NUCLEATION RATES OF ETHANOL AND METHANOL USING SAFT AND PC-SAFT EQUATIONS OF STATE

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NUCLEATION RATES OF ETHANOL AND METHANOL USING SAFT AND PC-SAFT EQUATIONS OF STATE

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DEDICATIONS

To My Family and My Dearest Friend, Tewfik

AKCNOLODGEMENTS

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF NOMENCLAURE

Symbol	Description
β	Absorption flux of monomer per unit area per unit time
P_v	Actual pressure of the supersaturated gas
Δ^{AB}	Associating strength
ε^{AB}	Association energy between site A and site B on another molecule
N_{AV}	Avogadro's number
k_B	Boltzmann's constant
Q_n	Canonical partition function
μ	Chemical potential
λ_n	Chemical potential of droplet as a single species
μ_1	Chemical potential of monomer
μ_l	Chemical potential per molecule of the droplet
μ_v	Chemical potential per molecule of the supersaturated gas
N_{tot}	Concentration of monomers
D_{tot}	Concentration of monomers
$f(n)$	Concentration of n-size droplet
$D(n)$	Concentration of n-size droplet at equilibrium
n^*	Critical number of molecules of the droplet
r^*	Critical radius of the droplet
ε	Dispersion energy of interaction between segments
α	Emission flux of monomer per unit area per unit time
S'	Entropy
P_{ve}	Equilibrium vapor-liquid pressure
v	Frequency
G	Gibbs free energy
F^{disp}	Helmhlotz free energy per mole after dispersion
F^{assoc}	Helmhlotz free energy per mole of the association model

F^{chain}	Helmhlotz free energy per mole of the chain model
F^{hs}	Helmhlotz free energy per mole of the hard sphere model
F	Helmholtz free energy
F^{*}	Helmholtz free energy per mole
F^{id}	Helmholtz free energy per mole of the ideal gas
P_l	Internal pressure in the droplet
W^{*}	Maximum work of formation
X^A	Mole fraction of components which are not bonded at site A
X^B	Mole fraction of components which are not bonded at site B
m'	Molecular mass
J	Nucleation rate
J_0	Nucleation rate when the whole system nucleates to the critical size (i.e., probability equals one)
ρ	Number density
ρ_l	Number density of the droplet
ρ_{ref}	Number density of the reference state
ρ_v	Number density of the supersaturated gas
N	Number of molecules
n	Number of molecules of the droplet
m	Number of segment (chain length)
η	Packing fraction or reduced mass
h	Planck's constant
P	Pressure
r	Radius of the droplet
ρ_g	Reduced molar density
T_g	Reduced temperature
v_l	Specific volume of the droplet
v_v	Specific volume of the supersaturated vapor
S	Supersaturation ratio
A	Surface area of the droplet
σ	Surface tension
σ_∞	Surface tension of flat surface
T	Temperature
d	Temperature-dependent segment diameter

σ'	Temperature-independent segment diameter
M	Total number of sites
R	Universal gas constant
V	Volume
K^{AB}	Volume of interaction
W	Work of formation

ABSTRACT

NUCLEATION RATES OF ETHANOL AND METHANOL USING SAFT AND PC-SAFT EQUATIONS OF STATE

By

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The two equations of state (EOS) called SAFT and PC-SAFT have been used with the most general Gibbsian form (P-form) of classical nucleation theory (CNT) are used to calculate the nucleation rate. It is found that using SAFT EOS and PC-SAFT EOS leads to good improvement in the calculation of nucleation rate of Methanol and Ethanol.

The SAFT and PC-SAFT EOSs improve the T-dependence and the S-dependence of the calculation of nucleation rate for both Methanol and Ethanol using the P-form.

Data obtained for Methanol gives better agreement when compared with experimental results.

CHAPTER I

1. INTRODUCTION

The basic definition of nucleation is that being a kind of phase transition from the vapor to the liquid phase, which means that the transition of the system from a state to another state as a result of changes in its thermodynamic properties. The nucleation process is isothermal phase transition similar to the condensation [1], which is usually associated with a critical size at which the probability of cluster formation is a maximum.

To understand the nucleation process which will be discussed in chapter two, some thermodynamic properties must be introduced such as thermodynamic properties related to equation of state (EOS). As an example, the ideal gas equation of state is given by

$$PV = Nk_{B}T = nRT \tag{1.1}$$

Where P is the pressure, V is the volume of the system, N is the number of molecules, k_{B} is the Boltzmann's constant, n is the number of moles, R is the universal gas constant, and T is the absolute temperature. The main use of the equation of state is that, knowing any three thermodynamic properties, enable one to find the fourth property. The efficiency of any equation of state depends on how close it can predict values to experimentally measured properties at equilibrium.

Because the nucleation process is an isothermal process, any change in the pressure will change the volume and the number of molecule of the phase. To image this process, assume that we have a container with a volume V occupied by a gas with a number of molecules N at a pressure P and a temperature T. If we increase the pressure on the system at the same temperature, the volume will decrease and the collisions among the molecules will increase, so, the molecules will start to condensate. This condensation will form clusters (i.e., microscopic droplets), which represent the embryos of the new phase (liquid phase).

As it is known, the foreign particles (impurities), often, aid the condensation process (i.e., the impurities assist the nucleation process). The nucleation process, which occurs without any impurities, is called homogeneous nucleation [2] process, and that occurs with the impurities is called heterogeneous nucleation [3] process.

Study of nucleation is widely used in cloud physics, material science, and crystal growth.

The first thermodynamic description of the nucleation process is due to Gibbs [4], who proved that the nucleation process depends on the work of formation. The formation consists of two terms: a bulk (volumetric) term and a surface term.

Practically, the nucleation rate which is defined as, the rate of formation of critical-size embryos per unit time per unit volume is the important

parameter (quantity) in our calculation, because it gives the rate of formation of the new phase. In 1926 Volmer and Weber [5] derived the first expression of the nucleation rate, by assuming that the nucleation should be proportional to the flux of molecules absorbed by the critical- size droplets. The theory of Volmer and Weber was derived kinetically by Becker and Döring [6], known in the literature as classical nucleation theory (CNT). The general expression of the nucleation rate is given by

$$J \propto \exp\left(\frac{-W^*}{k_B T}\right) \tag{1.2}$$

Where W^* is the maximum work of formation of critical-size droplet. Gibbs [4] was the first one who proved that the maximum work of formation can be given as

$$W^* = \frac{16\pi}{3} \frac{\sigma^3}{(P_l - P_v)^2} \tag{1.3}$$

Which is called P-form. Where σ is the surface tension of the critical droplet, P_l is the internal pressure of the droplet, and P_v is the actual pressure (the pressure after compression).

Since the surface tension can't be measured for small droplet, it is assumed to be equal to the measured surface tension for flat interface σ_∞.

The above equation is usually written as

$$W^* = \frac{16\pi}{3} \frac{\sigma_\infty^3}{(P_l - P_v)^2} \tag{1.4}$$

Which is known as the P-form.

If the droplet is incompressible (see equation A.3.2), equation 1.4 can be written as

$$W^* = \frac{16\pi}{3} \frac{v_l^2 \sigma_\infty^3}{(\Delta\mu)^2} \tag{1.5}$$

Which is called μ-form. Where

$$\Delta\mu = \mu_l(P_l) - \mu_l(P_{ve}) \tag{1.6}$$

Where $\Delta\mu$ is the difference in the chemical potential per molecule of the liquid phase and vapor phase, respectively (see equation A.4.4), v_l is the specific volume (volume per molecule) of the droplet, and P_{ve} is the equilibrium vapor-liquid pressure.

Assuming that the gas is ideal, the last equation can be written as

$$W^* = \frac{16\pi}{3} \frac{v_l^2 \sigma_\infty^3}{(k_B T \ln S)^2} \tag{1.7}$$

Where S is called the supersaturation ratio and defined as P_v / P_{ve}. Equation 1.7 is known as the standard form of nucleation or simply S-form.

The application of the S-form is straight forward since the equation requires a measured quantity, while using the P-form requires the knowledge of the internal pressure of the droplet, which can't be measured for a small droplet. Although, one can take advantage of Gibbs formula by using an appropriate EOS for $\sigma = \sigma_\infty$.

Application of the P-form requires the assumption that the chemical potential at constant temperature is the same for the liquid-vapor phases. According to this assumption, Gibbs [4] introduced the concept of the reference state at which the chemical potential is the constant of phase transformation.

$$\mu_v(\rho_v) = \mu_l(\rho_{ref}) \qquad (1.8)$$

This reference state is characterized by P_{ref} and ρ_{ref} as shown in the following figure
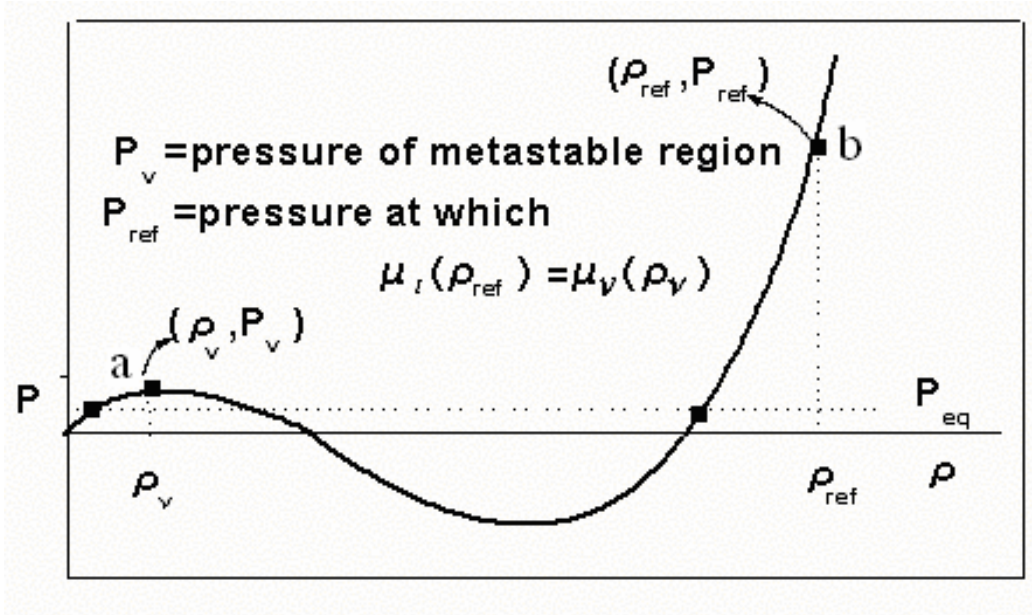
Figure 1.1. The pressure–density isotherm for a pure fluid using Van der-Waals's EOS.

Mathematically, we use the equation of state to find the vapor number density ρ_v at the actual pressure P_v, point a in the figure. According to Gibbs approach there is a point like b (ρ_{ref}, P_{ref}) which has the same μ as a. This μ when substituted in the EOS gives ρ_{ref} from which, P_{ref} is known.

Obeidat et al [7] are the first to use the P-form numerically. They calculated the nucleation rate of ethanol and methanol using cubic perturbed hard body CPHB [8] equation of state and they proved that, the P-form improves the results of S-form, but, the results of methanol and ethanol deviate from the experimental results. As shown in figure 1.2, P-form improve the results of S-form by one order of magnitude while the T-dependence and S-dependence did not improved.
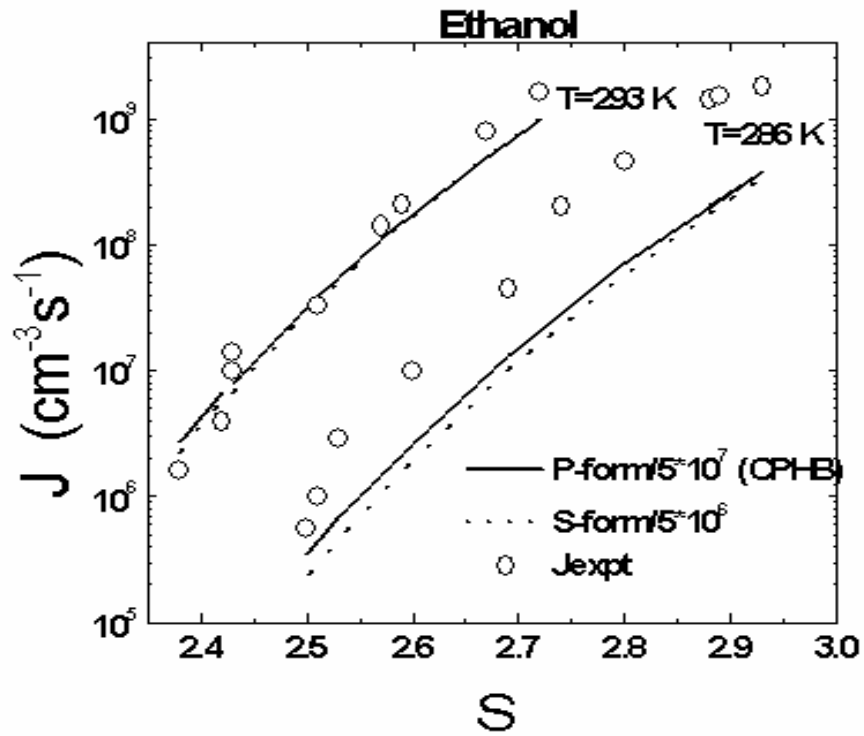
Figure 1.2. Experimental nucleation rates of ethanol compared to calculated rates using the S-form and the P-form of CNT with the CPHB EOS.

Since, methanol and ethanol have a wide range of applications in physics and chemistry, scientists have investigated the nucleation rate of these substances. But no solid explanation has been made using classical nucleation rates, so more work is needed regarding this aspect.

Recall that methanol and ethanol are not ideal gases and the CPHB EOS is not an accurate equation at low temperature, for these reasons, we will use a more accurate equations of state at low temperature which are called statistical associating fluid theory SAFT EOS [9-10] and perturbed chain-statistical associating fluid theory PC-SAFT EOS [11].

The layout of this thesis will be as follows; chapter two deals with general theoretical background of all thermodynamic properties mainly equation of state and nucleation rate "J".

Chapter three deals with kinetics that enable us to calculate the rates.

Chapter four explains in details the derivation of the work of formation in classical nucleation theory (CNT).

Chapter five deals with the numerical results obtained using two equation of state (SAFT [9-10] and PC-SAFT [11]) with parameters appropriate to methanol and ethanol.

Results of nucleation rates using SAFT and PC-SAFT will be discussed in chapter six.

CHAPTER II

2. THERMODYNAMICS OF NUCLEATION

2.1. THERMODYNAMIC SURVEY

If changes occur in the thermodynamic properties of a stable thermodynamic system, the system will transfer to a new more stable phase (minimum free energy). Where Gibbs free energy is given by

$$G = N\mu \tag{2.1}$$

The Helmholtz free energy is given by

$$F = G - PV = N\mu - PV \tag{2.2}$$

Where G is the Gibbs free energy, N is the number of molecules, μ is the chemical potential, F is the Helmholtz free energy, P is the pressure, and V is the total volume.

Figure 2.1 illustrates the pressure-volume diagram using Van der-Waal's equation of state EOS [12], given by

$$(P + \frac{a}{v^2})(v - b) = RT \tag{2.3}$$

Where a and b are characteristic parameters for the given substance.
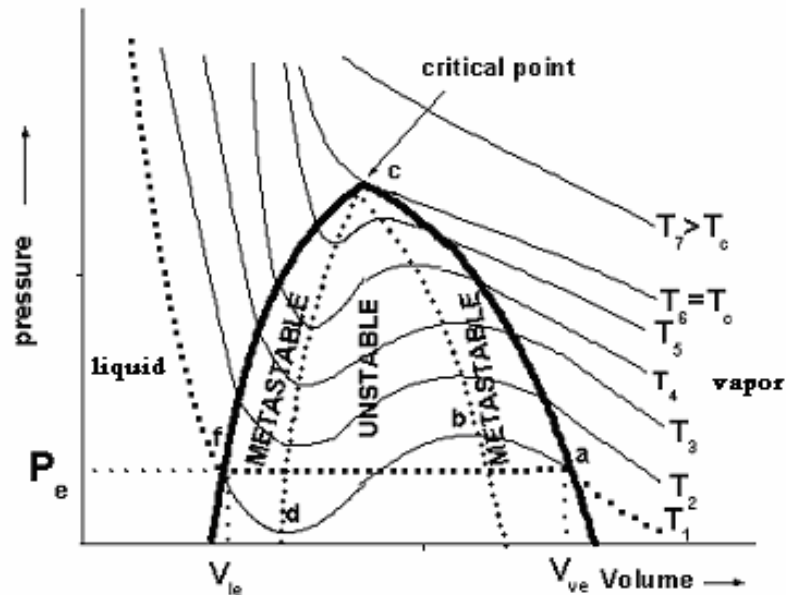
Figure 2.1. Pressure-volume phases for a pure substance.

From the figure 2.1[8], for each isothermal line, there is an equilibrium vapor-liquid pressure P_e (for example, the isothermal line at temperature T_1) has an equilibrium vapor-liquid pressure P_e at points a and f. The dashed line between a and f is the experimental line which represents the coexisting range of liquid and vapor at the equilibrium vapor-liquid pressure.

The heavy-line dome which passes through all the equilibrium vapor-liquid pressure points is called the binodal line and the peak of this dome is found at the critical point, which is the point at which the vapor and liquid are indistinguishable. For each theoretical isotherm, there are a maximum pressure of vapor (as b for T_1) and a minimum pressure of liquid (as d for T_1). The dotted-line dome which passes through all the points of maximum

pressure of vapor and minimum pressure of liquid for several temperatures is called the spinodal line and the two dome intersect at the critical point "c".

The vapor which has a pressure higher than P_e and the liquid which has a pressure lower than P_e will be in unstable state for some time and then each of them will return to its own stable region or transfer to the stable region of the other phase, from that, the region between the spinodal line and the binodal is called metastable region ($(\partial p / \partial V)_T < 0$), where the region between a and b for T_1 is the metastable region for the vapor phase and the region between f and d is the metastable region for liquid phase .

The region inside the spinodal dome is called unphysical region or unstable region, because the volume of the fluid increases with increasing the pressure ($(\partial p / \partial V)_T > 0$), this unstable region is for both vapor and liquid phases.

The vapor is said to be undersaturated, saturated or supersaturated if the actual pressure is less, equal or higher than the equilibrium vapor-liquid pressure respectively.

2.2. THERMODYNAMIC DESCRIPTION OF NUCLEATION

Since the free energy of the surface of the droplet is larger than that of the bulk of the droplet, the droplet starts to shrink. On the other hand if the molecule in the bulk of the droplet have enough excess free energy to transfer

from the bulk to the surface, the droplet starts to grow. This excess free energy can be obtained from an external work. The work which is needed to increase the surface of the droplet by unit area is known as the surface tension. Consequently, the surface of the droplet opposes the growth of the droplet.

Because the external work has a role in the formation of the droplet, we must use the Helmholtz free energy (see equation 1.2) to derive the expression of the total work needed to form the droplet.

Gibbs [4] is the first to show that the work of formation (i.e., free energy barrier) of the droplet equals the difference between the Helmholtz free energies before and after the formation, and he showed that, the work of formation consists of two terms: The bulk (volumetric) term and the surface term, where, the Gibbs's formula of the work of formation is given as (see appendix A),

$$W = \Delta F = -V_l(P_l - P_v) + A\sigma \tag{2.4}$$

Where W is the work of formation, F is the Helmholtz free energy, V is the volume of the droplet, P_l and P_v are the internal pressure of the droplet and the actual pressure, respectively, A is the surface area of the droplet, and σ is the surface tension.

Figure 2.2 [8] illustrates the reversible work (free energy barrier) of formation of the droplet with its number of molecules.
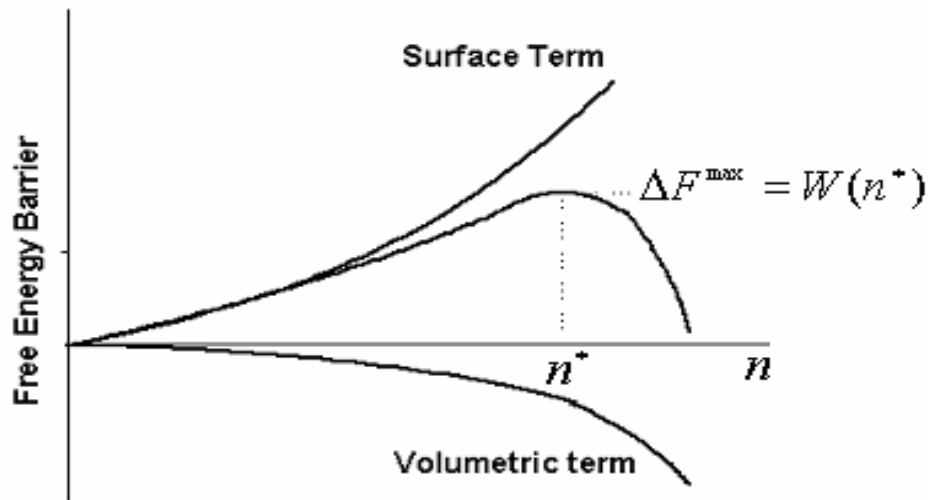
Figure 2.2. Work of formation of a droplet.

As we see in figure 2.2, the maximum reversible work of formation is found at point n^* and the growth of the droplet after n^* will be spontaneous. From that, the size of the droplet at n^* is called the critical-size droplet, because droplets with this size have the probability to transfer to the new phase (liquid) and the other droplets with sizes less than n^* will shrink (decay) to the old phase (gas), and the maximum reversible work which is needed to form this critical size droplet is the minimum work needed for phase transition.

The formation of the critical-size droplets (embryos) which have the probability of growth spontaneously is called the nucleation process, and the number of critical-size droplets generated per unit volume per unit time is called the nucleation rate "J".

CHAPTER III

3. KINETICS OF NUCLEATION RATE

3.1. BECKER AND DöRING THEORY

In 1935 Becker and Döring[6] introduced kinetic equations which can be used to describe the nucleation process of superheated vapor in metastable region. In this case we are dealing with two-component system (liquid and gas).

The kinetic equation can be applied to the two-component system where the concentration of the gas is much more than that of the liquid. The distribution of the molecules of the old phase component is described by assuming that they condensate locally in clusters or droplets of several sizes. We use a variable n for the sizes of the droplets to define the number of particles (molecules or atom) in the droplet. A cluster containing n molecules is called n-cluster.

Let the concentration of the n-cluster be represented by the notation $f(n)$. Clusters are assumed to be distributed uniformly and randomly, so $f(n)$ do not depend on the space variables.

To obtain equations of the time description of $f(n)$, Becker and Döring [6] assumed that the clusters change size by absorbing single molecule (1-

size) or by emitting single molecule (reversible process). As shown in figure 3.1.
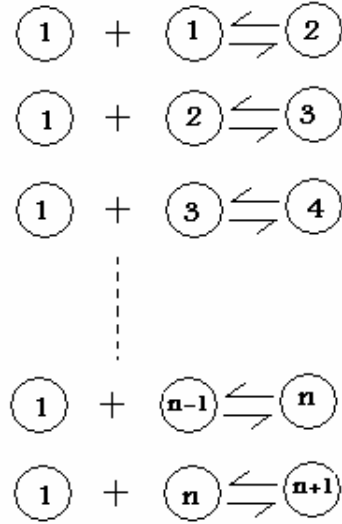
Figure 3.1. The formation of n-size droplet by single molecule absorption into $(n-1)$-size droplet or single molecule emission from $(n+1)$-size droplet.

From the above assumption, droplets can only grow or shrink by single events. Then $J(n)$ is the difference between the rate of formation of n-size droplets by single-molecule absorption into $(n-1)$-molecule droplet and the rate of destruction of n-size droplets by single-molecule emission, can be written as

$$J(n) = f(n-1)A(n-1)\beta(n-1) - f(n)A(n)\alpha(n) \tag{3.1}$$

Where $J(n)$ has dimension of (1/(volume.second)), $f(n)$ and $f(n-1)$ are the concentration of n-cluster and $(n-1)$-cluster, $A(n)$ and $A(n-1)$ are their respective surface areas, $\beta(n-1)$ is the flux per unit time per unit area of single molecules onto $(n-1)$-droplet(i.e., molecules arriving to the

droplet-vapor interface from the vapor) and $\alpha(n)$ is the flux of single molecule leaving the n–size droplet.

From kinetic theory β can be calculated (see appendix A, equation A.1.5), but α is not known in general, because its calculation depends on kinetics of molecules in the liquid phase and the interaction between the molecules of the liquid phase. To overcome this difficulty, equilibrium concentration is used. Where the equilibrium concentration can be obtained when the rate of formation of n-size droplets by single-molecules absorbed to $(n-1)$-droplets equals the rate of destruction of it by single-molecules emitted from n-droplets (i.e., $\Delta f(n) = 0$).

Assume that the equilibrium distribution of droplets in the bulk metastable phase can be established as long as the characteristic time for this establishment is short with respect to the lifetime of the metastable phase [13]. Because of microscopic reversibility, we can write,

$$D(n-1)A(n-1)\beta(n-1) = D(n)A(n)\alpha(n) \tag{3.2}$$

Where $D(n-1)$ and $D(n)$ are the equilibrium concentrations of $(n-1)$-droplets and n-droplet, respectively. By assuming that α and β do not depend on the number of molecules in the droplet (i.e., $\beta(n-1) = \beta$ and $\alpha(n) = \alpha$), we can solve equation 3.2 for α,

$$\alpha = \beta \frac{D(n-1)A(n-1)}{D(n)A(n)} \tag{3.3}$$

Substitute equation 3.3 into 3.1, we obtain,

$$J(n) = \beta A(n-1)D(n-1)\left[\frac{f(n-1)}{D(n-1)} - \frac{f(n)}{D(n)}\right] \qquad (3.4)$$

The first part in the right hand side of equation (3.4) represents the rate of formation of n-size droplet by single-molecule condensation onto $(n-1)$-size droplet and the second part represents the rate of destruction of it by single-molecule evaporation. But there is another method to form n-size droplet by evaporating single-molecule from $(n+1)$-droplet and destruction of it can be obtained by single-molecule absorption (i.e., $J(n+1)$), see figure 3.1. Then the total time-variation of concentration of n-size droplet is the difference between the two methods, so

$$\frac{\partial f(n,t)}{\partial t} = J(n) - J(n+1) \qquad (3.5)$$

At equilibrium distribution (i.e., $f(n)=D(n)$), the time-invariant population of droplets is established at $J(n)=J(n+1)$, therefore J is independent of n. The above result means that a steady-state is established.

Rewrite equation 3.4 with the sum taken from $n=2$ to $n=q$ to obtain equation 3.6.

$$\sum_{n=1}^{q}[J/\beta A(n)D(n)] = \sum_{n=1}^{q}\left[\frac{f(n)}{D(n)} - \frac{f(n+1)}{D(n+1)}\right] = \frac{f(1)}{D(1)} - \frac{f(q+1)}{D(q+1)} \qquad (3.6)$$

Where q is very large (undefined), $f(1)$ is the concentration of single-molecule (monomers), and $D(1)$ is the concentration of monomers at

equilibrium. From the definition of nucleation, we can conclude that, if the $(q+1)$-size droplet is larger than the critical size, then none equilibrium $(q+1)$-size droplet will grow until phase transition occurs and if it is less than the critical size, it will shrink to a monomer.

From that, the value of $f(n+1)$ vanishes and $f(1)$ nearly equals $D(1)$. So we can rewrite equation 3.6 as

$$J = \frac{1}{\sum\limits_{1}^{q} [1/\beta A(n)D(n)]} \tag{3.7}$$

Where equation 3.7 is the main equation used to derive the relation of nucleation rate. To derive the rate of nucleation, we must obtain the appropriate relation of the concentration at equilibrium $D(n)$ and replace the summation by an integral with suitable limits.

3.2. CONCENTRATION OF DROPLETS AT EQUILIBRIUM

Because the concentration of the clusters (dimers, trimers .etc) is much lower than the concentration of monomers (except when there are attractive forces between molecules). Clusters rarely collide, therefore no clusters form from union of two or more clusters. Assume that the system consists from equilibrium clusters is an ideal mixture (i.e., cluster considered as new species). These species are distributed following Maxwell-Boltzmann distribution [14], therefore

$$D(n) = \phi \exp\left(\frac{-W}{k_B T}\right) \tag{3.8}$$

Where, ϕ is the normalization factor and W is the work of formation. The work of formation for 1-cluster ($n=1$) equals zero, so the normalization factor ϕ equals $D(1)$. Then equation 3.8 can be written as

$$D(n) = D(1)\exp\left(\frac{-W}{k_B T}\right) \tag{3.9}$$

Because the concentration of the monomers $D(1)$ is much more than the other concentrations, the value of $D(1)$ nearly equals to the total number density of the bulk metastable phase before the condensation, therefore

$$D(1) = N_{tot}/V = D_{tot} \tag{3.10}$$

Where, N_{tot} is the total number of monomers and V is the total volume of the system. Assume that there is a mutual equilibrium between the clusters of all possible sizes. Then, the reversible reaction is very suitable because the thermodynamic condition for equilibrium is fulfilled. This condition is written as,

$$\mu_n = n\mu_1 = n\mu_v \tag{3.11}$$

Where μ_n is the chemical potential of n-size clusters and μ_1 is the chemical potential of the vapor μ_v (monomers or single-molecules). Suppose that the chemical potential of the cluster as a one species (i.e., single body) is λ_n and using the following thermodynamic relation,

$$\Delta\mu_v = \mu_v(P_v) - \mu_v(P_{ve}) = k_B T \ln\left(\frac{P_v}{P_{ve}}\right) \tag{3.12}$$

The value of μ_n can be written as (see appendix A, equation A.2.7)

$$\mu_n = \lambda_n + k_B T \ln\left(\frac{D(n)}{D_{tot}}\right) \qquad (3.13)$$

The entropy of the canonical ensemble [14] equals $-k_B \ln Q_n$, where Q_n is the partition function of the ensemble. Given as:

$$Q_n = \sum_n \exp\left(\frac{-W}{k_B T}\right) \qquad (3.14)$$

Using equations (3.9 and 3.10) the partition function can be written as

$$Q_i = \frac{\sum_i D(n_i)}{D_{tot}} \qquad (3.15)$$

Then the entropy equals to

$$S' = -T \ln(\sum_i D(n_i) / D_{tot}) \qquad (3.16)$$

This result illustrates that the logarithmic term in equation 3.13 allows for the entropy of the mixing in the absence of cluster-cluster interaction. The solution of equation 3.13 yields:

$$D(n) = D_{tot} \exp\left(\frac{n\mu_v - \lambda_n}{k_B T}\right) \qquad (3.17)$$

This implies that:

$$W = \lambda_n - n\mu_v \qquad (3.18)$$

But the value of W (see appendix A, equation A.3.4) equals,

$$W = \sigma A + n\Delta\mu \qquad (3.19)$$

Where A is the surface area of the droplet. Then equations (3.18 and 3.19) lead to,

$$\lambda_n = \sigma A + n \mu_l \qquad (3.20)$$

Thus the chemical potential of the droplet containing n molecules considered as a distinct molecular species differs from the chemical potential of n molecules in liquid phase by the surface term of the work of formation.

3.3. HOMOGENUOUS NUCLEATION RATE

The homogeneous nucleation rate is obtained by substituting the equilibrium distribution equation 3.9 into equation 3.7, it is customary to replace the summation by an integral, to obtain,

$$J = \beta D_{tot} \left(\int_{n \langle\langle n^*}^{n \rangle\rangle n^*} \exp\left(\frac{-W}{k_B T}\right) \frac{1}{A(n)} dn \right)^{-1} \qquad (3.21)$$

Where n^* represents the critical-size droplet appropriate to the maximum work of formation. Since the exponential has a peak at n^*, therefore the work of embryo formation can be expanded about the unstable equilibrium point n^*, the expansion of W is

$$W(n) = W(n^*) + W'(n^*)(n - n^*) + W''(n^*)(n - n^*)^2 / 2 \qquad (3.22)$$

Because $W(n^*)$ is an extreme value, the first derivative vanishes, then

$$W(n) = W(n^*) + W''(n^*)(\delta n)^2 / 2 \qquad (3.23)$$

Change the variable of integral in equation 3.21 by δn (i.e., $n - n^*$), if $n \ll n^*$, the lower limit of integral of equation 3.21 is $-\infty$ and if $n \gg n^*$,

the upper limit of integral is ∞. Then, the integral is written as

$$J = \beta D_{tot} A(n^*) \exp\left(-\frac{W(n^*)}{k_B T}\right) \int_{-\infty}^{\infty} \exp\left[\left(\frac{W''(n^*)}{2k_B T}\right)(\delta n)^2\right] d(\delta n) \quad (3.24)$$

Knowingthat

$$\int_{-\infty}^{\infty} \exp(-\alpha x^2) dx = \sqrt{\frac{\pi}{\alpha}} \quad (3.25)$$

Then,

$$J = \beta A(n^*) \sqrt{\frac{-W''(n^*)}{2\pi\, k_B T}} \left(D_{tot} \exp\left(\frac{-W(n^*)}{k_B T}\right) \right) \quad (3.26)$$

For a spherical model. The work of formation of the droplet is given by

$$W = 4\pi r^2 \sigma + n\Delta\mu \quad (3.27)$$

Where the radius of the sphere r can be calculated using the following relation,

$$V = \frac{4}{3}\pi r^3 = n v_l \quad (3.28)$$

Use the above relation of the work and the value of β from appendix A (equation A.1.5), the result of J is

$$J = \frac{2 P_v D_{tot}}{\sqrt{2\pi\, m' k_B T}} \sqrt{\frac{\sigma v_l^2}{k_B T}} \exp\left(\frac{-W(n^*)}{k_B T}\right) \quad (3.29)$$

From the ideality of the mixture, we get

$$D_{tot} = \rho_v = 1/v_v \ , \quad P_v = D_{tot} k_B T = \rho_v k_B T \quad (3.30)$$

By using the results in equation 3.30, we obtain

$$J = \rho_v^2 / \rho_l \sqrt{2\sigma / \pi \ m'} \ \exp[-W(n^*)/k_B T] \qquad (3.31)$$

Or

$$J = J_o \exp\left(\frac{-W^*}{k_B T}\right) \qquad (3.32)$$

Where, W^* equals $W(n^*)$ and, J_0 is given as

$$J_o = \rho_v^2 / \rho_l \sqrt{2\sigma / \pi \ m'} = \sqrt{2\sigma / \pi \ m'} \ v_l (P_v / k_B T)^2 \qquad (3.33)$$

The final form of the rate is given by

$$J = \sqrt{2\sigma / \pi \ m'} \ v_l (P_v / k_B T)^2 \exp\left(\frac{-W^*}{k_B T}\right) \qquad (3.34)$$

CHAPTER IV

4. VERSIONS OF CLASSICAL NUCLEATION RATE

4.1. THEORY

There are three versions of classical nucleation rate based on the form of the work of formation [8], thus there are three forms of formation work. These versions are the chemical potential form μ-form (equation 1.3), the saturation ratio form S-form (equation 1.4) and the pressure form P-form (equation 1.5). In this thesis comparison will be made between the results obtained by using the S-form and P-form with the experimental results. To perform these comparisons, one should use an equation of state to calculate the difference between the pressure of the vapor and the internal pressure of the droplet. This equation of state (EOS) must give acceptable results of binodal at low temperature at which the nucleation process occurs.

4.2. WORK OF FORMATION

The nucleation process occurs because the system tends to have a minimum free energy. Consequently, the work of formation equals the difference between the Helmholtz free energy before and after the formation. To calculate this difference, consider a container of volume V having N molecules of a vapor at a chemical potential μ_v and a pressure P_v. The Helmholtz free energy before formation [8], is

$$F_b = N\mu_v - P_v V \tag{4.1}$$

The Helmholtz free energy after formation of a droplet of n molecules after ignoring the very small changes in μ_v and P_v, [8], is written as:

$$F_a = (N-n)\mu_v + n\mu_l - (V-V_l)P_v - V_l P_l + A\sigma \tag{4.2}$$

Where, μ_l is the chemical potential of the molecules inside the droplet, P_l is the internal pressure, V_l is the droplet volume, A is the surface area of the droplet and, σ is the surface tension.

The surface term is added because the bulk (volumetric part of the droplet) and the surface of the droplet are considered to be different phases, so the molecules must have excess energy to move from the bulk to the surface. The difference in the free energy between the old system and the new system is

$$\Delta F = F_a - F_b = n(\mu_l(P_l) - \mu_v(P_v)) - (P_l - P_v)V_l + A\sigma \tag{4.3}$$

The chemical potential part will vanish at equilibrium where droplet is at the critical-size, because the droplet has the same chemical potential of the supersaturated vapor according to the equilibrium assumption. From the above result, the maximum difference of free energy which equals to the maximum work of formation for spherical droplet model is given by [13]:

$$\Delta F^{max} = W^{max} = -(P_l - P_v)\frac{4\pi}{3}r^{*3} + 4\pi r^{*2}\sigma \tag{4.4}$$

Where r^* is the radius of critical-size droplet.

Equation 4.3 represents the maximum energy barrier which must be overcome to form the droplet in a spatial region .Using appendix A (equation A.3.2), equation 4.4 can be approximated as

$$\Delta F = -\frac{4\pi r^3}{3}\frac{\Delta\mu}{v_l} + 4\pi r^2 \sigma \tag{4.5}$$

Where $\Delta\mu$ is the difference in chemical potential between the initial metastable phase and the final stable phase and v_l is the molecular volume of stable (liquid) phase. Figure 4.1 shows the free energy barrier as a function of the droplet radius.
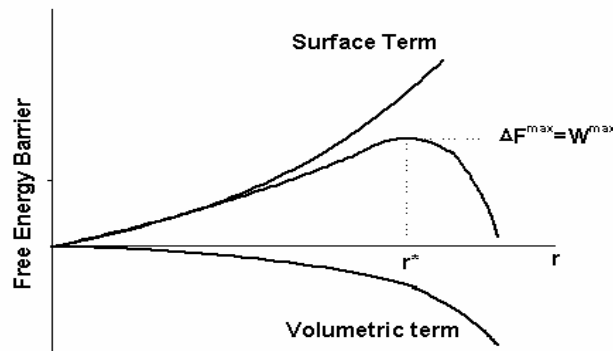
Figure 4.1. Free energy barrier as a function of droplet radius.

Use the Laplace's relation [15], which introduces the pressure across a curved interface (see appendix A, equation A.5.2), specifically, $P_l - P_v = 2\sigma/r^*$. Because the droplet has a spherical surface (curved interface), the Laplace relation [15] is suitable. The work of formation is written as

$$W^{max} = W^* = \frac{16\pi}{3}\frac{\sigma^3}{(P_l - P_v)^2} \tag{4.6}$$

From Laplace relation [15], we note that the surface tension σ depends on the radius of the droplet r. If we assume that the surface tension of the curved surface of droplet is nearly equal to experimental surface tension of a flat interface (i.e., $r = \infty$ and, $\sigma = \sigma_\infty$). Then equation 4.6 becomes

$$W^{\max} = W^* = \frac{16\pi}{3} \frac{\sigma_\infty^3}{(P_l - P_v)^2} \tag{4.7}$$

If the droplet is incompressible then v_l is invariant with pressure, so

$$\Delta\mu = \int_{P_v}^{P_l} v_l dP = v_l (p_l - p_v) \tag{4.8}$$

Substitute 4.8 in 4.7, we obtain the μ-form

$$W^{\max} = W^* = \frac{16\pi}{3} \frac{\sigma_\infty^3 v_l^2}{(\Delta\mu)^2} \tag{4.9}$$

If the gas is ideal, it is easy to derive the following relation (see appendix A, equation A.4.7).

$$\Delta\mu = k_B T \ln S - v_l (p_v - p_{ve}) \approx k_B T \ln S \tag{4.10}$$

Substituting equation 4.10 in 4.9 gives the S-form

$$W^{\max} = W^* = \frac{16\pi}{3} \frac{\sigma_\infty^3 v_l^2}{(k_B T \ln S)^2} \tag{4.11}$$

Equations 4.7, 4.9, and 4.11 form the backbone of our numerical calculations for the rate equation appropriate to experimental available data to methanol and ethanol.

CHAPTER V

5. RESULTS OF EQUATIONS OF STATE

5.1. SAFT EOS

Chapman et al [9-10] proposed an equation of state of associating fluids based on statistical associating fluid theory known as (SAFT).

For polar fluids, SAFT based on Lennard-Jones (LJ) potential [14] which treats the molecules as spherical segments of equal-size and equal – interaction strength. Then the Helmholtz molar free energy of the system can be written as

$$F' = F^{id} + F^{res} \tag{5.1}$$

F^{id} is the ideal Helmholtz molar free energy per mole, and F^{res} is the residual Helmholtz molar free energy per mole at the same temperature and density. The residual term is a sum of three terms due to contributions of different intermolecular forces. The first of which, F^{seg}, represents the segment-segment interaction. The second term, F^{chain}, is due to the presence of covalent chain-forming bonds among the LJ segments. The third term, F^{assoc}, is due to site-site specific interaction. The general expression of the total Helmholtz molar free energy per mole can be written as

$$F' = F^{id} + F^{seg} + F^{chain} + F^{assoc} \tag{5.2}$$

5.1.1. SEGMENT TERM

The segment Helmholtz molar free energy per mole was calculated [9] as

$$F^{seg} = m(F_o^{hs} + F_o^{disp})$$
(5.3)

Where m is the number of segments per molecule, F_o^{hs} is the hard sphere term, and F_o^{disp} is the dispersion term.

The hard sphere term for one species is given as

$$\frac{F_o^{hs}}{RT} = \frac{4\eta - 3\eta^2}{(1-\eta)^2}$$
(5.4)

Where R is the universal gas constant and η is a segment packing fraction defined as

$$\eta = \frac{\pi N_{AV}}{6} \rho d^3 m$$
(5.5)

$$d = \sigma' \frac{1 + 0.2977 \dfrac{k_B T}{\varepsilon}}{1 + 0.33163 \dfrac{k_B T}{\varepsilon} + \left(0.0010477 + 0.025337 \dfrac{m-1}{m}\right)\left(\dfrac{k_B T}{\varepsilon}\right)^2}$$
(5.6)

Where ρ is the molar density, d is the effective hard sphere diameter, σ' is the temperature-independent sphere diameter, N_{AV} is the Avogadro's number, and ε is the intermolecular energy (LJ) energy.

The dispersion term is given as

$$F_o^{disp} = \frac{\varepsilon R}{k_B}\left(F_{o1}^{disp} + \frac{F_{o2}^{disp}}{T_R}\right)$$
(5.7)

$$F_{o1}^{disp} = \rho_R(-8.5959 - 4.5424\rho_R - 2.1268\rho_R^2 + 10.285\rho_R^3)$$
(5.8)

$$F_{o2}^{disp} = \rho_R(-1.9075 + 9.9724\rho_R - 22.216\rho_R^2 + 15.904\rho_R^3) \tag{5.9}$$

Where $\rho_R = [6/\sqrt{2}\pi]\eta$ is the reduced density and $T_R = k_B T / R$ is the reduced temperature.

5.1.2. CHAIN TERM

The chain term [9-10] is given as

$$\frac{F^{chain}}{RT} = (1-m)\ln\left(\frac{(2-\eta)}{2(1-\eta)^3}\right) \tag{5.10}$$

5.1.3. ASSOCIATION TERM

The association term [9-10] for a polar fluid is given as

$$\frac{F^{assoc}}{RT} = \sum_A\left(\ln X^A - \frac{A^A}{2}\right) + \frac{1}{M} \tag{5.11}$$

Where M is the total number of sites on each molecule, X^A is the mole fraction of molecules not bonded at site A, and $\sum_A$ represents a sum over all associating sites on the molecules.

The mole fraction of molecules not bonded at site A can be calculated as

$$X^A = [1 + N_{AV}\sum_B \rho X^B \Delta^{AB}]^{-1} \tag{5.12}$$

Where the sum runs over all sites and Δ^{AB} is the associating strength, given as

$$\Delta^{AB} = d^3\left(\frac{2-\eta}{2(1-\eta)^3}\right)K^{AB}\exp\left(\frac{\varepsilon^{AB}}{k_B T} - 1\right) \tag{5.13}$$

Where, K^{AB} is the associating volume and ε^{AB} is the associating energy.

To find the mole fraction of methanol and ethanol molecules not bonded at a given site, we follow Radosz et al [10] approach using 2B-type .

This approach gives the following mole fraction as

$$X^A = [1 + N_{AV}\rho(X^B\Delta^{AB} + X^A\Delta^{AA})]^{-1} \tag{5.14}$$

Where Δ^{AA} equals zero and Δ^{AB} is given by 5.12, then

$$X^A = [1 + N_{AV}\rho X^B\Delta^{AB}]^{-1} \tag{5.15}$$

Using the same approach, X^B is given by

$$X^B = [1 + N_{AV}\rho X^A\Delta^{BA}]^{-1} \tag{5.16}$$

Substituting 5.16 in 5.15 gives

$$X^A = \frac{-1 + (1 + 4\rho N_{AV}\Delta)^{1/2}}{2\rho N_{AV}\Delta} \tag{5.17}$$

Equation 5.11 gives for the association free energy the following

$$\frac{F^{assoc}}{RT} = 2\ln X^A - X^A + 1 \tag{5.18}$$

The parameters that have been used for ethanol and methanol are given in table 5.1.

Table 5.1. Parameters of SAFT EOS

compound	σ	ε/k_B	m	ε^{AB}/k_B	k^{AB}	source
methanol	3.203	163.25	1.6	2964	0.053	[1]
ethanol	3.416	199.9	1.8	2614.7	0.0373	fitting

These parameters were used to test the accuracy between experimental equilibrium values with theoretically computed numerically.

The pressure and chemical potential can be derived from the reduced Helmholtz free energy as:

$$P(\rho) = \rho^2 \left(\frac{\partial F'(\rho)}{\partial \rho} \right)_T \qquad (5.19)$$

$$\mu(\rho) = \rho \left(\frac{\partial F'(\rho)}{\partial \rho} \right)_T + F'(\rho) \qquad (5.20)$$

To calculate the equilibrium vapor-liquid pressure, two conditions must be applied for each isothermal line in $P-V$ or $P-\rho$ diagram (figure 1.1 and 2.1):

$$P(\rho_l) = P(\rho_v) \qquad (5.21)$$

$$\mu(\rho_l) = \mu(\rho_v) \qquad (5.22)$$

Figures 5.1was obtained by applying the above conditions (equation 5.21and, 5.22) using SAFT EOS, which indicates excellent agreement between theory and experiment especially at low temperatures as shown in the insito of figure 5.1.

Small deviation from experimental values [16] was observed on binodal at high temperature (T >400), this motivated us to say that SAFT EOS is an excellent EOS to explain the experimental results at low temperature where nucleation usually occurs.
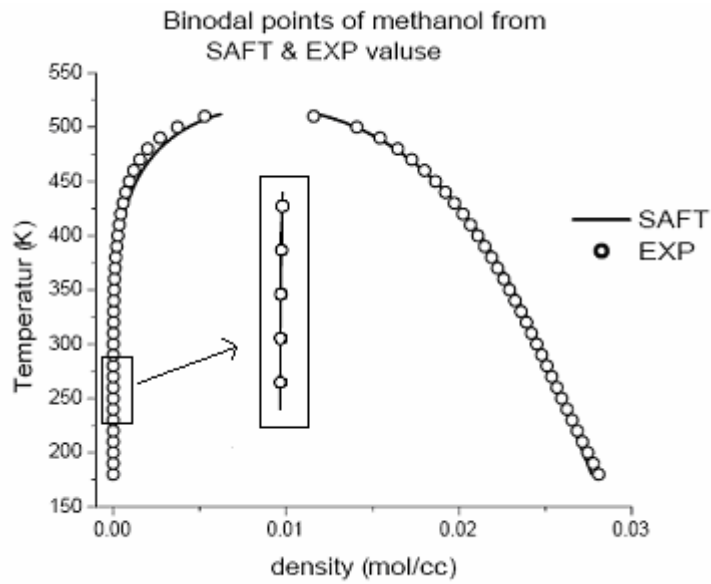
Figure 5.1. Binodal points of methanol Using SAFT EOS.

Figure 5.2 was obtained for ethanol by applying the same conditions as methanol using SAFT EOS, which indicates excellent agreement between theory and experiment [16] at all temperatures.
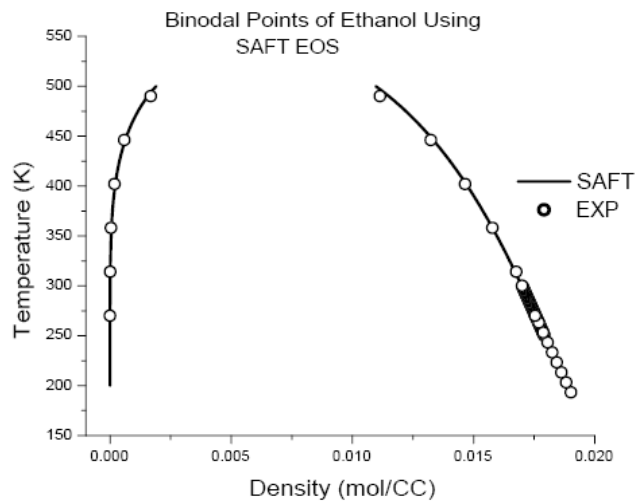

Figure 5.2. Binodal points of ethanol Using SAFT EOS.

5.2. PC-SAFT EOS

SAFT EOS was modified by Gross and Sadowski [11], they added a small perturbing term due to dispersion in the chain formation. The added dispersion term can be written as

$$\frac{F^{disp}}{RT} = \frac{F_1}{RT} + \frac{F_2}{RT} \tag{5.23}$$

Where

$$\frac{F_1}{RT} = -2\pi\rho I_1 m^2 \left(\frac{\varepsilon}{k_B T}\right)\sigma^3 \tag{5.24}$$

And

$$\frac{F_2}{RT} = -\pi\rho \frac{I_2}{C_1} m^3 \left(\frac{\varepsilon}{k_B T}\right)^2 \sigma^3 \tag{5.25}$$

Where

$$C_1 = 1 + m\frac{8\eta - 2\eta^2}{(1-\eta)^4} + (1-m)\frac{20\eta - 27\eta^2 + 12\eta^3 - 2\eta^4}{[(1-\eta)(2-\eta)]^2} \tag{5.26}$$

$$I_1 = \sum_{i=0}^{6} a_i(m)\eta^i \tag{5.27}$$

$$I_2 = \sum_{i=0}^{6} b_i(m)\eta^i \tag{5.28}$$

Where

$$a_i(m) = a_{0i} + \frac{m-1}{m}a_{1i} + \frac{m-1}{m}\frac{m-2}{m}a_{2i} \tag{5.29}$$

$$b_i(m) = b_{0i} + \frac{m-1}{m}b_{1i} + \frac{m-1}{m}\frac{m-2}{m}b_{2i} \tag{5.30}$$

Parameters appear in equations (5.27-5.30) are given in table 5.2.

Table 5.2. Universal constants [11], a_{0i}, a_{1i}, a_{2i} and b_{0i}, b_{1i}, b_{2i}

i	a_{0i}	a_{1i}	a_{2i}	b_{0i}	b_{1i}	b_{2i}
0	0.79198281	-0.62311554	-0. 06777556	0.79198281	-0. 62311554	-0. 06777556
1	1. 07148651	0.48573437	0. 02837411	2.14297303	0. 97146874	0. 05674823
2	0. 91474661	1.12485267	0. 09612281	2.74423982	3. 37455809	0. 28836841
3	-7. 81060651	-.09485016	0. 06815027	-31. 2424260	-8. 37940062	0. 27260110
4	25.7855977	9.45049823	0. 05980187	128. 927988	47. 2524911	0. 29900933
5	-6. 9822877	-7.1027262	0. 28660979	-341. 893726	-102. 616357	1. 71965874
6	41. 9308941	7.77610281	-0.74701698	293. 516259	54. 4327197	-5. 22911885

Parameters shown in table 5.3 were used in the numerical calculations of thermodynamic properties of methanol and ethanol using PC-SAFT EOS.

Table 5.3. parameters of PC-SAFT EOS.

compound	σ	ε / k_B	M	ε^{AB} / k_B	k^{AB}	source
methanol	3.230	188.90	1.5255	2899.5	0.035176	fitting
ethanol	3.0438	198.24	2.7	2753.4	0.0323	fitting

Figures 5.3 illustrate the binodal points of methanol obtained, numerically, using conditions stated in equations 5.21 and 5.22 using PC-SAFT EOS [11]. It is observed that the binodal equilibrium points are not sensitive to the modified SAFT EOS.

As in SAFT EOS, the conditions (equations 5.21 and 5.22) were applied for methanol using PC-SAFT EOS to obtain figure 5.3, which indicates

excellent agreement between theory and experiment [16] especially at low temperatures as shown in the insito of figure 5.3. Small deviation was observed at high temperatures (T >410 K).
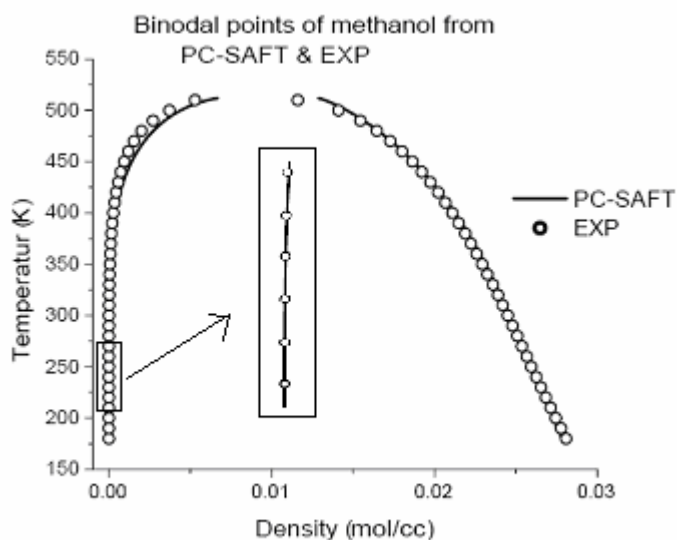

Figure 5.3. Binodal points of methanol Using PC-SAFT EOS.

Figure 5.4 indicates that, there is an excellent agreement between experiment [16] and theory at all temperatures. Consequently, PC-SAFT EOS is an excellent EOS to explain the experimental results at law temperatures.
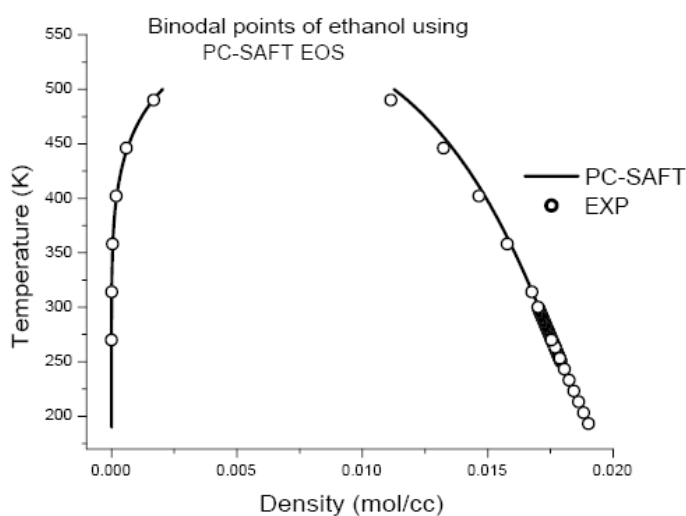

Figure 5.4. Binodal points of ethanol Using PC-SAFT EOS.

CHAPTER VI

6. RESULTS OF HOMOGENEOUS NUCLEATION RATE

6.1. RESULTS OF METHANOL

The excellent fit obtained from SAFT [9-10] or PC-SAFT [11] EOSs for the equilibrium binodal motivated us to extend the calculation to include the dependence of the nucleation rate on supersaturation ratio and temperature. Although the binodal equilibrium points were insensitive to the perturbation due to chain, the nucleation rate was found to be sensitive to the form of EOS.

Figure 6.1 depicts the results for methanol using SAFT EOS. It is clear that SAFT EOS improves the S-dependence while the T-dependence was improved at high Temperature.
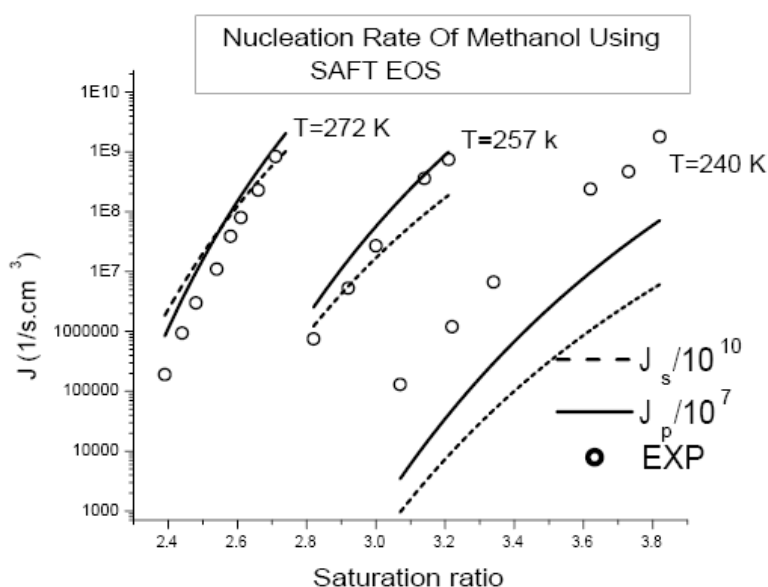

Figure 6.1. Nucleation rates of methanol using SAFT EOS.

As in figure 6.1, figure 6.2 depicts the results for methanol using PC-SAFT EOS. It is clear that PC-SAFT EOS improves the S-dependence while the T-dependence was improved at high Temperature.
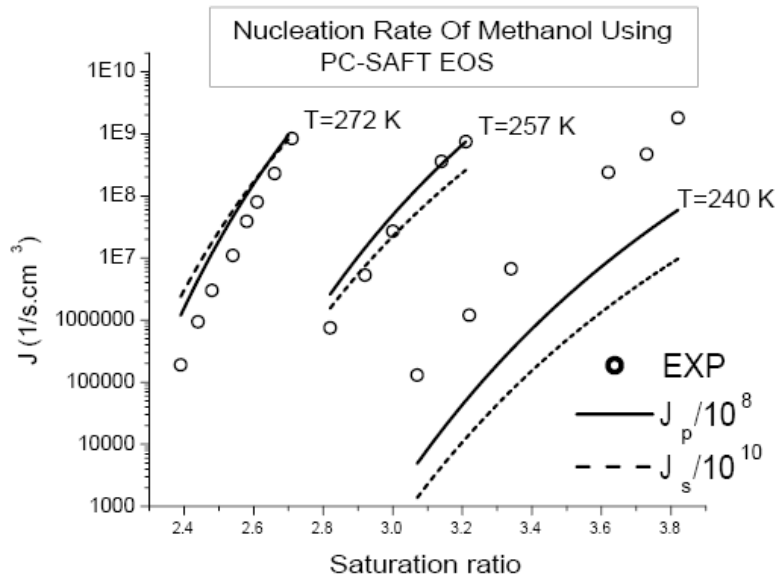
Figure 6.2. Nucleation rates of methanol using PC-SAFT EOS

These results were expected because the standard form requires the gas to be an ideal, where methanol and ethanol are not ideal gases.

Note that, the fitted values of nucleation rate used in SAFT EOS was improved by one order of magnitude when compared to PC-SAFT EOS.

6.2. RESULTS OF ETHANOL

Because the SAFT and PC-SAFT EOSs are suitable for ethanol as discussed in chapter five, we used these EOSs to calculate the nucleation rate of ethanol applying P-form and S-form methods.

Figure 6.3 depicts the results for ethanol using SAFT EOS. It is clear that, the improvement of SAFT EOS on the S-dependence is small while the T-dependence was improved at high Temperature.
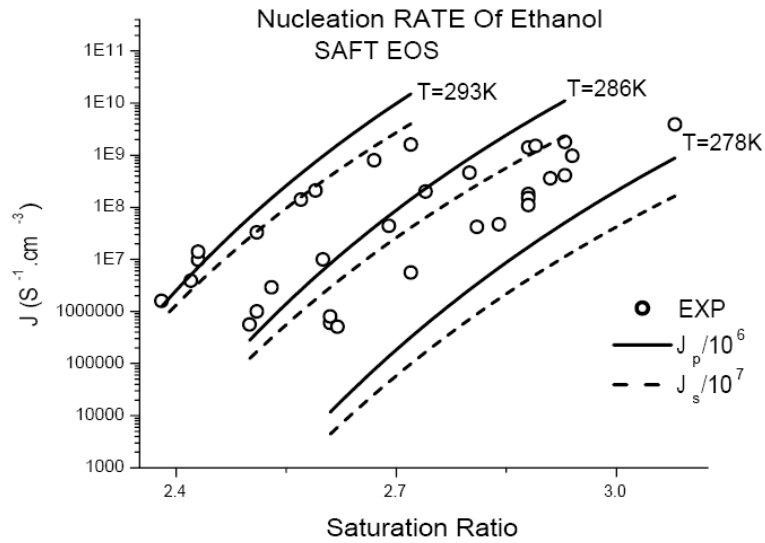
Figure 6.3. Nucleation rates of ethanol using SAFT EOS.

Figure 6.4 depicts the results for ethanol using PC-SAFT EOS. We note that, there is a very small differ between SAFT EOS (figure 6.3) and PC-SAFT EOS. The clear improvement is on T-dependence, whereas the improvement on S-dependence is small.
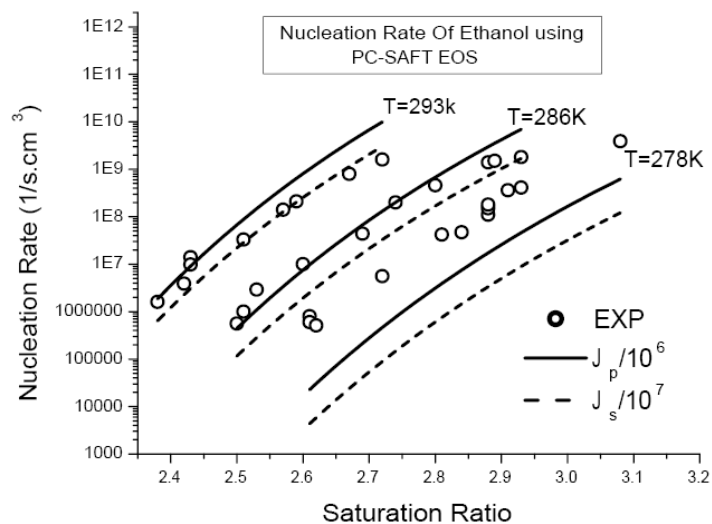

Figure 6.4. Nucleation rates of ethanol using PC-SAFT EOS.

All the experimental values of nucleation rate for ethanol and methanol are taken from [17].

6.3. DISCUSSIONS AND CONCLUSIONS

Since the gases of methanol and ethanol are not ideal, it is expected that the P-form of CNT will give better calculated results of nucleation than the S-form, where in the last form the gas is assumed to be an ideal.

From the results of EOSs in chapter five, we note that SAFT and PC-SAFT EOSs improve the theoretical binodals for methanol and ethanol at low temperature where the deviation from the experimental values approach zero.

Our results of nucleation rates show that SAFT EOS gives better values for the nucleation rates by one order of magnitude when compare with PC-SAFT EOS for methanol, that was clear in fitting value of nucleation rates for SAFT EOS was 10^7 and PC-SAFT EOS was 10^8.

6.4. RECOMMENDATIONS

These exact EOSs are not used yet to calculate the nucleation rate for many gases of industrial importance applications as water and, water-ethanol.

In our theoretical calculations of nucleation rates using the classical versions, we assumed that the surface tension is that of the flat interface, but we noted in our numerical calculations that the calculated results are very sensitive to the surface tension.

Then further work is needed.

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APPENDICES

APPENDIX A

IMPORTANT RELATIONS

A.1. ABSORPTION FLUX

To calculate the absorption flux per unit time per unit volume β, kinetically. Suppose a single molecule with a distance d from a spherical droplet and its average velocity c, see figure A.1.
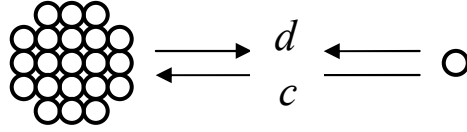
Figure A.1. Schematic depiction of the absorption of a single molecule by a droplet in metastable phase.

From the definition of β (i.e., the flux of a single molecule per unit area per unit time [6]), we can represent it by the following relation,

$$\beta = \frac{1}{At} \qquad (A.1.1)$$

Or

$$\beta = \frac{d}{Atd} = \frac{c}{Ad} \qquad (A.1.2)$$

Where A is the surface area of the droplet and t is the time for reaching the molecule to the droplet.

From thermal De broglie assumption [6] which represents the motion of

molecules of fluids as a wave motion, we can rewrite the value of c as follow.

$$c = \lambda v \tag{A.1.3}$$

Where λ is thermal De brogli wave length [6] and v is the frequency (i.e., number of collisions per unit time), then

$$\beta = \frac{hv}{Ad\sqrt{2\pi m' k_B T}} \tag{A.1.4}$$

Where h is planck's constant and m' is the molecular mass.

But hv equals the work which is needed to move the molecule by a distance d ($hv = P_v Ad$), substitute the relation of work in A.1.4, the absorption flux of a single molecule [10] can be written as

$$\beta = \frac{P_v}{\sqrt{2\pi m' k_B T}} \tag{A.1.5}$$

A.2. CHEMICAL POTENTIAL OF DROPLET IN IDEAL MIXTURE

To derive the chemical potential of a droplet in ideal mixture, we can start from the following thermodynamic relation [8].

$$\mu_v(p_v) - \mu_v(p_{ve}) = k_B T \ln S = k_B T \ln \frac{P_v}{P_{ve}} \tag{A.2.1}$$

Where S is the supersaturation ratio. Before the condensation, the droplet of n-size was a number of vapor molecules which equals n (see figure A.2.a), so its chemical potential equals the summation of the chemical

potentials for n vapor molecule basis on the reversible interaction principle. then its chemical potential equals

$$\mu_v(p_{ve}) = n\mu_1(p_{ve}) = \mu_n \tag{A.2.2}$$

After the condensation occur the droplet is considered as a single species of the ideal mixture (see figure A.2.b), then represent its chemical potential by (λ_n).

$$\mu_v(p_v) = \lambda_n \tag{A.2.3}$$
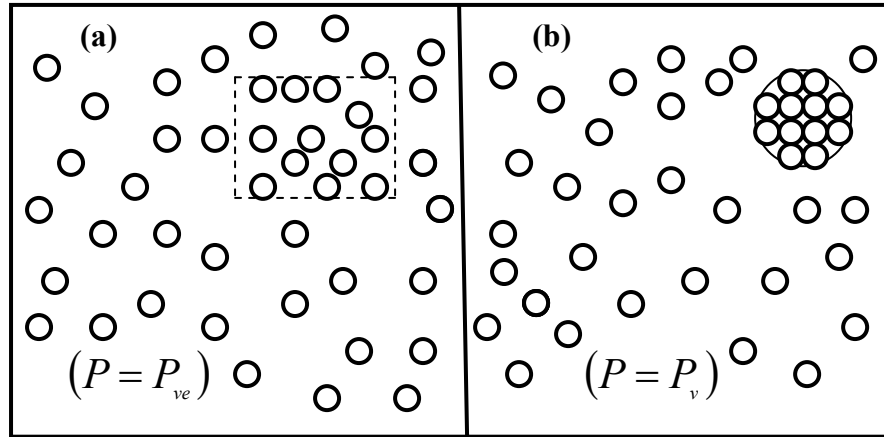
Figure A.2. Schematic depiction of the droplet (a) before the formation (b) after the formation.

