.

Creation of interface between two immiscible fluids is due to the difference in chemical nature of intermolecular interactions in each fluid or difference in molecular density in evolved fluids [2]. So that as these differences between two contiguous fluids decrease, the interface between these fluids would be weaker and weaker until the interface would be invisible and the fluids would be commingled in which they are called miscible fluids. For example, this condition usually occurs in mixtures of water and alcohols in which the mentioned differences are very small [1]. Contrary, in the mixtures of oils and water, an obvious interface is created between two phases because of mentioned differences. In other word as the mentioned differences increase between two contiguous fluids, the created interface between the fluids would be stronger. In some of the sources, the interface creation between two fluids is expressed by the Gibbs free energy concept. In this point of view, considering one fluid, each of the fluid molecules are in the same interactions with the other same molecules from all sides and so that the resultant is zero. Now, considering a molecule in the interface of the two immiscible fluids, the molecule is in the different interactions applied by different molecules from different sides which results the non-zero resultant force. In this case, the system tries to minimize own Gibbs free energy so that it tries to decrease the number of high energy molecules in the interface so that it creates a curved interface toward the phase that applies the stranger interactions [3].

Interfacial tension (IFT) is an quantitative index of molecular behavior in the interface between two fluids [1] which determines the stability and performance of the interface. In this way, as the IFT

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http://dx.doi.org/10.1016/j.fluid.2016.01.037
0378-3812/

increased, the interface would be stronger and vice versa until in the complete miscible condition the IFT would be zero. The IFT is usually expressed as the mN/m or dyne/cm^2 which are the units for the energy required to extend the interface between the fluids y unit area.

IFT is one of the important parameters in pharmacology, chemistry, chemical engineering and petroleum engineering [2] especially in separation processes design, multiphase flow design, enhanced oil recovery, petroleum production process design, emulsion creation and distortion [2,4–7]. IFT between pure hydrocarbons and water has a very important role in the processes like liquid–liquid extraction and hydrocarbon Stream sweetening [2,7]. Also some of the theoretical and empirical models for interfacial tension prediction between water and hydrocarbon mixtures, require the IFT between pure hydrocarbons and water as their input arguments [8]. Regarding these reasons, IFT determination between pure hydrocarbons and water is very necessary and important.

The main way for determination of the hydrocarbon-water IFT is to measure it experimentally in the laboratory but it is usually time consuming, expensive and needs a lot of attention in conducting it to make accurate and reproducible results. So that it is not desirable in many of the IFT applications especially when it is needed immediately [3] like what is happened in routine engineering calculations.

The other method for hydrocarbon-water IFT determination is to use the theoretical models and procedures [4,6,9–17]. These models (such as gradient theory) refer to the molecular feature of two phase and their interface which need data about molecular energy, chemical potential and the equilibrium densities of the coexisting phases [18]. Some of these models only give very rough estimate of the IFT and the others, require advanced parameters of the fluids [4,13,16,17] to result the accurate values which these parameters are not common; so that they are not desirable in routine engineering calculations.

The density gradient theory (DGT) is a well-known theoretical model which is based on relating an equation of state (EOS) to surface properties of homogeneous and inhomogeneous systems of substances [19]. This theory has its origin in the work of van der Waals [20] and was developed by Cahn and Hilliard [21]. Density and stress distributions in the interface inhomogeneous fluids can be computed by this theory. For this purpose, the theory converts statistical mechanics into a boundary value problem. Using Cahn and Hilliard model, the interfacial tension of heterogeneous systems can be calculated using Helmholtz free energy of system [22]; therefore, Helmholtz free energy density is one of the gradient theory inputs that can be computed by thermodynamic models such as equations of state. Panayiotou combined the quasi chemical hydrogen bonding (QCBH) equation of state with the gradient theory to compute surface tensions. The obtained results were satisfactory for pure and non-polar fluids [23]. Another approach for estimating the interfacial tension of mixtures is to use the statistical associated fluid theory. Statistical Association Fluid Theory EOS (SAFT) proposed by Huang and Radosz [24] is a molecular based EOS which accounts the molecular association effects (repulsion and dispersion, hydrogen-bonding and charge transfer, etc) and chain structure in calculating the free energy of the system. For heterogeneous mixture, this EOS can properly determine DGT essential input parameters and leads to accurate IFT calculation. Kahl and Enders [19] and Fu [25] demonstrated that the SAFT EOS leads to satisfactory results for alcohols and gives better modeling results at lower temperatures.

Cubic plus association (CPA) is a new equation of state in the family of equations of state like APACT and SAFT that is the combination of the Wertheim association contribution with the Soave-Redlich-Kwong (SRK) EOS. In the following the combination of DTG with CPA is discussed for modeling the interfacial tension value.

Miqueu et al. [26] generalized the gradient theory for multicomponent mixtures as follows [18]:

$$\sigma = \int_{n_N^{vap}}^{n_N^{liq}} \sqrt{2\Delta\Omega(n)\sum_i\sum_j c_{ij}\frac{dn_i}{dn_N}\frac{dn_j}{dn_N}}dn_N \tag{1}$$

$$\Delta\Omega(n) = \Omega(n) + p \tag{2}$$

Where, σ is the interfacial tension, p is the equilibrium pressure, n^{liq} and n^{vap} are the liquid and vapor densities, c is the influence parameter, N is the so-called mixture reference component, n is the pure component chemical potential and Ω(n) is the grand thermodynamic potential and is defined as [18]:

$$\Omega(n) = f_o(n) - \sum_i n_i\mu_i \tag{3}$$

In the above equation $f_0(n)$ is the Helmholtz free energy density for homogeneous fluids at n, and μ_i is the pure component chemical potential.

The influence parameter, c, is correlated from surface tension data and is determined after vapor–liquid equilibrium [18].

$$c_{ii} = \frac{1}{2}\left[\frac{\sigma_{\exp}}{\int_{n^{vap}}^{n^{liq}}\sqrt{f_o(n) - n\mu + p}dn}\right]^2 \tag{4}$$

The cross influence parameters, c_{ij}, are computed using the following equation which considers the binary interaction coefficients [18].

$$c_{ii} = \left(1 - k_{ij}\right)\sqrt{c_{ii}c_{jj}} \tag{5}$$

In order to determine the chemical potentials, equilibrium densities and the Helmholtz free energy in the gradient theory, it is necessary to use an accurate model like CPA equation of state. The CPA EOS is expressed as follow, in terms of compressibility factor, which is the sum of physical interactions and Wertheim association contribution [18].

$$\begin{aligned} Z &= Z^{phys} + Z^{assoc} \\ &= \frac{1}{1-b\rho} - \frac{a\rho}{RT(1+b\rho)} - \frac{1}{2}\left(1+\rho\frac{\partial \ln g}{\partial\rho}\right)\sum_i x_i\sum_{A_i}(1 - X_{Ai}) \end{aligned} \tag{6}$$

Where, *a* is the energy parameter, ρ the density, *b* the co–volume parameter, *g* the radial distribution function, X_{Ai} the mole fraction of pure component *i* not bonded at site *A* and *xi* is the mole fraction of component *i*. The energy parameter of CPA, a(T), is defined as follow. It must be noticed that the parameters a_0, c_1 and b are found from liquid density and vapor pressure data [18].

$$a(T) = a_0\left[1 + c_1\left(1 - \sqrt{T_r}\right)\right]^2 \tag{7}$$

X_{Ai} is calculated by solving the following equations [18]: