The Prediction of Vapour Liquid Equilibrium Behaviour of Propane Butane Mixture

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ABSTRACT

This paper is a contribution to the development of mathematical model for the prediction of vapour liquid equilibrium behaviour of propane butane mixture at non-ideal state. The proposed model is based on the generalized virial equation of state and Gamma/Phi formulation. Mathematical modeling, Mathcad is used to numerically solve for fugacity, fugacity coefficient, activity coefficient and vapour-phase composition of propane butane mixture by taking into consideration the effects of temperature and pressure. A temperature range of 263.15K to 313.15K chosen in this modeling is of practicability for propane butane mixture in cylindrical storage. The prediction of vapour liquid equilibrium behaviour for propane butane mixture is illustrated in *Pxy* diagram at different system temperatures. It is clearly shown that solution fugacity coefficient decreases steadily as system temperature and pressure increase. It is also shown that the solution fugacity increases with system temperature and pressure. Activity coefficient of butane in mixture becomes larger as system temperature and pressure increase. Meanwhile, there is insignificant decrease in activity coefficient of propane with temperature and pressure. As system temperature and pressure go higher, vapour-phase composition of propane decreases while for butane, its concentration in vapour phase becomes richer.

LIST OF NOMENCLATURE

γ	Activity coefficient
ϕ	Fugacity coefficient of pure species
$\hat{\phi}$	Fugacity coefficient of species in solution
$\hat{f}$	Fugacity of pure species
f	Fugacity of species in solution
x	Liquid phase mole fraction
P	Pressure
T	Temperature
y	Vapor phase mole fraction
Subscripts	
i	Component i
Superscripts	
L	Liquid
sat	Saturated condition
v	Vapor

INTRODUCTION

The accurate prediction of phase equilibrium of fluid mixtures is extremely important in many industrial applications, such as reservoir modeling, process design, and gas processing and separation. One practicable example of phase equilibrium is the primary process in an oil refinery which involves the separation of the crude oil into the more valuable fractions i.e., gasoline, kerosene, diesel fuel, etc. by distillation. Equilibrium is a static condition in which no changes occur in the properties of a system with time. A state of equilibrium is a state of rest (Lewis and Randall, 1961). Phase-equilibrium thermodynamics seeks to establish the relations among the various properties, in particular, temperature, pressure and composition, that ultimately prevail when two or more phases reach a state of equilibrium wherein all tendencies for changes have ceased.

Most of the initial work in vapor liquid equilibrium (VLE) behaviour of hydrocarbon mixture was with the system at low pressure and low temperature where an ideal state was usually assumed. Based on the previous researches, there are no studies carried out on the hydrocarbon system, especially the light hydrocarbon system, at non-ideal condition. Ideal model like Raoult's law model is applied to the hydrocarbon system at ideal state. Situations change when the said system is not at ideal state since ideal systems hardly exist in real life. The deviations from mixture ideality should be accounted in the prediction of VLE for propane butane mixture.

LITERATURE REVIEW

Fugacity and Fugacity Coefficient

The fugacity is a quantity that corresponds to the pressure for a non-ideal gas. Fugacity is a pseudo or effective pressure. It is the pressure at which the chemical potential of an ideal gas is the same as that of the real gas at the true pressure. Fugacity of a component in a gas mixture is a pseudo or effective partial pressure for that component.

Fugacity f_i is a property of a pure material and it depends upon temperature and pressure, which must be uniform throughout both phases at equilibrium. The criterion of vapour liquid equilibrium for multicomponent system is as follows:

$$f_i^L\left(T, P_i^{sat}\right) = f_i^V\left(T, P_i^{sat}\right) \tag{1}$$

Fugacity coefficient is another new property, which is dimensionless. The fugacity coefficient of pure species i, ϕ_i is defined as:

$$\phi_i = \frac{f_i}{P} \tag{2}$$

When dealing with ideal gas, $\phi_i = 1$ and $f_i^{ig} = P$. On the other hand, the definition of the fugacity of a species in solution is parallel to the definition of the pure-species fugacity. Fugacity coefficient of species i in solution is expressed as:

$$\hat{\phi}_i \equiv \hat{f}_i / y_i P \tag{3}$$

Activity Coefficient

In contrast to fugacity, activity coefficient is inherently a multicomponent concept that is useful only for mixtures. It is introduced into Raoult's law to account for liquid-phase non-idealities. In non-ideal mixtures, activity coefficients depend strongly on liquid-phase composition. Ideal solution serves as a standard to which real-solution behaviour can be compared. Activity coefficient is defined in the following expression:

$$\gamma_i = \frac{\hat{f}_i}{x_i f_i} \tag{4}$$

Gamma/Phi Formulation of VLE

Modified Raoult's law includes the activity coefficient to account for liquid-phase non-idealities, but it is limited by the assumption of vapour-phase ideality. This can be overcome by introducing the vapour-phase fugacity coefficient. For species i in vapour mixture and in liquid solution, fugacity of species i in vapour phase and in liquid phase can be represented by:

$$\hat{f}_i^v = y_i \hat{\phi}_i P \text{ and } \hat{f}_i^l = x_i \gamma_i f_i \tag{5}$$

The criterion for phase equilibrium is that these be equal:

$$y_i \hat{\phi}_i P = x_i \gamma_i f_i \tag{6}$$

Prediction of VLE

In order to calculate with confidence the fugacities in a gas mixture, it is advantageous to use an equation of state where the parameters have physical significance, i.e. where the parameters can be related to intermolecular forces. One equation of state that has this desirable ability is the virial equation of state. The fundamental advantage of the virial equation is that it directly relates fugacities in mixtures to intermolecular forces (Prausnitz et al., 1999). Vapour phase non-idealities in the calculation of thermodynamics properties near atmospheric pressure and often up to about 1.5MPa can be represented by the virial equation of state with the inclusion of the second virial coefficient only (Virendra et al., 1995). The generalized virial equation has been widely used because it only requires the substance-dependent critical parameters and acentric factor. Generalized virial equation is of greater applicability to all gases. The most important advantage of the virial equation of state for application to phase equilibrium is its direct extension to mixtures (Prausnitz et al., 1999). Mixing rules should be included when dealing with mixture. For two-term truncated form, mixture second virial coefficient is a function of temperature only.

MATHEMATICAL MODELING

This research project involves mathematical modeling. Mathcad is used to numerically solve fugacity, fugacity coefficient and activity coefficient for propane butane mixture. All the required inputs like properties of propane and n-butane should be defined in the early stage. Then suitable equations are listed in correct sequences in order to get the final results. There are four parameters to be solved in this study. They are fugacity, fugacity coefficients, activity coefficients and vapour phase compositions for each species in propane butane mixture. Liquid phase composition and system temperature are set before solving the above parameters. In order to establish a mathematical model, appropriate assumptions are made. The generalized virial equation of state method is suitable for propane butane mixture. That is, the operating condition of propane butane mixture at 10 bars is assumed as moderate pressure while applying this method. Limitation of this method is its applicability to low and moderate pressure. In this study, 10 bars is considered high pressure for propane butane system but in the other way round it is considered as moderate pressure when applying this method. Next, the required liquid composition of propane butane mixture is referred to the composition at equilibrium state which is obtained through the composition analyzer. Besides, butane in the mixture is actually consisting of n-butane and isobutane. In this project, butane is referred to a mixture of 50% of n-butane and 50% of isobutane. In addition, propane and butane are chemically similar species and both species are non-reactive in a mixture. Therefore, an assumption of fugacity coefficient in gas phase ($\hat{\phi}^{v}$) equals to the fugacity coefficient in liquid phase ($\hat{\phi}^{L}$) is made. This assumption is based on the fact that the pure species fugacity coefficient in gas phase (ϕ^{v}) equals to the pure species fugacity coefficient in liquid phase (ϕ^{L}).

RESULTS AND DISCUSSIONS

This research study focuses on the effect of temperature and pressure on the vapour liquid equilibrium behaviour of propane butane mixture. Mathematical modeling has been developed in order to predict the VLE behaviour. The model currently proposed can be used for the prediction of VLE of propane butane mixture in the full composition range.

Effect of Composition

A typical *Pxy* diagram for six different temperatures can be seen in Figure 1. It clearly shows that when there is an increase in temperature, there is an increase in system pressure. For each temperature, the upper curve represents bubble point line while the lower curve represents dew point line. A temperature range of 263.15 K to 313.15 K chosen in this modeling is of practicability for propane butane mixture in cylindrical storage.

Effect of Temperature

Figure 2 displays the effect of temperature changes on the fugacity coefficient. Here, it is assumed that mole fractions in liquid phase for both the propane and butane are 0.6 and 0.4, respectively. The same assumption also goes to Figures 3, 4 and 6. It can be seen clearly that fugacity coefficients of solution as well as of individual species in mixture decreases steadily as the system temperature increases. That is, the deviation of fugacity coefficient from unity becomes larger as the system temperature becomes higher.

Figure 3 shows the effect of temperature changes on fugacity as well as system pressure. As shown in Figure 3, solution fugacity increases as the system temperature increases. It is showed that the solution fugacity appears very closely to the fugacity of propane in mixture.

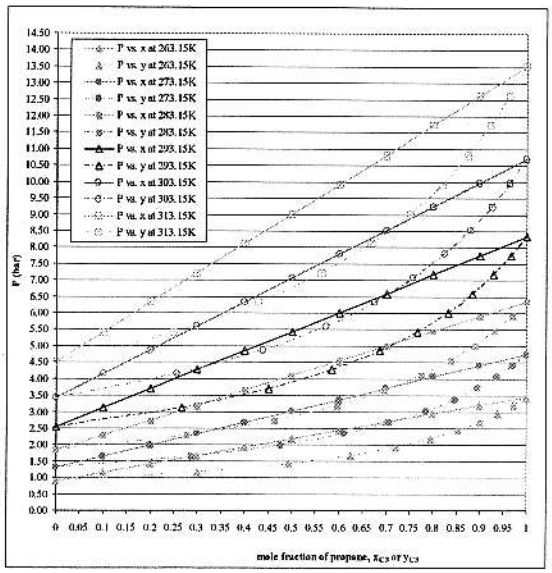

Figure 1: *Pxy* diagram for several temperatures

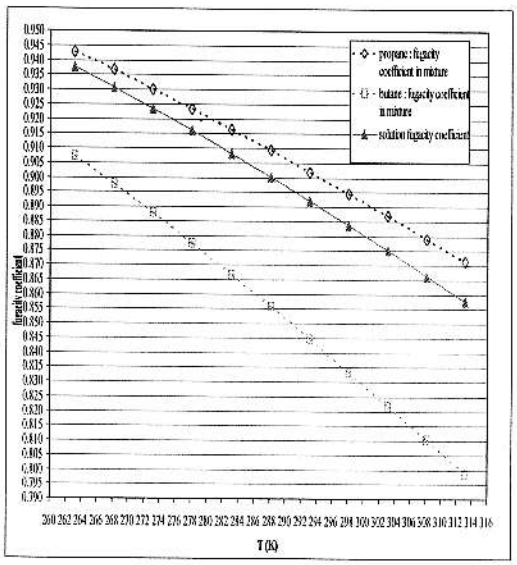

Figure 2: Fugacity coefficients at different temperatures

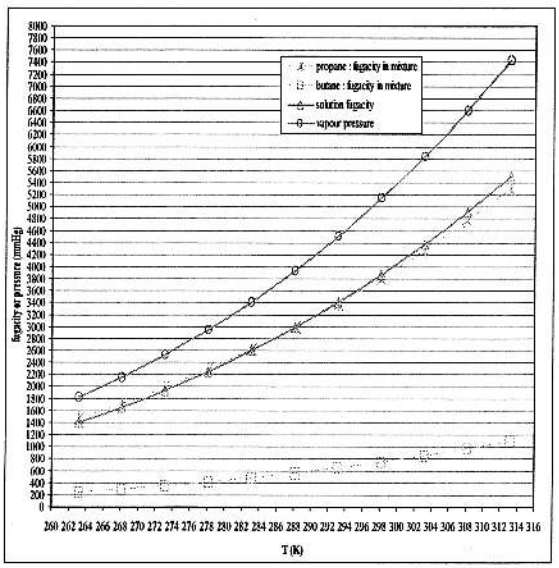

Figure 3: Fugacity and vapour pressure at different temperatures

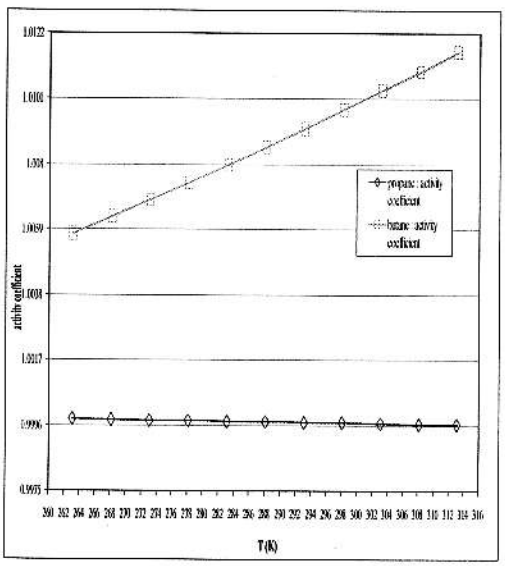

Figure 4: Activity coefficients at different temperatures

This is because fugacity is known as a parameter representing the effective pressure in vapour phase (Prausnitz et al., 1999). Since there is more propane in vapour phase, therefore both the solution fugacity and fugacity of propane in mixture show the similar trend. That is, there is negligible gap between these two parameters. On the other hand,

Figure 3 shows clearly that the system pressure always greater than the solution fugacity. A system is considered as an ideal system when these two parameters show negligible difference. As shown in Figure 3, difference between system pressure and solution fugacity becomes larger when system temperature becomes higher. That is, deviation from ideality for propane butane mixture is more apparent at higher temperature.

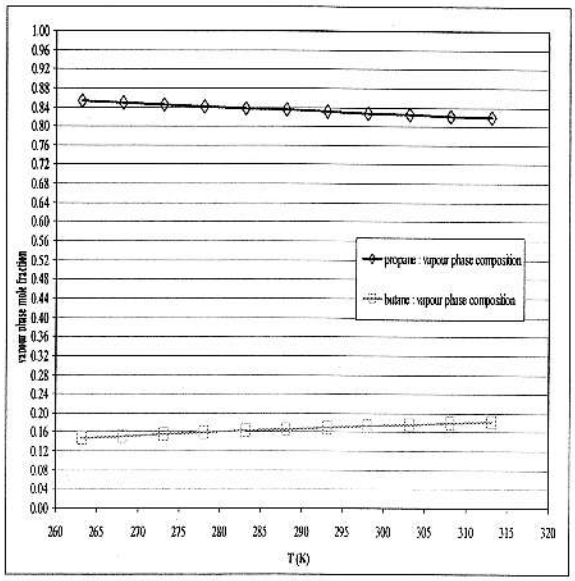

Figure 5: Vapour phase compositions at different temperatures

As can be seen from Figure 4, it is known that activity coefficient of butane increases appreciably as temperature grows higher. Meanwhile, there are only insignificant decreases in activity coefficient of propane with temperature. As can be seen, activity coefficient of propane stays closely to unity while the activity coefficient of butane deviates from unity. Activity coefficient is a parameter used to account for liquid-phase non-idealities. In general, there is more butane in liquid phase. Therefore, the effect of temperature on activity coefficient of propane in liquid solution is quite insignificant while the effect of temperature brings relatively significant changes on butane. Figure 5 shows the effect of temperature on vapour phase composition. As temperature becomes higher, more butane vaporizes therefore the vapour phase composition of butane increases while the vapour phase composition of propane decreases. However, there is always more propane in vapour phase due to its higher vapour pressure. These vapour

phase compositions are then used in the study of discharging process of propane butane mixture from cylindrical storage.

Effect of Pressure

Figure 6 displays the effect of pressure on activity coefficient at different temperatures. At constant temperature, as pressure goes higher deviations of activity coefficient for butane become more noticeable. Even though there is a deviation from unity, the said deviation can actually be neglected because, as can be seen from Figure 6, the highest value of activity coefficient is less than 1.02 for these six temperatures. This value is actually not far from unity. Sometimes, this value can even be approximated to unity. Unless near the critical region, activity coefficient is little affected by pressure and is strongly affected by the nature of pure chemicals comprising the liquid solution (Alvarado, 1993). This statement clearly explains that it is reasonable to neglect the deviation of activity coefficient when pressure changes. Meanwhile, activity coefficient of propane approaches unity at certain pressure. Apart from that particular pressure, it is clearly shown that activity coefficient goes larger than unity at lower pressure and smaller than unity at higher pressure. Besides, larger range of value of activity coefficient is accounted as temperature increases.