Use the following equation of state which represents the ideal mixture.

$$P = \sum_n \frac{N_n}{V} k_B T = \sum_n D(n) k_B T \tag{A.2.4}$$

Where N_n is the number of n-size species, V is the total volume of the system, k_B is the Boltzmann's constant, and $D(n)$ is the concentration of the n-size species (i.e., number density of each n-size species).

At equilibrium pressure the condensation does not occur, which means that all the species are monomers (i.e., single-molecule), so the equilibrium pressure can be given as

$$P_{ve} = D(1)k_B T = D_{tot} k_B T \qquad (A.2.5)$$

Substitute the equations A.2.2, A.2.3, A.2.4 and A.2.5 in A.2.1, we get

$$\lambda_n = \mu_n + k_B T \ln \frac{D_{tot}}{D(n)} \qquad (A.2.6)$$

Or

$$\mu_n = \lambda_n + k_B T \ln \frac{D(n)}{D_{tot}} \qquad (A.2.7)$$

A.3. THE WORK OF FORMATION

Start from equation 4.3, the difference in the Helmholtz free energy can be given as

$$\Delta F = F_a - F_b = n\left(\mu_l(P_l) - \mu_v(P_v)\right) - (P_l - P_v)V_l + A\sigma \qquad (4.3)$$

Where ΔF equals the work of formation, use the following thermodynamic identity

$$\left(\frac{\partial \mu_l}{\partial p}\right)_T = v_l \qquad (A.3.1)$$

Where v_l is the specific volume of liquid. If the droplet is incompressible the value of v_l does not depend on the pressure, so

$$\int_{P_v}^{P_l}\left(\frac{\partial \mu_l}{\partial p}\right)_T dp = \mu_l(p_l) - \mu_l(p_v) = \Delta\mu = v_l(p_l - p_v) \qquad (A.3.2)$$

But v_l equals V_l / n, then

$$n(\mu_l(p_l) - \mu_l(p_v)) = V_l(p_l - p_v) \tag{A.3.3}$$

Equations A.3.3 and 4.3 lead to

$$W = n(\mu_l(P_v) - \mu_v(P_v)) + A\sigma = n\Delta\mu + A\sigma \tag{A.3.4}$$

A.4. THE RELATION BETWEEN THE SUPERSATURATION RATIO AND THE CHEMICAL POTENTIAL DIFFERENCE

Use the following thermodynamic identity at constant temperature for an ideal gas

$$d\mu = -sdT + v_v dP = v_v dp \tag{A.4.1}$$

Where

$$v_v = k_B T / P \tag{A.4.2}$$

Substitute the above result in A.4.1, and solve the integral between P_{ve} and P_v, then

$$\mu_v(p_v) - \mu_v(p_{ve}) = k_B T \ln\left(\frac{p_v}{p_{ve}}\right) = k_B T \ln S \tag{A.4.3}$$

But

$$\Delta\mu = \mu_l(P_l) - \mu_l(P_v) \tag{A.4.4}$$

Then use the relation A.3.1 to get

$$\mu_l(p_v) = \mu_l(p_{ve}) + v_l(p_v - p_{ve}) \tag{A.4.5}$$

The equations A.4.4 and A.4.5 lead to,

$$\Delta\mu = \mu_l(p_l) - \mu_l(p_{ve}) + v_l(p_v - p_{ve}) \tag{A.4.6}$$

At unstable equilibrium (critical size) $\mu_l(p_l) = \mu_v(p_v)$ (i.e., gibbs reference assumption) and at equilibrium of the bulk two-phases $\mu_l(p_{ve}) = \mu_v(p_{ve})$ and the pressure difference $(P_v - P_{ve})$ is negligible, then the difference in the chemical potential can be given as

$$\Delta\mu = \mu_v(p_v) - \mu_v(p_{ve}) = k_B T \ln S \qquad (A.4.7)$$

A.5. THE LAPLACE EQUATION

Starting from equation 3.4, the first derivative of ΔF^{max} with respect to the radius of the droplet equals zero, where

$$\Delta F^{max} = -(p_l - p_v)\frac{4\pi}{3}r^{*3} + 4\pi r^{*2}\sigma \qquad (3.4)$$

Then, derive the equation 3.4 to give,

$$\frac{d}{dr^*}\Delta F^{max} = -(p_l - p_v)4\pi r^{*2} + 8\pi r^*\sigma = 0 \qquad (A.5.1)$$

Solve the above equation to get the Laplace equation

$$(p_l - p_v) = \frac{2\sigma}{r} \qquad (A.5.2)$$

APPEDIX B
NUMERICAL PROGRAMS OF SAFT AND PC-SAFT

B.1 List of symbols

```
R           Universal constant of gases (Mpa.cc/k.mol)
N           Avogadros's number
S           LJ interaction energy (kelvin)
m           Segment numer or chain length
L           Association energy (kelvin)
w           Association volume (dimensionless)
v           Temp-independent segment diameter (cm)
Kl          Boltzmann's constant (pa.m**3/K)
MM          Molar mass (kg/mol)
b           pi=Л
d           Temperature-dependence segment diameter
row         Molar density
eta         Segment packing fraction
g           6*eta/[√2*b*row]
c           eta/row
T           Temperature
Guess       Guessing value for Gibbs reference density
Guess1      Guessing value for liquid density
Guess2      Guessing value for vapor density
Guess3      Guessing value for supersaturated vapor density
rowg        supersaturated vapor density
Pg,Pv       Actual pressure
rowl        Density of Gibbs reference state
mewg        Chemical potential of supersaturated vapor
Jo          Pre-exponential of nucleation rate
Jp          Nucleation rate by P-form
Js          Nucleation rate by S-form
Pl          Pressure of Gibbs reference state
gama        surface tension
W1          Work of formation for P-form
W2          Reduced work of formation for P-form
W3          work of formation for S-form
dp          First derivative of pressure by row
dmew        First derivative for mew by row
K           square matrix includes dp and dmew
i           Number of iteration
error       Error equals 10⁻¹°
Kl          Boltzmann's constant
satu        Saturation ratio
row(1),equl Equilibrium liquid density
row(2),equg Equilibrium vapor density
```

B.2 Densities of equilibrium vapor-liquid pressure
```
do
row(1)=guess1
row(2)=guess2
k(1,1)=dp(row(1),t)
```

```
k(1,2)=-dp(row(2),t)
k(2,1)=dmew(row(1),t)
k(2,2)=-dmew(row(2),t)
f(1)=p(row(2),t)-p(row(1),t)
f(2)=mew(row(2),t)-mew(row(1),t)
z=k(2,1)/k(1,1)
k(2,1)=0.0d0
f(2)=f(2)-(z*f(1))
k(2,2)=k(2,2)-(z*k(1,2))
u(2)=f(2)/k(2,2)
u(1)=(f(1)-k(1,2)*u(2))/k(1,1)
row=row+u
error1=0.0d0

do i=1,2
error1=error1+f(i)**2
end do
error1=dsqrt(error1)

if (error1<error) exit
guess1=row(1)
guess2=row(2)
end do
```

B.3 Density of supersaturated vapor

```
Pg=satu*p(equg,T)
guess3=1.20d0*equg
fun1=p(guess3,t)-Pg
dfun1=dp(guess3,t)
do while(dabs(fun1/dfun1)>error)
fun1=p(guess3,t)-Pg
dfun1=dp(guess3,t)
root1=guess3-fun1/dfun1
guess3=rowg
```

B.4 Density of Gibbs reference state

```
mewg=mew(rowg,t)
guess=1.2d0*equl
fun=mew(guess,t)-mewg
dfun=dmew(guess,t)
do while(dabs(fun/dfun)>error)
fun=mew(guess,t)-mewg
dfun=dmew(guess,t)
root=guess-fun/dfun
guess=rowl
end do
```

B.5 Nucleation Rate by P-form

```
gama=(24.23d0-0.09254d0*(T-273.15d0))*1.0d-3    !(N/m)=(pa.m)
Vl=(1.0d0/(rowl*N))
W1=((16.0d0/3.0d0)*b*(gama**3)/((Pl-Pv))**2) !(n.m)(work of formation)
W2=(W1/(Kl*T))
Jo=(dsqrt((2.0d0*gama)/(b*(MM/N)))*Vl*(Pv/(Kl*T))**2)*1.0d-12
Jp=(Jo*dexp(-W2))
```

B.6 Nucleation rate by S-form

```
gama=(24.23d0-0.09254d0*(T-273.15d0))*1.0d-3    !(N/m)=(pa.m)
W3=((16.0d0/3.0d0)*b*(Vl**2)*(gama**3)/&
&((Kl*T*dlog(satu))**2))*1.0d-12 !(n.m)
W4=(W3/(Kl*T)) !Work of formation
Jo=(dsqrt((2.0d0*gama)/(b*(MM/N)))*Vl*(Pv/(Kl*T))**2)*1.0d-12
Js=Jo*dexp(-W3/(Kl*T))  !Nucleation rate
```

B.7 SAFT EOS and its related parameters

B.7.1 Temperature-dependent segment diameter

```
d=v*((1.0d0+0.2977*(T/S))/(1.0d0+0.33163d0*(T/S)&
&+(0.0010477d0+0.025337d0*(m-1.0d0)/m)*(T/S)**2))
```

B.7.2 C parameter (simplification parameter)

```
c=(b*N*(d**3)*m)/6.0d0
```

B.7.3 Segment packing fraction

```
eta=c*row
```

B.7.4 Association strength

```
H=row/2.0d0*d**3*((2.0d0-eta(row))/(1.0d0-eta(row))**3)*w&
&*(dexp(L/T)-1.0d0)
```

B.7.5 Mole fraction of molecules not bonded at site A

```
X=(-1.0d0+dsqrt(1.0d0+4.0d0*H(row,t)*N))/(2.0d0*H(row,t)*N)
```

B.7.6 First derivative of associating strength

```
dH=d**3*((2.0d0*eta(row)+2.0d0-(eta(row))**2)&
&/(2.0d0*(1-eta(row))**4))*w*(dexp(L/T)-1)
```

B.7.7 second derivative of associating strength

```
ddH=c*(d)**3*((5.0d0+2.0d0*eta(row)-(eta(row))**2.0d0)&
&/(1-eta(row))**5.0d0)*w*(dexp(L/T)-1)
```

B.7.8 First derivative of mole fraction of molecules not bonded at site A

```
dX=(((4.0d0*H(row,t)*N**2/dsqrt(1.0d0+4*N*H(row,t)))&
&-2.0d0*N*(-1.0d0+dsqrt(1.0d0+4.0d0*H(row,t)*N))))*dH(row,t)&
&/(4.0d0*N**2*H(row,t)**2)
```