Figure 7 depicts the effect of system pressure on solution fugacity at different temperatures. It is clearly shown that as the pressure increases, solution fugacity increases at constant temperature. At higher temperature, solution fugacity becomes larger and it obviously accounts for larger range of values. Figure 7 clearly tells that solution fugacity is always smaller than system pressure due to the non-idealities in propane butane mixture. However, the difference between these two parameters for propane butane mixture is always small. Judging from the modeling, the ratio between solution fugacity and system pressure (f/P) always ranges from 0.73 to 0.87. Figure 8 depicts the effect of system pressure on solution fugacity coefficient at different temperatures. It is clearly shown that as the pressure increases, solution fugacity

coefficient decreases at constant temperature. At higher temperature, solution fugacity coefficient accounts for larger range of values and the deviations from unity are larger.

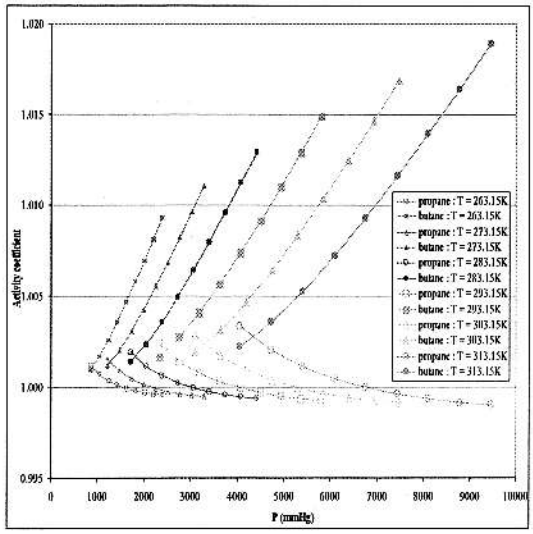

Figure 6: Effect of pressure on activity coefficient at different temperatures

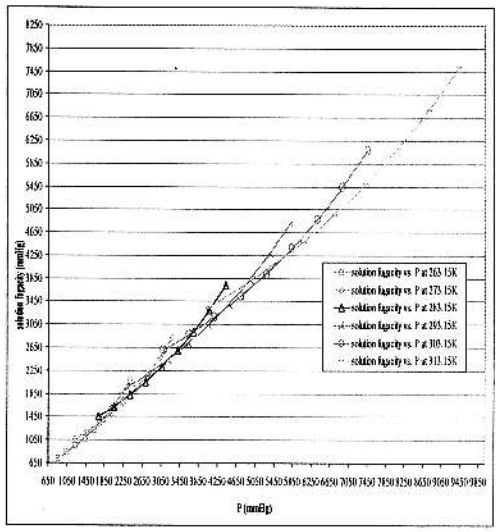

Figure 7 : Effect of pressure on solution fugacity at different temperatures

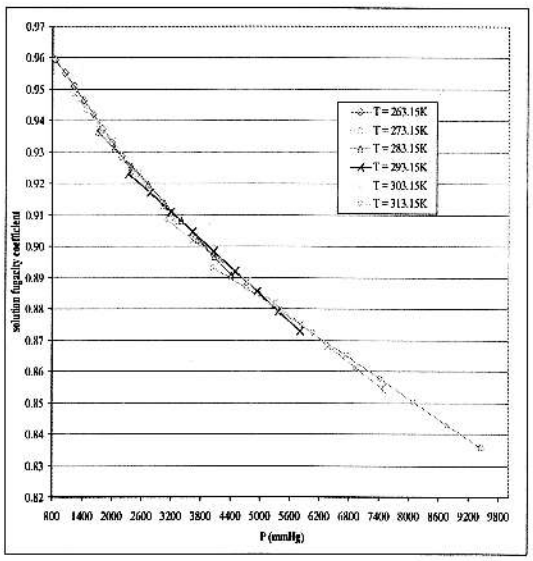

Figure 8 : Effect of pressure on solution fugacity coefficient at different temperatures

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