B.7.9 second derivative of mole fraction of molecules not bonded at site A

```
ddX=((-32.0d0*N**5*H(row,t)**3*(1.0d0+4.0d0*N*H(row,t))**(-1.5)&
&-32*N**4*H(row,t)**2&
&/dsqrt(1.0d0+4.0d0*N*H(row,t))-16.0d0*N**3*H(row,t)&
&+16.0d0*N**3*H(row,t)*dsqrt(1.0d0+4.0d0*N*H(row,t)))*&
&(dH(row,t)**2/(16.0d0*N**4*H(row,t)**4)))+dX(row,t)*ddH(row,t)&
```

```
&/dH(row,t)
```

B.7.10 Ideal term of Helmholtz free energy

```
A1=R*T*dlog(row)
```

B.7.11 Hard sphere term of Helmholtz free energy

```
A2=(R*T*m)*((4.0d0*eta(row)-3.0d0*(eta(row))**2)&
&/(1.0d0-eta(row))**2)
```

B.7.12 SAFT Dispersion term of Helmholtz free energy
```
A3=R*T*(((S/T)*m*(-8.5959d0*g*row-4.5424d0*g**2*row**2-&
&2.1268d0*g**3*row**3+10.285d0*g**4*row**4)+&
&(S/T)**2*m*(-1.9075d0*g*row+9.9724d0*g**2*row**2-&
&22.216d0*g**3*row**3+15.904d0*g**4*row**4)))
```

B.7.13 Hard chain term of Helmholtz free energy

```
A4=R*T*(((1.0d0-m)*dlog((1.0d0-0.5d0*eta(row))&
&/(1.0d0-eta(row))**3)))
```

B.7.14 Association term of Helmholtz free energy

```
A5=R*T*((2.0d0*dlog(X(row,t))-X(row,t)+1.0d0))
```

B.7.15 Total term of Helmholtz free energy

```
A=A1(row,t)+A2(row,t)+A3(row,t)+A4(row,t)+A5(row,t)
!Total term of reduced free Helmholtz free energy
```

B.7.16 First derivative of ideal term of Helmholtz free energy

```
dA1=R*T/row
```

B.7.17 First derivative of hard sphere term of Helmholtz free energy

```
dA2=(R*T*m*c)*((4.0d0-2.0d0*eta(row))/(1.0d0-eta(row))**3)
```

B.7.18 First derivative of SAFT Dispersion term of Helmholtz free energy

```
dA3=R*T*(((S/T)*m*(-8.5959d0*g-2.0d0*4.5424d0*g**2*row&
&-3.0d0*2.1268d0*g**3*row**2+4.0d0*10.285d0*g**4*row**3)+&
&(S/T)**2*m*(-1.9075d0*g+2.0d0*9.9724d0*g**2*row-&
&3*22.216d0*g**3*row**2+4*15.904d0*g**4*row**3)))
```

B.7.19 First derivative of hard chain term of Helmholtz free energy

```
dA4=R*T*(1.0d0-m)*c*((5.0d0-2.0d0*eta(row))/&
&(2.0d0-3.0d0*eta(row)+(eta(row))**2))
```

B.7.20 First derivative of associating term of Helmholtz free energy

dA5=R*T*(((2.0d0/X(row,t)-1.0d0)*dX(row,t)))

B.7.21 First derivative of total term of Helmholtz free energy

dA=dA1(row,t)+dA2(row,t)+dA3(row,t)+dA4(row,t)+dA5(row,t)

B.7.22 First derivative of ideal term of Helmholtz free energy

ddA1=-R*T/row**2

B.7.23 second derivative of hard sphere term of Helmholtz free energy

ddA2=R*T*m*c**2*((10.0d0-4.0d0*eta(row))/(1.0d0-eta(row))**4)

B.7.24 second derivative of SAFT dispersion term of Helmholtz free energy

ddA3=R*T*(((S/T)*m*(-2.0d0*4.5424d0*g**2&
&-6.0d0*2.1268d0*g**3*row+12.0d0*10.285d0*g**4*row**2)+&
&(S/T)**2*m*(2.0d0*9.9724d0*g**2-&
&6.0d0*22.216d0*g**3*row+12.0d0*15.904d0*g**4*row**2)))

B.7.25 second derivative of hard chain term of Helmholtz free energy

ddA4=R*T*((1.0d0-m)*c**2*((11.0d0-10.0d0*eta(row)+2.0d0*&
&eta(row)**2)/(2.0d0-3.0d0*eta(row)+(eta(row))**2)**2))

B.7.26 second derivative of associating term of Helmholtz free energy

ddA5=R*T*(((2.0d0/X(row,t)-1.0d0)*ddX(row,t))-&
&(2.0d0/X(row,t)**2)*(dX(row,t))**2)

B.7.27 second derivative of total term of Helmholtz free energy

ddA=ddA1(row,t)+ddA2(row,t)+ddA3(row,t)+ddA4(row,t)+ddA5(row,t)

B.8 PC-SAFT dispersion term and its parameters

B.8.1 alpha parameter (simplification parameter)

alpha=-2.0*b*m**2*(S/T)*v**3*N

B.8.2 Beta parameter (simplification parameter)

beta=-b*m**3*((S/T)**2)*v**3*N

B.8.3 Temperature-dependent segment diameter

```
d=v*(1.0d0-0.12d0*dexp(-3.0d0*S/T))
```

B.8.4 C$_1$ parameter

```
c1=(1.0d0+m*(8.0d0*eta(row)-2.0d0*eta(row)**2)&
&/(1.0d0-eta(row))**4+(1.0d0-m)*(20.0d0*eta(row)&
&-27.0d0*eta(row)**2+12.0d0*eta(row)**3-2.0d0*eta(row)**4)/&
&((1.0d0-eta(row))*(2.0d0-eta(row)))**2)
```

B.8.5 first derivative of C$_1$ parameter

```
dc1=m*c*((8.0d0+20.0d0*eta(row)-&
&4.0d0*eta(row)**2)/(1.0d0-eta(row))**5)&
&+(1.0d0-m)*c*((80.0d0-216.0d0*eta(row)+&
&208.0d0*eta(row)**2-&
&80.0d0*eta(row)**3+6.0d0*eta(row)**4+2.0d0*eta(row)**5)&
&/(4.0d0-12.0d0*eta(row)+13.0d0*eta(row)**2&
-6.0d0*eta(row)**3+eta(row)**4)**2)
```

B.8.6 second derivative of C$_1$ parameter

```
ddc1=m*c**2*(((420.0d0+72.0d0*eta(row)-12.0d0*eta(row)**2)/&
&(1.0d0-eta(row))**6))+(1.0d0-m)*c**2*((((4.0d0-12.0d0*&
&eta(row)+13.0d0*eta(row)**2-6.0d0*eta(row)**3+eta(row)**4)&
&**2*(-216.0d0+416.0d0*eta(row)-240.0d0*eta(row)**2&
&+24.0d0*eta(row)**3+10.0d0*eta(row)**4)-2.0d0*(80.0d0-&
&216.0d0*eta(row)+208.0d0*eta(row)**2-&
&80.0d0*eta(row)**3+6.0d0*eta(row)**4+2.0d0&
&*eta(row)**5)*(4.0d0-12.0d0*eta(row)&
&+13.0d0*eta(row)**2&
&-6.0d0*eta(row)**3+&
&eta(row)**4)*(-12.0d0+26.0d0*eta(row)-&
&18.0d0*eta(row)**2+4.0d0*eta(row)**3)))&
&/(4.0d0-12.0d0*eta(row)+13.0d0*eta(row)**2&
&-6.0d0*eta(row)**3+eta(row)**4)**4)
```

B.8.7 I$_1$ parameter

```
I1=a00+a11*eta(row)+a22*eta(row)**2+a33*eta(row)**3+a44*eta(row)**4&
&+a55*eta(row)**5+a66*eta(row)**6
```

B.8.8 First derivative of I1 parametere

```
dI1=c*(a11+2.0d0*a22*eta(row)+3.0d0*a33*eta(row)**2&
&+4.0d0*a44*eta(row)**3+5.0d0*a55*eta(row)**4+6.0d0*a66*eta(row)**5)
```

B.8.9 Second derivative of I1 parametere

```
ddI1=c**2*(2.0d0*a22+6.0d0*a33*eta(row)+12.0d0*a44*eta(row)**2&
&+20.0d0*a55*eta(row)**3+30.0d0*a66*eta(row)**4)
```

B.8.10 I2 parametere

```
I2=b00+b11*eta(row)+b22*eta(row)**2+b33*eta(row)**3+b44*eta(row)**4&
&+b55*eta(row)**5+b66*eta(row)**6
```

B.8.11 First derivative of I2 parameter

```
dI2=c*(b11+2.0d0*b22*eta(row)+3.0d0*b33*eta(row)**2&
&+4.0d0*b44*eta(row)**3&
&+5.0d0*b55*eta(row)**4+6.0d0*b66*eta(row)**5)
```

B.8.12 Second derivative of I2 parameter

```
ddI2=c**2*(2.0d0*b22+6.0d0*b33*eta(row)+12.0d0*b44*eta(row)**2&
&+20.0d0*b55*eta(row)**3+30.0d0*b66*eta(row)**4)
```

B.8.13 Dispersion term

```
A3=R*T*(alpha*row*I1(row)-beta*row*I2(row)/C1(row))
```

B.8.14 First derivative of dispersion term

```
dA3=R*T*(alpha*I1(row)+alpha*row*dI1(row)+beta*I2(row)/C1(row)+&
&beta*row*dI2(row)/C1(row)-beta*row*I2(row)*dC1(row)&
&/C1(row)**2)
```

B.8.15 Second derivative of dispersion term

```
ddA3=R*T*(2.0d0*alpha*dI1(row)+alpha*row*ddI1(row)&
&+2.0d0*beta*dI2(row)/C1(row)-2.0d0*beta*I2(row)*dC1(row)&
&/C1(row)**2-2.0d0*beta*row*dI2(row)*dC1(row)&
&/C1(row)**2+beta*row*ddI2(row)/C1(row)&
&+2.0d0*beta*row*I2(row)*dC1(row)**2/C1(row)**3-&
&beta*row*I2(row)*ddC1(row)/C1(row)**2)
```

B.9 Thermodynamic properties and its first derivatives

B.9.1 Pressure

```
p=row**2*dA(row,t)
```

B.9.2 First derivative of pressure

```
dp=row**2*ddA(row,t)+2.0d0*row*dA(row,t)
```

B.9.3 Chemical potential

```
mew=row*dA(row,t)+A(row,t)
```

B.9.4 First derivative of chemical potential

```
dmew=dA(row,t)+ddA(row,t)*row+dA(row,t)
```

معدلات التحول للايثانول و الميثانول باستخدام معادلتي الحالة (SAFT) و(PC-SAFT)

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مشرفاً مشاركاً: د. حسن الغانم

الملخص:

من أجل معرفة مدى التحسن في معدلات التحول المرتقبة من الحالة الغازية إلى الحالة السائلة سيتم استخدام معادلتي الحالة الموسومة بـ(PC-SAFT) و (SAFT) جنباً إلى جنب مع صيغة جيبس العامةP-Form للنظرية التقليدية في تكوين الأنوية (Nucleation) . بينت النتائج النظرية لمعدلات التكوين المستخلصة من معادلتي الحالة (PC-SAFT) و(SAFT) وجود تطابق جيد عند مقارنتها بالنتائج العملية للميثانول و الايثانول. مع ملاحظة تحسين معدلات التكوين على درجات الحرارة وقيم الاشباع للضغط. وجد أن التطابق بين الكميات النظرية و العملية كان جيداً في حالة الميثانول.